A SPECTROSCOPIC STUDY OF
SOME ARYLIMIDATE COMPOUNDS

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by

MICHAEL IVAN ALLNUTT

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ABSTRACT

A spectroscopic study of 25 arylimidate compounds has been carried out. The assignments were arrived at by comparing the spectra of the arylimidates and the products of rearrangement of the N-aryl substituted compounds. Spectra of several related esters were examined to enable a description of the skeletal modes of the imidates to be obtained.

The dipole moments of the simpler imidates and some related esters were measured for comparison and in order to obtain structural information about the imidates.

Temperature studies were performed on the ν (C=N) absorption of some imidates. Ultra violet and nuclear magnetic resonance spectra of the imidates were recorded in an attempt to obtain information on the electronic nature of the aryl rings and the (C=N) group.

Some anilides were examined by dielectric and infrared techniques to obtain structural information. 15 previously unmeasured dipole moments were measured during the course of this study.

SUMMARY

Ethyl benzimidate, ethyl meta- and para-chlorobenzimidates, ethyl meta- and para-toluimidates and their analogous ethyl benzoates were prepared. The dipole moments of all compounds were measured at 25°C in benzene and vector calculations made using group moments to obtain preliminary structural information.

The infrared spectra were recorded on liquid film samples and the spectra analysed in the light of previous assignments of ethyl benzoate and ethyl benzimidate. N-phenyl phenyl benzimidate was prepared together with seventeen other N-aryl aryl arylimidates by substituting each position of each ring in turn with chlorine and then methyl groups. The disc spectra were recorded together with solution spectra in both cyclohexane and tetrachloroethylene. The compounds were rearranged by the Chapman rearrangement into benzoyl diphenylamines and the infrared spectra were recorded as they had been for the parent arylimidates from which they were derived. The presence of three aromatic rings complicated the spectra of these compounds, because of three overlapping patterns of absorptions characteristic of substituted benzene rings. The skeletal modes could be distinguished by comparing the spectra with those of the rearranged compounds. The skeletal modes were described by studying the spectra of specific related simple molecules. The description obtained could be simply adapted to describe the ethyl benzimidate skeletal modes in which there was more extensive mixing of modes. The skeletal modes of the N-benzoyl diphenylamines were not unambiguously described due to complications in this spectral region from other modes and due to lack of published spectra of analogous compounds.

Anomolous effects in the γ(C-H) modes of the imidates and esters were noticed and an explanation proposed in terms of repulsions due to the (O=C-O) and (O-C=N-H) groups. The vibrations thought to be reasonably localised in such bonds as (C=O) and (C=N) were studied by temperature variation and its effect on the absorptions. The compounds were studied by their ultra violet and nuclear magnetic resonance spectra which unfortunately were of little help in elucidating the structure.

The dipole moments of acetanilide and nine chlorine substituted derivatives were measured in benzene and some repeated in dioxan. Vector calculations showed that the preferred structure was trans(N-H, C=O) in all cases.

The infrared spectra of all compounds were recorded using high dilution to obtain monomeric species. The ν(N-H) and ν(C=O) absorptions were recorded. This study was extended to some 2'6'-dialkyl substituted acetanilides where two ν(N-H) and two ν(C=O) absorptions were observed.

As in the case of simple acetanilides 2-chlorine substitution was found to result in the molecules existing predominantly in the trans form. Substitution of the 2-position by three methyl groups again results in a trans structure being preferred, even when the ring was 2'6'-dialkyl substituted. The ultra violet spectra of the compounds were recorded in ethanol and showed a dramatic decrease in intensity of the absorption bands when the ring was alkyl substituted in the 2' and 6' positions.

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CHAPTER I

INTRODUCTION

1. Importance and History.
2. Background to Vibrational Analysis and Infrared Spectroscopy.
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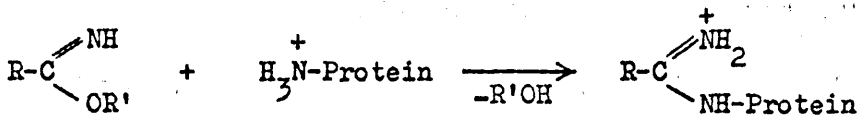
1. Importance and History

Compounds containing the (C=N) group, although having been known for almost a century, e.g.[1] and playing an important part in biological systems, have not been studied as comprehensively as analogous (C=O) and (C=C) systems.

Biochemically the use of imidates as starting material for peptide synthesis[2] and modification of proteins by reaction with imidates under mild conditions may become important.



The (-C=N-H) group appears also in several systems of pharmaceutical interest.

Generally these compounds are only reported as intermediates in synthesis and this is the case for the N-aryl aryl arylimidates which seem only to have received attention as starting reagents for rearrangement into benzoyl diphenylamines by the Chapman Rearrangement[3-6].

Hughes[7] has made a spectroscopic study of some aliphatic imidates and two benzimidates. There appears to have been no such study of the N-aryl aryl arylimidates. Despite the size of these compounds they represent an interesting system in which, because of the disposition of heavy masses on the imidate skeleton, there should be little coupling of the skeletal modes. With the exception of Prichard[8,9] and Hughes[7] the spectroscopic studies of imidate systems has been restricted to studies of the ν (C=N) and ν(N-H) group absorptions.

It was hoped that a complete vibrational analysis of the arylimidates and their products of rearrangement should enable one to estimate whether or not the Chapman Rearrangement reaction had gone to completion.

The products of rearrangement of the N-aryl aryl arylimidates have in some cases been found to exhibit optical activity by restricted rotation in the molecule[10].

2. Background to Vibrational Analysis and Infrared Spectroscopy

The Born Oppenheimer approximation, introduced to allow solution of the wave equation for molecular systems, states that the motions of the electrons in a molecule are so rapid that in studying the electronic properties of molecules the nuclei may be regarded as fixed. It is a consequence of this that electronic and vibrational motion can be separated. Thus the wave equation would be written:

$$\Psi \text{ total} = \Psi \text{ electronic} \cdot \Psi \text{ vibrational and rotational}$$

If during a vibration there is a change in dipole moment, the oscillation of charge produced may interact with the electric vector of electromagnetic radiation of the correct frequency. The appropriate radiation falls within the infrared region of the electromagnetic spectrum. Energy may be exchanged between the vibration and the applied radiation such that absorption of energy from the beam takes place according to the Planck equation. The energy of the quantum of radiation absorbed

$$\Delta E = h\nu \qquad \ldots\ldots \quad 1,1$$

being proportional to the frequency via Planck's constant h.

The simplest vibrating system is the diatomic oscillator. The potential energy of such a system U is given by:

$$U = \frac{1}{2} f q^2 \qquad \ldots\ldots \quad 1,2$$

f is the stretching force constant of the bond.

q is a displacement coordinate describing the extent of distortion of the bond from the equilibrium position.

Substitution in the Schrödinger wave equation yields the energies of the allowed vibrational states.

$$\varepsilon_v = (v + \tfrac{1}{2}) \quad \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \qquad v = 0,1,2 \qquad \ldots\ldots \quad 1,3$$

v is the vibrational quantum number.

μ is the reduced mass of the system.

Transitions are allowed between these energy levels governed by the selection rule that the vibrational quantum number can only change by $\pm$ 1.

Applying Boltzmann's distribution function it is found that nearly all the molecules are found in the ground (v = 0) state. One absorption frequency is allowed corresponding to a change of v = 0 to v = 1. The frequency of such an absorption can be calculated from equations 1,1 and 1,3.

Actual diatomic systems do not have the simple parabolic potential energy function. The spectra reveal the presence of overtone frequencies near integral multiples of the fundamental frequency in violation of the selection rule of the simple harmonic oscillator.

The potential energy is a function of the displacement coordinate q and may be expanded in a Maclaurin's series.

$$U(q) = U_{q=0} + \left(\frac{dU}{dq}\right)_{q=0} q + \frac{1}{2!}\left(\frac{d^2U}{dq^2}\right)_{q=0} q^2 + \frac{1}{3!}\left(\frac{d^2U}{dq^3}\right)_{q=0} q^3 + \qquad \ldots\ldots \quad 1,4$$

The first term defines the zero value of the system. Setting U = 0 at r = r equil., q = 0, sets $U_{q=0} = 0$.

At q = 0 the potential energy is a minimum and so the derivative is zero and the second term is zero.

If only the third term is used the approximation is that of simple harmonic motion. When the third and fourth terms are used to describe the potential energy which is substituted into the Schrödinger equation the energy levels obtained are:

$$\bar{\varepsilon}_v = \bar{\omega}_e \left(v + \tfrac{1}{2}\right) - \overline{\omega_e X_e} \left(v + \tfrac{1}{2}\right)^2 \qquad \ldots\ldots \quad 1,5$$

$$\text{where } \bar{\omega}_e = \frac{1}{2\pi c}\sqrt{\frac{k_e}{\mu}} \qquad k_e = \left(\frac{d^2U}{dq^2}\right)_{q=0}$$

$\bar{\omega}_e$ is the spacing of the energy levels in cm^{-1} if the potential curve were a parabola.

The coefficient $\overline{\omega_e X_e}$ of the squared quantum number term is the anharmonicity constant ($<< \bar{\omega}_e$) which describes the departure from the simple anharmonic system.

In the anharmonic system overtones are allowed. These are the result of the system absorbing one quantum of radiation, and before this is lost, receiving a second quantum. Thus their intensity is controlled by the chance of a double quantum absorption. The intensity of the fundamental absorption depends on the change of dipole μ of the bond with respect to its displacement coordinate q.

A polyatomic molecule containing N atoms will have (3N-6) normal modes of vibration; (3N-5) if the molecule is linear.

These normal modes of vibration involve displacements of several atoms in the molecule. If these coordinates are used in the expressions for the potential and kinetic energies these energy functions involve no cross terms of the form Q_iQ_j. This has the effect that the Schrödinger equation can be factorised into 3N-6 equations, one in each normal coordinate Q.

However, the form of the normal coordinates is usually not known.

The polyatomic vibrating system can be described in terms of any convenient set of coordinates. In terms of these coordinates the kinetic and potential energy expressions are formulated and substituted into the Lagrange equation of motion.

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{q}_i}\right) + \frac{\partial U}{\partial q_i} = 0 \qquad \ldots\ldots (1,6)$$

which leads to a set of 3N-6 simultaneous linear equations[11].

Wilson[12] showed that setting up the kinetic energy equation in terms of cartesian displacement coordinates and the potential energy equation (using the simple harmonic approximation, valid for amplitudes of vibration that are small compared with the interatomic distances) in terms of internal displacement coordinates, the secular equation, relating the absorptions of the system with the force constants, was of the form:

$$[G\,F - E\lambda] = 0 \qquad \ldots\ldots\ldots (1,7)$$

The F matrix contains the force constants of the system. The G matrix contains the masses and geometric information of the system and is defined[13] as:

$$G_{kl} = \sum_{i=1}^{3n} \frac{B_{ki}B_{li}}{M_i} \qquad \ldots\ldots (1,8)$$

The B matrix is the transformation matrix between the internal coordinates and the cartesian coordinates. The elements of the G matrix can be found readily from equations given by Wilson, Decius and Cross[13].

E is a unit matrix.

$\lambda = 4\pi^2\nu^2$ and ν is the vibrational frequency.

The Wilson equation (1,7) is mostly used in a computer programme to compare the absorption frequencies calculated from a trial set of force constants with the actual experimentally measured ones and to continue adjusting the trial set to obtain the optimum agreement. The form of the equation is such that there are as many unknown quantities as known ones so that there is an infinity of possible solutions. The eigenvectors yielded by the equation define the displacements of the various atoms involved in each normal mode and so describe the normal vibrations.

It is possible to make several approximations without attempting a full force field calculation of a system which is often not possible for large systems. The Wilson equation can be written:

$$\begin{bmatrix} D_{11}-\lambda & D_{12} & D_{13} & \cdots \\ D_{21} & D_{22}-\lambda & D_{23} & \cdots \\ D_{31} & D_{32} & D_{33}-\lambda & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{bmatrix} = 0 \qquad \ldots\ldots \quad 1,9$$

The GF terms have been rewritten as D.

$$D_{ij} = \sum G_{it} F_{tj}$$

It is the off-diagonal terms D_{ij} $i \neq j$ that determine the extent of coupling between the various vibrations. If all these terms are zero with the exception of D_{11} then one root is obtained:

$$D_{11} = \lambda$$

This means that the normal vibration involves only one coordinate. Such vibrations are characteristic frequencies of the bond in which the vibration is localised. It is sometimes possible that a normal mode is localised within a group of atoms, e.g. CH_3 and are termed group frequencies characteristic of the group in which they are localised. Normal vibrations, however, in general involve motions of several atoms within a molecule. The vibrations of the bonds within these groups of atoms are said to be coupled.

If λ is close to D_{11} the approximate solution of the secular equation is:

$$\lambda = D_{11} + \frac{D_{12} \cdot D_{21}}{D_{11} - D_{22}} + \frac{D_{13} \cdot D_{31}}{D_{11} - D_{33}} +$$

The difference $(D_{11} - \lambda)$ will be small if each of the members of the right hand side are small. This will be so if either the difference $D_{11} - D_{ii}$ is large or the product $D_{1i} \cdot D_{i1}$ is small.

The diagonal elements are given by

$$D_{11} = G_{11} F_{11} + G_{12} F_{21} + G_{13} F_{31} +$$

$$D_{22} = G_{12} F_{21} + G_{22} F_{22} + G_{23} F_{32} +$$

the major contribution is from members of the type $G_{ii} F_{ii}$ so it is a reasonable approximation to discuss the differences of the sort

$$G_{11} F_{11} - G_{22} F_{22}$$

This difference will be large if G_{11} and G_{22}, or F_{11} and F_{22} are very different.

The implication of this is that there will be little coupling between the vibration of a light atom and that of a heavier atom provided the force constants of the bonds containing these atoms are similar.

Alternatively if the masses of two vibrating atoms are similar but the force constants of the two bonds are different again coupling would be small.

Volkenstein, Elyashevitch and Stepanov[14] give some empirical rules for predicting the effects of the D_{ij} D_{ji} products.

1. Coupling can be extensive between stretching vibrations only if the bonds have a common atom.
2. Coupling is possible between angle deformation and bond stretching if the bond forms one side of the angle.
3. Angle deformations may couple only if they have a common bond.
4. Strong coupling may occur between angle deformation vibrations involving hydrogen and the stretching of an adjacent bond with a heavier atom. The coupling diminishes with increasing mass of the hydrogen bearing atom.

The possibility of coupling is decided by the shape of the molecule. Using the above rules it is possible to decide which vibrations are liable to couple. The extent to which coupling takes place is decided by force constants and masses involved. If a force constant is known in a molecule it can only be transferred to another molecule if the bond in the second molecule is in a similar chemical environment. Whenever possible interaction force constants of the type f_{ij} are transferred. These off-diagonal elements of matrix F give a measure of the coupling of two vibrations described by coordinates q_i and q_j.

To determine the vibrational independence of a group vibration the characteristic group frequencies are calculated for the group attached to an infinite mass and compared with the experimentally measured values. This was done by King and Crawford for the methyl group[15]. Bratôz and Besnainou[16] resolved the carbonyl frequency for various compounds into contributions from the (C=O) oscillator force constant 10.5×10^{2} N m^{-1} and contributions from next neighbours. In the compounds studied the main contribution was from adjacent ν(C-C). For saturated ketones the carbonyl absorption 1706 cm^{-1} was found to comprise 1574 cm^{-1} from the ν(C=O) oscillator, 47.1 cm^{-1} from adjacent ν(C-C), 6.8 cm^{-1} from β(O=C-C) 7.2 cm^{-1} from β(C-C-C) and 2.5 cm^{-1} from β(C-H). Thus there are contributions from stretching and in-plane bending modes.

Changes in hybridisation of the carbon orbitals have a marked effect on the force constant of the (C-C) bond, for example:

Herzberg[17] quotes the force constant of the (C≡C) bond as 15.59×10^{2} N m^{-1}, the (C=C) bond as 9.6×10^{2} N m^{-1} and the (⪧C-C⪦) bond as 4.5×10^{2} N m^{-1}. Intermediate values of the force constant of a (C-C) bond obtained from the appropriate diagonal entry of an adjusted force constant matrix would give some indication of the multiplicity of the bond.

For a transition from the ground state to the first excited state, where the molecule has one quantum of energy in one vibrational mode, the probability of such a transition is dependent on the integral

$$\int \psi_o \, \mu \, \psi_i \, dt$$

μ is the dipole moment of the molecule.

ψ_o is the ground state wave function.

ψ_i is the excited state wave function.

If the integral is zero then the probability of the transition is zero and the transition is forbidden in the infrared.

The integral will be zero unless the product $\psi_o \, \mu \, \psi_i$ is totally symmetric.

The dipole moment μ is a vector quantity and can be split into components along the three cartesian axes, i.e. μ_x, μ_y, μ_z. Only one of the integrals

$$\int \psi_o \mu_k \psi_i \, dt \quad (k = x,y \text{ or } z)$$

need be non-zero.

The ground state wave function ψ_o is always totally symmetric. μ_k and ψ_i must have the same symmetry to give a totally symmetric product. The symmetry properties of the dipole moment components are those of translation vectors along the same axis. The wave function ψ_i has the same symmetry properties as those of the vector describing the vibrational mode i of which ψ_i is the wave function. Thus if the vibrational mode has the same symmetry properties as translation in the x,y or z directions the vibrational transition from the ground state of that mode will be infrared active.

In the case of Raman active transitions the transition probability depends on the vibrational mode having the same symmetry properties as that of the polarisability of the molecule. The polarisability, a measure of the ease with which the molecular electron distribution can be distorted is a tensor quantity, i.e. a 3 x 3 array of components α_x^2, α_{xy}, α_{xz}, α_{yz}, α_y^2, α_{yz}, α_{zx}, α_{zy} and α_z^2. Thus there are 6 distinct integrals of which one must be non-zero for the transition to be Raman active. For this to be so, the vibrational mode i must have the same symmetry properties as a binary combination of translations.

The intensity of an infrared absorption depends on the change of dipole moment with respect to changes in the displacement coordinate q. The Raman intensity depends on the corresponding derivative of the polarisability. It is found that polar bonds, e.g. (C=O) give strong infrared absorptions whereas more symmetric bonds e.g. (C=C) give a strong Raman shift.

In addition to the absorptions described by the normal coordinates of the system, the spectrum of a compound can often contain absorptions due to overtones. These are due to the fortuitous absorption of a second quantum whilst in an excited state, these are of low intensity. Combination tones can also occur, these being due to two vibrational modes receiving quanta at the same time and again these will show low intensity. Difference bands have been observed; these being the result of a molecule absorbing a quantum of energy whilst in the process of losing that already obtained. Sometimes two vibrations can have the same frequency and lead to only one absorption due to the accidental degeneracy. If they are of different symmetries the two absorptions are merely superimposed. If, however, the symmetries are the same, exchange of energy can take place between the two, this is termed Fermi resonance. When two such vibrations are almost of the same frequency the effect of such energy exchange is to decrease the frequency of the lower and raise that of the higher whilst equalising the intensities of the absorption bands.

It is possible to use a product rule, derived by Teller and Redlich and a sum rule derived by Decius and Wilson to check the various assignments made during the course of a study. These rules become particularly useful where deuteration studies are made.

Deuteration was not carried out on the ethyl benzimidates as it was only possible to deuterate the (N-H) this would have had little effect on the simplification of the spectrum.

When the ~~secular determinant~~ determinantal equation (1,9) is expanded a polynomial in λ of degree n is obtained. The coefficient of λ^n is unity and the constant term is obtained when $\lambda = 0$. This constant term is equal to the product of the roots λ_k of the polynomial.

Thus $$\prod_k \lambda_k = \left|GF\right| = \left|G\right|\cdot\left|F\right| \qquad \text{......} \quad 1,10$$

If the molecule is substituted isotopically and such substitution is assumed to have negligible effect on the force field (reference 17, Table 39)

$$\prod_k \lambda_k^i = \left|G^i\right| \left|F\right| \qquad \text{......} \quad 1,11$$

The superscript i refers to the isotopic species.

$$\frac{11}{10} \text{ gives } \quad \frac{\prod_k \lambda_k^i}{\prod_k \lambda_k} = \frac{\left|G^i\right|}{\left|G\right|} \qquad \text{......} \quad 1,12$$

Teller[18] and Redlich[19] derived the general product rule.

$$\frac{\nu_1^i \nu_2^i \text{.....}}{\nu_1 \nu_2 \text{.....}} = \left[\left(\frac{m_1}{m_1^i}\right)^{\alpha} \left(\frac{m_2}{m_2^i}\right)^{\beta} \text{....} \left(\frac{M^i}{M}\right)^{t} \left(\frac{I_x^i}{I_x}\right)^{\delta x} \left(\frac{I_y^i}{I_y}\right)^{\delta y} \left(\frac{I_z^i}{I_z}\right)^{\delta z} \right]^{\frac{1}{2}}$$

ν are the vibrational frequencies; $\lambda = 4\,\pi^2\,\nu^2$.

M is the total molecular mass.

m_1 m_2 .... etc., are the masses of the individual atoms in sets of identical nuclei transformed into each other by the symmetry operations of the group to which the molecule belongs.

t is the number of translations of the species considered.

$\delta x, \delta y, \delta z$ the powers to which the inertia moments I are raised, they are 1 or 0 depending on whether rotation about the axes x,y,z has the same symmetry as the vibrations considered, α and β terms are the numbers of vibrations each set of atoms contributes to the symmetry species considered.

If the potential and kinetic energies of the system are set up in external symmetry coordinates (reference 13, section 6,4) the G elements $G_{kk} = \mu_k$, μ_k being the reciprocal mass of the atom of the set (transformed into each other by the symmetry operations), from which the coordinates are constructed. This has the effect that

$$\frac{\prod \lambda^{i}}{\prod \lambda} = \frac{\mu_1' \mu_2' \cdots\cdots \mu_k'}{\mu_1 \mu_2 \cdots\cdots \mu_k}$$

over k.

This is then only valid if the symmetry species considered involve no translation or rotation. If so the ν_k related to these modes would be zero and the product indeterminate. To overcome this the two conditions eliminating the ratios of the vanishing frequencies are introduced.

$$\frac{\nu_t^{i}}{\nu_t} = \left(\frac{M}{M'}\right)^{\frac{1}{2}} \qquad \text{for translation}$$

$$\frac{\nu_R^{i}}{\nu_R} = \left(\frac{I}{I'}\right)^{\frac{1}{2}} \qquad \text{for rotation}$$

M is the total mass of the molecule, I the moment of inertia about the principal axis.

In addition to the Product Rule there is the Sum Rule of Decius and Wilson[20]. The sum of the roots of the polynomial obtained by expanding the secular determinant in the form

$$\begin{vmatrix} F_{11}/m_1 - \lambda & F_{12}/(m_1 m_2)^{\frac{1}{2}} & \cdots\cdots \\ F_{21}/(m_2 m_1)^{\frac{1}{2}} & F_{22}/m_2 - \lambda & \cdots\cdots \\ \cdots\cdots & \cdots\cdots & \end{vmatrix} = 0$$

(set up using cartesian displacement coordinates) is given by the coefficient of the λ^{n-1} term. This can be seen to be of the form

$$\sum_j F_{jj}/m_j = \sum_j \lambda_j \qquad \cdots\cdots \; 1,13$$

For chemical exchange reactions involving isotopic substitution, e.g. $H_2O + D_2O = 2HDO$ the rule is stated as

$$\Sigma_\alpha n_\alpha \Sigma_k \nu_{\alpha k}^2 = 0 \qquad \ldots\ldots \quad 1,14$$

The subscript α identifies an isotopic form with specified isotopic atoms in each of the identified atomic positions, n_α is an integer +ve for reactants -ve for products. The chemical isotopic exchange reaction is balanced at each atomic position separately. The sum is over the molecular forms α and over the fundamental modes of vibration k. For the exchange reaction above the rule is written

$$\sum_i \nu^2 H_2O + \sum_i \nu^2 (D_2O) = 2 \sum_i \nu^2 HDO$$

are the fundamental absorption frequencies. The sum of the λ's in terms of the ν's is

$$4\pi^2 \Sigma_\alpha \Sigma_k n_\alpha \nu_{\alpha k}^2 = \Sigma_\alpha \Sigma_k n_\alpha \lambda_k^{(\alpha)}$$

$$= \Sigma_j F_{jj} (\Sigma_\alpha n_\alpha / m_j^{(\alpha)})$$

from (1,13)

$\Sigma_\alpha n_\alpha / m_j^{(\alpha)}$ is the sum of the masses^{-1} on both sides of the equation with coefficient +1 for reactants and -1 for products. Thus the sum is zero for the balanced exchange reaction and

$$4\pi^2 \Sigma_\alpha \Sigma_k n_\alpha \nu_{\alpha k}^2 = 0$$

so $$\Sigma_\alpha \Sigma_k n_\alpha \nu^2_{\alpha k} = 0 \qquad \text{which is (1,14)}$$

The ideal phase for studying the spectra of molecules is the gas phase. At low pressure the molecules can move without significant intermolecular interaction and the energy levels of the system are determined by intramolecular effects. The effects of rotational changes, which occur during the individual vibrations, can be observed as fine structure on the vibrational absorptions.

The band shapes produced can lead to useful structural information.

It was not possible to obtain gas phase spectra of the ethyl benzimidates because of their low stability and the N-aryl aryl imidates rearranged before they vapourised.

In solution molecules undergo transitions between their energy levels which are perturbed by the dielectric field of the solvent. Rotations tend to be hampered, leading to the loss of fine structure on the vibrational absorptions but because the rotations are not completely restricted the absorption bands appear broad. In certain solvents interaction in the form of hydrogen bonding between solute and solvent can occur. The absorptions due to such systems are broader than those observed in the unbonded system. At high concentration of solute, solute-solute interactions can take place leading to aggregation and intermolecular hydrogen bonding which again broadens the relevant absorptions. On dilution of such solutions with further solvent the broadening can be observed to decrease until eventually the solute molecules are sufficiently diluted with solvent that individual molecules are again observed in the dielectric field of the solvent.

In the solid phase the molecules are packed into crystal lattices. There is no freedom for rotations of the molecules which leads to a sharpening of the absorption bands. The molecule is now in strong crystal fields which can have a marked influence on the appearance of the spectrum.

The symmetry and number of molecules in the unit cell now become significant in determining the activity of a particular mode. In addition to this overtones and combination tones usually weak or unobserved can become apparent due to the intensity no longer being spread over the rotational band contour. The symmetry is generally lower in the solid state making more vibrations infrared active.

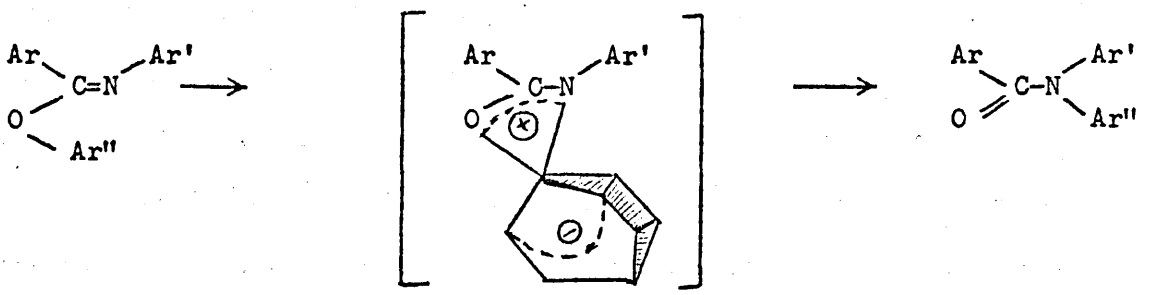
In the liquid phase the molecules are in a similar state to that of a high pressure gas. There is usually no preferred orientation rather a range of environments. There is then considerable freedom and the possibility that the molecular symmetry be distorted during collisions. In the crystal the selection rules tend to be rigidly obeyed but in the liquid state molecular symmetry can be completely removed due to collisions so that all vibrations become infrared active to some degree.

In this study an attempt was made to assign the spectra of some arylimidates. It was not possible to carry out a normal coordinate analysis on these compounds because of their size. It was felt that it was unreasonable to consider the benzene rings as point passes and the presence of three rings made the systems too large to handle.

The assignments were therefore made by comparison with related structures. To help the assignments the N-aroyl diarylamines were prepared by Chapman rearrangement of the arylimidates.

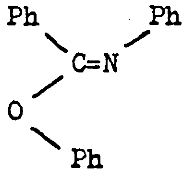
3. The Chapman Rearrangement

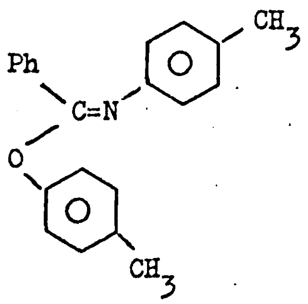
The thermal rearrangement of N-aryl aryl benzimidates to N-benzoyl diphenylamines is known as the Chapman rearrangement. This rearrangement is shown schematically below, A being rearranged into C.

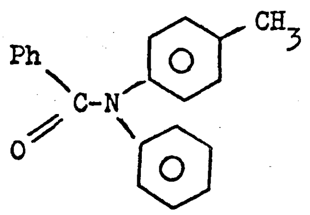


(A) (B) (C)

Chapman showed that the rearrangement was intramolecular by heating a mixture of (D) and (E) and obtaining no mixed product (F).

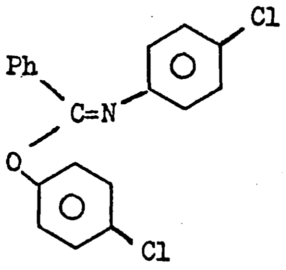






(D) (E) (F)

This was later confirmed by Wiberg and Rowland[22] using X-ray crystallographic techniques and infrared spectroscopy to examine the products of heating (D) and (G).



(G)

Chapman's original kinetic study of the rearrangement was carried out in the solid state using the freezing point of the melts to follow the rearrangement. The rearrangement was found to follow first order kinetics.

From the study of the rates of rearrangement of N-aryl aryl benzimidates varying only in the nature and position of the aryloxy substituent, Chapman[4] found that the rate was associated with the acidity of the phenol from which the imidate was derived.

Bennet[23] suggested that the reaction could be initiated by a nucleophilic attack by nitrogen on the aryloxy ring. This was confirmed by Chapman[6].

When the aryl group on the nitrogen was varied Chapman[4] found that electron withdrawing substituents made the nitrogen electrons less available for nucleophilic attack. Wiberg and Rowland[22] studied the rearrangement in solution in diphenyl ether, verifying that the rearrangement followed first order kinetics and that it was essentially a nucleophilic displacement of an aryl ring. They also discussed the entropy effect that caused ortho-substituents on the aryloxy ring to increase the rate of rearrangement over that of the analogous para-substituted compound.

This was ascribed to steric factors tilting the ring and thus lowering the entropy decrease required to go from reactant to the four-membered intermediate. This effect was examined more closely by Relles[24].

CHAPTER II

EXPERIMENTAL

1. Infrared Studies

(a) Instrumental.

(b) Solvents.

(c) Sample preparation:
solid, liquid, solution.
Cells. Calibration.

2. Dipole Moment Studies

(a) Instrumental.

(b) Solvents.

(c) Sample preparation and procedure.

(d) Treatment of results and derivation
of equations.

3. Preparation of Compounds

(a) Anilides.

(b) Esters.

(c) Imidates.

(d) N-aryl imidates.

(e) N-aroyl diarylamines.

1. Infrared Studies

(a) Instrumental

Infrared spectra were recorded using the Perkin Elmer 457 and the Beckman IR9 spectrometers.

The P.E.457 instrument is a double beam optical null grating spectrometer. The optical system utilises an f/5 monochromator two gratings and a reflecting optical system employing planar and aspheric mirrors. The range of the instrument is from 4000 to 250 cm^{-1}. Using a normal slit the resolution is 4 cm^{-1} at 3000 cm^{-1} and 2 cm^{-1} at 1000 cm^{-1}. The chart drive is synchronised with the monochromator so that readings may be taken from the chart scale. The P.E.457 also incorporates a x 10 abscissa expansion unit. This instrument was used to record solution spectra and spectra of compounds in KBr matrix form.

The Beckman IR9 instrument employs a double beam optical null mode of operation. High resolution is obtained by the prism grating optical system with a double monochromator. The range of the instrument is from 4000 - 400 cm^{-1}. Readings are made directly from the grating and eliminate chart errors. The instrument allows a choice of slit programme and gain settings so that an optimum resolution can be obtained. For narrow slit widths a much higher gain is required so a longer period response and scan speed are required to compensate for the increase in instrument noise. The IR9 is capable of resolving to 0.25 cm^{-1} throughout most of its range. The IR9 was used for accurate determinations on liquid samples and for some temperature studies.

For the variable temperature study the Beckman TEM 1C temperature controller was used. Dry-ice acetone was used as the coolant in this study over the range -20°C - +20°C. The coolant was removed for temperature studies above 20°C.

(b) Solvents

Dilute solutions were required to minimise the extent of aggregation of solute. It was necessary to use pure solvents to minimise interaction of impurities with the solute under study. The study of monomeric species involved examination of the spectra for the effects of intramolecular hydrogen bonding, it was thus essential to have dry solvent to avoid added complications of intermolecular hydrogen bonding between solute and water.

Carbon tetrachloride

Spectrosol carbon tetrachloride was allowed to stand overnight over phosphorus pentoxide. The solvent was then distilled using a system that excluded water vapour. The dry solvent was then stored in a glove box containing nitrogen under a pressure of 5 lb in^{-2} and calcium chloride desiccant.

Solutions were made up under these conditions.

Cyclohexane

Spectroscopic grade cyclohexane was dried by distillation from phosphorus pentoxide.

Tetrachloroethylene

Spectroscopic tetrachloroethylene was used directly from a fresh bottle without any drying.

(c) Sample preparation

KBr discs

Spectroscopic grade KBr was baked at 180°C for several hours. It was allowed to cool in a desiccator where it was subsequently stored.

10 mg of sample was finely ground in an agate pestle and mortar. 100 mg of KBr was added and the mixture ground together. 50 mg of the mixture was transferred to a Wilks Scientific Corporation mini-press and

compacted under a torque of 12 lb ft^{-1} for 1 min. When the spectrum was recorded a beam attenuator was used in the reference beam.

Liquid samples

Routine liquid spectra were recorded using a thin film of the sample between KBr plates. Accurate spectra were recorded using a film of path length 0.007 mm between KBr plates using the Perkin Elmer demountable cells 0482 - 0986, (being semi-permanent cells with a series of replaceable teflon spacers of varying path length). A beam attenuator was used in the reference beam.

Solution studies

For the low concentration study of monomeric anilides special cells were used. These were cells of a fixed path length of 12 mm made from teflon machined to take KBr windows. They were found to be well matched by recording a baseline spectrum with both cells containing carbon tetrachloride.

For the other solution spectra the Perkin Elmer demountable cells described above were used with spacers of 1 mm, 0.5 mm and 0.1 mm.

The variable temperature studies were carried out using sealed cells incorporating silver chloride windows with a path length of 0.1 mm.

Before any spectrum was recorded a spectrum of polystyrene was recorded and compared with a standard spectrum.

Anilides

The anilides were recrystallised again from chloroform, finely ground and baked at 80°C under reduced pressure.

0.002 mol dm^{-3} solutions of each compound in dry carbon tetrachloride were made up in a glove box containing dry nitrogen under a pressure of 5 lb in^{-2} and transferred to the 12 mm path length cells described.

The infrared spectrum of each solution was recorded over the ranges 3300 - 3600 cm^{-1} and 1650 - 1750 cm^{-1} with dry carbon tetrachloride as reference using the Perkin Elmer 457 instrument on slow scan with x 10 abscissa expansion.

A routine KBr matrix spectrum of each compound was recorded on the same instrument.

Ethyl esters and imidates

A routine liquid film spectrum of each compound between KBr plates was recorded using the P.E.457 spectrometer.

An accurate spectrum of each compound, in the form of a film of path length 0.007 mm between KBr plates, was recorded using the Beckman IR9 spectrometer.

N-aryl aryl arylimidates and N-aroyl diarylamines

A KBr matrix spectrum of each compound was recorded using the P.E.457. 0.02 mol dm^{-3} solutions of each of the compounds were made using cyclohexane and tetrachloroethylene as solvents. The spectra of these solutions were recorded using the P.E.457 over the range 4000 - 250 cm^{-1} in the cells described, using pure solvent in the reference beam.

To aid the assignments the infrared spectra of various related compounds were recorded in the phase prevailing at room temperature, using the P.E.457 instrument.

Raman spectra

The Raman spectra were recorded using the Carey 81 Laser Raman spectrometer. This instrument, part of the Intercollegiate Research Service at Imperial College, uses an argon-krypton laser as the source. Samples of any colour can be processed, the principal wavelengths available for excitation being 488, 514.5, 568.2 and 647.1 nm.

The solid state spectra were recorded using a powder sample pressed on to a concave recess in a steel rod and were illuminated directly. Liquid samples were held in a glass capillary which was inserted into the laser beam.

2. Dipole Moment Studies

(a) Instrumental

The dielectric permittivities of a series of solutions were determined using the Dipolmeter, Type DMO1, manufactured by the Wissenschaftlich-Techniche Werkstatten, GMbH. This instrument is an internally thermostatted, heterodyne beat apparatus in which the arithmetic difference in the frequency of two oscillators is detected as a trace on a cathode ray tube. The oscillations are brought into superposition and after amplification the resulting beats are made visible on the cathode ray tube. Observations can be made to within fractions of a beat frequency of one cycle.

The dielectric measuring cell with a capacity of 20 cm^3 has gold coated interior plates. This cell is connected in parallel with a measuring condenser and forms part of one oscillating circuit. By tuning the measuring condenser the two capacitances can be adjusted so that the resulting frequency is equal to that of the standard oscillator. The result is a straight line on the cathode ray tube.

Internal standard condensers allow control of the calibration independently of the measuring condenser. A precision dial can be read with an accuracy of 1 in 10^5 which gives an accuracy of ± 0.0002 in the relative permittivity value calculated. For liquids a measuring frequency of 1800 kHz is used and the indicating and measuring sensitivities are 1×10^{-6} and 4×10^{-4} respectively. This instrument was calibrated by determining the scale reading of the measuring condenser for two pure liquids of known dielectric permittivity. A linear relationship between dielectric permittivity and scale reading was observed and hence the slope of the graph was determined and used for subsequent evaluation of dielectric permittivity.

The densities of the solutions were measured using a Warden's Pyknometer, the volume of which was determined at 25°C using boiled out deionised water. The specific volume of the pure solvent was determined for each series of measurements.

Table 1

Calibration of Dipolmeter

Solvent	Scale Reading	Dielectric Permittivity at 25°C (mean literature value)
Benzene	3747.8	2.2725
Carbon Tetrachloride	3636.0	2.2274
Air	591.9	1.0006

Benzene/air; $\frac{\Delta\varepsilon}{\Delta S} = \frac{1.2719}{3155.9} = 4.0304 \times 10^{-4}$

$\Delta\varepsilon$ difference in dielectric permittivity.

ΔS difference in scale reading

Carbon tetrachloride/air $\frac{\Delta\varepsilon}{\Delta S} = \frac{1.2268}{3044.1} = 4.0304 \times 10^{-4}$

Hence:

$$\varepsilon_x = 2.2725 - 4.03 \times 10^{-4} \left(\overset{S_x - S_{C_6H_5}}{\cancel{2.2725 - S}_x}\right)$$

ε_x and S_x are the dielectric permittivity and scale reading (respectively) for the unknown solution.

(b) Solvents

Benzene

Analar benzene was cooled until $\frac{4}{5}$ of the bulk had frozen. The remaining $\frac{1}{5}$ was discarded. The solid benzene was thawed out and used without further purification.

Dioxan

A Winchester of dioxan was cooled until $\frac{4}{5}$ of it had frozen. The remaining $\frac{1}{5}$ was discarded. 600 cm^3 of the thus freeze dried dioxan was refluxed for $\frac{1}{2}$ hr with anhydrous stannous chloride to remove traces of peroxide. The dioxan was filtered and cooled before 2 g of sodium wire was added. It was then refluxed for $\frac{1}{2}$ h to dry it further. Finally the dry dioxan was distilled and used immediately.

(c) Sample preparation

Anilides

The solubility of these compounds in carbon tetrachloride (the solvent used for the infrared study) was too low to allow accurate measurements to be made.

Benzene was used as solvent.

The compounds were finely ground before use. Accurately weighed amounts of the sample were transferred to a series of conical flasks of known weight. Warm, dry benzene was added to each and the flasks gently swirled to dissolve each sample. The flasks were stoppered and allowed to cool before being reweighed. The dielectric permittivity of each solution was then determined.

Esters and imidates

Careful weighing of each liquid sample allowed a series of solutions of each, of known weight fraction in benzene, to be prepared.

Experimental procedure

The dipole meter was switched on and allowed to stand for two hours to reach its working temperature of 40°C. The cell was connected via a pump to a water bath maintained at 25.0 ± 0.02°C. A series of solutions in benzene of the compound whose dipole moment was required were prepared, each of accurately known weight fraction. Before each measurement the cell was rinsed out with sodium dried ether and the vapour removed by a current of dry nitrogen gas. The solution under test was poured slowly into the cell to avoid trapping air bubbles. The solution was allowed to reach 25°C. At equilibrium several determinations of scale reading were made and an average taken. The readings were corrected for non-linearity of the measuring condenser/dielectric permittivity relationship, using a calibration graph supplied with the instrument. The dielectric permittivity was calculated from this scale reading.

The density of each solution was measured at 25°C. Dielectric permittivities were found to be linear with weight fraction over the range of concentrations studied.

3. Preparation of Compounds

(a) Anilides

Preparation of 2,2,2-trichloroacetanilide

1 mol equivalent quantity of freshly distilled aniline was dissolved in a solution of 5 parts v/v glacial acetic acid and 5 parts v/v of saturated sodium acetate solution.

The mixture was chilled by standing in ice water. It was then treated slowly and with constant shaking with a $1\frac{1}{2}$ mol. equivalent quantity of trichloroacetyl chloride. After being allowed to stand for a few minutes the product was removed by filtration. It was washed with a 50% v/v solution of aqueous acetic acid and crystallised from ethanol. It was then recrystallised to constant melting point from the same solvent.

By this general method the following compounds were prepared:

	m.p/°C	Literature m.p/°C	Reference
2-chloroacetanilide	135-6	135-8	89
2-chloro-4'-chloroacetanilide	168-9	168	90
2-chloro-4'-bromoacetanilide	175-6	170-3	89
2,2-dichloroacetanilide	115.5-6.5	116-7	91
2,2-dichloro-4'-chloroacetanilide	134-5	137-8	92
2,2-dichloro-4'-bromoacetanilide	146-7	146-7	93
2,2,2-trichloroacetanilide	94-5	94.5-5.5	94
2,2,2-trichloro-4'-chloroacetanilide	126-7	127-8	92
2,2,2-trichloro-4'-bromoacetanilide	129-30.5	129-30.1	95
2-chloro-2',6'-diethylacetanilide	133-4	133.4-34	96
2,2-dichloro-2',6'-diethylacetanilide	168-9	†	†
2-chloro-2',6'-dimethylacetanilide	145-5.5	†	†
2,2,2-trimethylacetanilide	130-1	127-9	98
2,2,2-trimethyl-2',6'-dimethylacetanilide	197-8	†	†
2,2,2-trimethyl-4'-chloroacetanilide	148.5-9	148-9	92

† Not recorded in the literature.

The following compounds were commercially available and were recrystallised to constant melting point from ethanol.

	m.p/°C	Literature m.p/°C	Reference
Acetanilide	115-7	115-6	98
4'-chloroacetanilide	175-6	172-3	98
4'-bromoacetanilide	165-7	168	98

The preparation of 2',6'-diethylacetanilide

2',6'-diethylaniline was dissolved in sodium dried diethyl ether and the solution cooled using an ice-salt bath. A $1\frac{1}{2}$ mol equivalent quantity of acetyl chloride dissolved in diethyl ether was carefully added dropwise with constant cooling and shaking.

The aniline chloride formed by reaction of the aniline with evolved HCl was removed by filtration and the product crystallised from the ether filtrate. The product was recrystallised to constant melting point from the same solvent.

Using this general method the following were prepared.

	m.p/°C	Literature m.p/°C	Reference
2',6'-diethylacetanilide	138-9	137-8	97
2',6'-dimethylacetanilide	178-9	177	98
2-methylacetanilide	108-8.5	105-6	98

(b) Esters

A series of esters were prepared using the following general method.

25 g of the relevant acid was refluxed for 16 h with 250 cm^3 of 95% ethanol and 10 cm^3 of concentrated sulphuric acid. The product was poured into 250 cm^3 of water and the crude ester extracted three times with 200 cm^3 of diethyl ether. The 600 cm^3 extract was washed with 400 cm^3 of saturated sodium bicarbonate solution. The ethereal layer was

washed with 600 cm^3 of water and dried over anhydrous sodium sulphate overnight. The ether was removed and the ester distilled under reduced pressure.

By this method the following esters were prepared.

Ethyl-ortho-toluate
Ethyl-meta-toluate
Ethyl-para-toluate
Ethyl-ortho-chloro-benzoate
Ethyl-meta-chloro-benzoate
Ethyl-para-chloro-benzoate

Ethyl benzoate was prepared by distillation of a commercial sample which had been dried over anhydrous sodium sulphate.

(c) Imidates

Ethyl benzimidate

The hydrochloride

Absolute ethanol was dried by the method described by Vogel[25]. Dry HCl was passed into a mixture of 51 cm^3 of benzonitrile and 100 cm^3 of sodium dried ether which was maintained at -5°C by an ice-salt bath. When 18 g of gas had been absorbed 23 g of dry absolute ethanol were added. The flask was sealed and transferred to a refrigerator and left until the hydrochloride crystallised.

The imidate

The hydrochloride was removed by filtration, quickly ground and stored at 0°C. A paste of twice the quantity of potassium carbonate required to neutralise the yield of hydrochloride was transferred to a conical flask cooled by standing in an ice-salt bath. 150 cm^3 of sodium dried ether was added.

The hydrochloride was added slowly over $\frac{1}{2}$ h to the contents of the conical flask, with continual stirring at -5°C. The ether layer was then decanted on to anhydrous sodium sulphate and dried for 2 h. The ether was removed by distillation under reduced pressure. The crude imidate was distilled without using an air leak, bumping stones used to control the bumping, at the lowest pressure available.

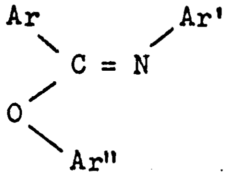
The following were prepared by a similar method. More ether was required initially to keep the solid cyanides in solution.

Ethyl benzimidate
Ethyl-meta-chloro-benzimidate
Ethyl-para-chloro-benzimidate
Ethyl-meta-toluimidate
Ethyl-para-toluimidate

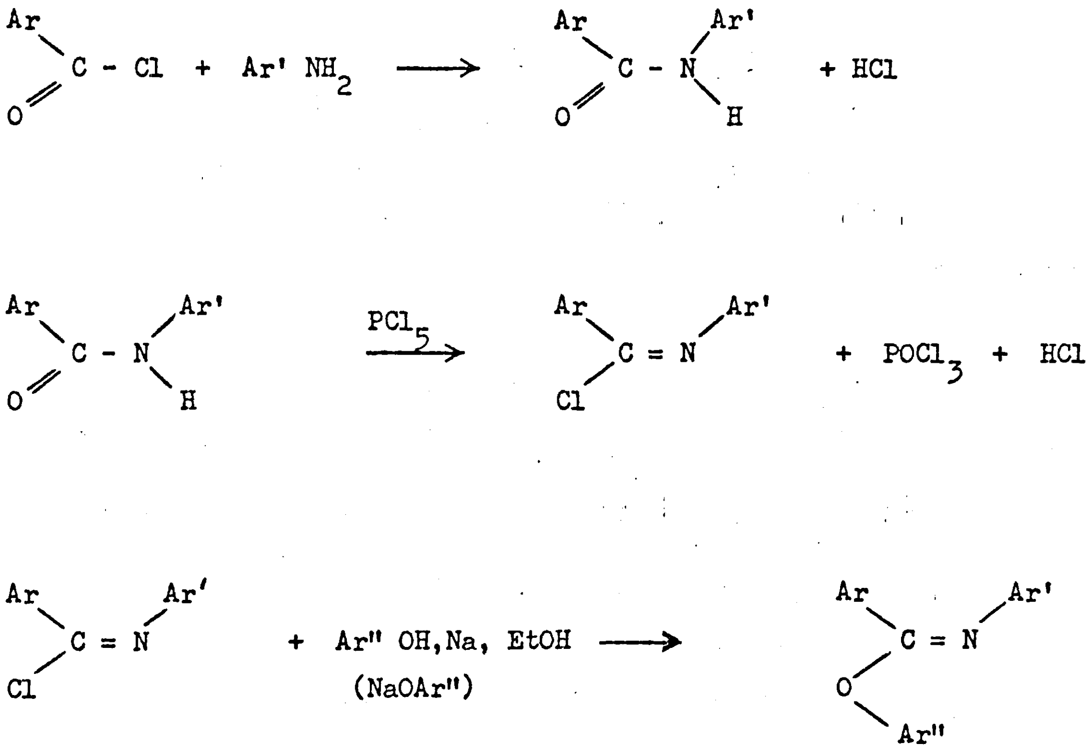
The ortho derivatives could not be prepared by this method.

Fig. 1.

N-Aryl Aryl Arylimidates



General Reaction Scheme:



(d) N-Phenyl arylbenzimidates

N-Phenyl benzimidoyl chloride

25 g of freshly dried benzanilide and 25.5 g of phosphorus pentachloride were heated together on a water bath in a flask carrying a reflux condenser and calcium chloride tube, cell joints being liberally greased to exclude moisture. When the evolution of hydrogen chloride had ceased the by-product, phosphorus oxychloride was removed by distillation under reduced pressure. Finally the product N-phenyl benzimidoyl chloride was distilled at 160°C under a pressure of 12 mmHg coming over as a golden liquid which crystallised in the receiving flask with a yield of 85%.

N-Phenyl phenyl benzimidate (I)

2 g of sodium metal were dissolved in 250 cm^3 of absolute ethanol then 8.2 g of freshly crystallised phenol were added and dissolved to give a solution of sodium phenate.

This solution was cooled and 19.05 g of N-phenyl benzimidoyl chloride dissolved in sodium dried ether was added with cooling and stirring. There was a clouding of the solution. Thus mixed the solution was left to stand at room temperature in a sealed flask. The excess solvent was then removed on a rotary evaporator and the residue, a thick oil, poured into 1500 cm^3 of water where the oil slowly solidified.

The crude product was crystallised from ethanol and recrystallised from the same solvent to constant melting point m.p. 105-105.5°C (lit.[22] 104.2 - 105°C) [Found: C, 83.18; H, 5.72; N, 5.16%; $C_{19}H_{15}NO$ requires C, 83.49; H, 5.50 and N, 5.12%].

By the same general method the following compounds were prepared using equimolar quantities.

	Compound	Experimental m.p/°C	Literature m.p/°C	Reference
II	N-phenyl-p-chlorophenyl benzimidate	93 - 3.5	92 - 3	3
III	N-phenyl-m-chlorophenyl benzimidate	70.5 - 1	71	4
IV	N-phenyl-o-chlorophenyl benzimidate	90 - 90.5	88	3
V	N-phenyl-p-tolyl benzimidate	59 - 60	58.8 - 9.8	6
VI	N-phenyl-m-tolyl benzimidate	64 - 5	62.7 - 3.2	6
VII	N-phenyl-o-tolyl benzimidate	73 - 4	73.4 - 3.8	6

Analyses

Calculated %		Found %		
$C_{19}H_{14}ClNO$ requires:		II	III	IV
C	74.15	73.79	73.79	74.03
H	4.59	4.68	4.62	4.71
N	4.55	4.55	4.56	4.60
Cl	11.52	11.44	11.55	11.28
$C_{20}H_{17}NO$ requires:		V	VI	VII
C	83.60	83.42	83.37	83.39
H	5.96	6.03	6.03	6.00
N	4.87	4.90	4.83	4.89

N-aryl phenyl benzimidates and N-phenyl phenyl arylimidates

The starting materials were prepared by the usual Schotten Bauman method. These were used in place of benzanilide in the general preparative method described. Freshly recrystallised phenol was used for each.

	Compound	Experimental m.p/°C	Literature m.p/°C	Reference
VIII	N-ortho-chlorophenyl phenyl benzimidate	64.5 - 5.5	65 - 6	3
IX	N-para-chlorophenyl phenyl benzimidate	110 - 11	110	3
X	N-ortho-tolyl phenyl benzimidate	56 - 7	54 - 6	27
XI	N-meta-tolyl phenyl benzimidate	60 - 1	60	28
XII	N-para-tolyl phenyl benzimidate	119.5 - 20	117 - 19	29

Analyses

Calculated %		Found %	
$C_{19}H_{14}ClNO$ requires:		VIII	IX
C	74.15	73.90	73.91
N	4.59	4.78	4.51
H	4.55	4.65	4.50
Cl	11.52	11.90	11.44

$C_{20}H_{17}NO$ requires:		X	XI	XII
C	83.60	83.63	83.54	83.58
H	5.96	5.99	5.94	5.98
N	4.87	4.96	4.90	4.87

	Compound	Experimental m.p/°C	Literature m.p/°C	Reference
XIII	N-phenyl-phenyl-ortho-chlorobenzimidate	99 - 100	100	4
XIV	N-phenyl-phenyl-meta-chlorobenzimidate	95.5 - 6	†	†
XV	N-phenyl-phenyl-para-chlorobenzimidate	63 - 3.5	64 - 5	4
XVI	N-phenyl-phenyl-ortho-toluimidate	87.5 - 8	89 - 90	30
XVII	N-phenyl-phenyl-meta-toluimidate	68.5 - 9	†	†
XVIII	N-phenyl-phenyl-para-toluimidate	85 - 5.5	86 - 7	30

Analyses

Calculated %		Found %		
$C_{19}H_{14}ClNO$ requires:		XIII	XIV	XV
C	74.15	73.96	74.00	73.92
H	4.56	4.48	4.44	4.45
N	4.55	4.49	4.44	4.46
Cl	11.52	11.32	11.71	11.29
$C_{20}H_{17}NO$ requires:		XVI	XVII	XVIII
C	83.60	83.34	83.56	83.31
H	5.96	6.11	6.02	5.99
N	4.87	4.96	4.90	5.08

† not recorded in the literature.

The preparation of N-phenyl ethyl benzimidate

An ethereal solution of N-phenyl benzimidoyl chloride prepared as described previously was added to the calculated quantity of sodium dissolved in absolute ethanol and the mixture left overnight. Precipitated sodium chloride was removed by filtration and the excess solvent removed by distillation. The crude product was then distilled under reduced pressure. The pure compound was a yellow liquid.

The ethyl benzimidate compounds were found to hydrolyse fairly readily especially in the presence of acid. The N-aryl aryl arylimidates were stable to hydrolysis and were prepared as oils which crystallised in a large quantity of water. The extra stability of the aryl aryl imidates to hydrolysis by water is most likely due to the (C=N) being shielded from attack by the three aromatic rings. The kinetics of hydrolysis of some ethyl benzimidates in acid solution have been studied by de Wolfe and Augustine[31] who suggest that the rate determining stage is the base catalysed dissociation of a tetrahedral hydrated conjugate acid into an ethyl benzoate and ammonium ion.

(e) The preparation of N-aroyl diarylamines

The preparation of N-benzoyl diphenylamine

5 g of N-phenyl phenyl benzimidate were heated in a boiling tube at 305 - 310°C for one hour by partially immersing the tube in a Wood's metal bath held at around 312°C.

The solid crystallised on cooling and was taken up in warm absolute ethanol and boiled with charcoal. The solution was filtered and allowed to crystallise. It was then purified by repeated crystallisation from absolute ethanol to constant melting point.

The pure product, a white needle shaped crystalline material melted at 180 - 80.5°C (Lit.[26] 178 - 82°C).

By a similar method the following were prepared:

	Experimental m.p/°C	Literature m.p/°C	Reference
N-benzoyl-p-chlorodiphenylamine by heating N-phenyl-p-chlorophenylbenzimidate at 305 - 10°C for 1.5 h.	109 - 9.5	109 - 9.5	3
N-benzoyl-m-chlorodiphenylamine by heating N-phenyl-m-chlorophenylbenzimidate at 255 - 60°C for 1.5 h.	101 - 1.5	101 - 2	3
N-benzoyl-o-chlorodiphenylamine by heating N-phenyl-o-chlorophenylbenzimidate at 270°C for 1.5 h.	92 - 2.5	95	3
N-m-chlorobenzoyldiphenylamine by heating N-phenyl-phenyl-p-chlorobenzimidate at 270°C for 1.5 h.	140 - 40.5	138 - 8.5	4
N-m-chlorobenzoyldiphenylamine by heating N-phenyl-phenyl-m-chlorobenzimidate at 270°C for 1.5 h.	123 - 3.5	†	†
N-o-chlorobenzoyldiphenylamine by heating N-phenyl-phenyl-o-chlorobenzimidate at 270°C for 1.5 h.	141.5 - 2	142 - 3	4
N-benzoylphenyl-p-tolylamine by heating N-p-tolylphenylbenzimidate at 290°C for 2 h.	98.5 - 9	†	†
N-benzoylphenyl-m-tolylamine by heating N-m-tolylphenylbenzimidate at 290°C.for 2 h.	106 - 6.5	104 - 6	28

	Experimental m.p/°C	Literature m.p/°C	Reference
N-benzoylphenyl-o-tolylamine by heating N-o-tolylphenylbenzimidate at 290°C for 2 h.	110.5 - 111	110 - 11	27
N-o-toluoyldiphenylamine by heating N-phenyl-phenyl-o-toluimidate at 275°C for 1.5 h.	114 - 14.5	†	†

The compounds were not sent for analysis as this would not show up any impurity due to starting material, which has the same formula.

† Not recorded in the literature.

CHAPTER III

RESULTS AND DISCUSSION

1. Dipole Moment Study of some Esters and Imidates

The dipole moments of four simple benzimidates were measured and some related esters in a hope that this would enable one to ascertain the stereochemistry of the imidates.

The polarisation data are given in Table 2. From these data the dipole moments were calculated.

A graph of dielectric permittivity against weight fraction and of specific volume against weight fraction was drawn for each compound. The slope of each was measured and recorded.

For a solution sufficiently dilute for the solute molecules to be free of influence on each other Debye expressed the molar polarisation of the solution P_{12} as:-

$$P_{12} = P_1f_1 + P_2f_2 = \frac{\varepsilon - 1}{\varepsilon + 2} (M_1f_1 + M_2f_2)v \qquad \ldots\ldots (3,1)$$

where P_1 = molar polarisation of solvent
P_2 = molar polarisation of solute
ε = dielectric permittivity of the solution
v = specific volume of the solution
f_1, f_2 = mole fractions of solvent and solute respectively.

From dielectric permittivity and specific volume measurements on solutions of a polar solute in a non-polar solvent, values of the total polarisation P_{12} may be calculated. On the assumption that P_1 remains constant and equal to the polarisation of the pure solvent, values of P_2 may be obtained. These may be plotted against f_2 and extrapolated to $f_2 = 0$ to give $_\infty P_2$ - the polarisation of the solute at infinite dilution.

The dipole moment μ of the solute may then be obtained from the Debye equation.

$$\infty P_2 = \frac{4}{3}\pi N\alpha + \frac{4}{3}\pi N\mu^2/3kT \qquad \ldots\ldots (3,2)$$

α = Polarisability of the solute.

N = Avogadro Constant

k = Boltzmann Constant

The term $\frac{4}{3}\pi N\alpha$ is known as the distortion polarisation P_D, and is the sum of the electron polarisation P_E and atom polarisation P_A. Usually P_D is computed as R_2 the molar refraction from measurements of refractive index n_D, measured at the wavelength of the sodium D line. For dilute solutions the Lorenz-Lorentz equation is written:

$$R_{12} = R_1f_1 + R_2f_2 = \frac{n_D^2 - 1}{n_D^2 + 2}(M_1f_1 + M_2f_2)v \qquad \ldots\ldots (3,3)$$

R_{12}, R_1, R_2 = molar refractions of the solution, solvent and solute.

Alternatively R_2 may be calculated as the sum of the bond refractions of the solute. Hence:

$$\frac{4\pi N\mu^2}{9kT} = \infty P_2 - R_2$$

and therefore:

$$\mu = 0.012812\ [(\infty P_2 - R_2)T]^{\frac{1}{2}} \qquad \ldots\ldots (3,4)$$

The chief disadvantage of this method is that the error in the values of P_2 increase as the solution becomes more dilute. Consequently the values which are most important for the extrapolation are the most inaccurate.

Halverstadt and Kumler [32] assumed that in dilute solution dielectric permittivity ε_{12} and specific volumes v_{12} of the solution are linear functions of the weight fraction of solute w_2 so that:

$$\varepsilon_{12} = \varepsilon_1 + a w_2 \qquad \text{......} \ (3,5)$$

$$v_{12} = v_1 + \beta w_2 \qquad \text{......} \ (3,6)$$

ε_1 and v_1 are the dielectric permittivities and specific volume of pure solvent.

a and β are constants.

The Clausius Mosotti equation may be written in the form:

$$p_{12} = \left(\frac{\varepsilon_{12} - 1}{\varepsilon_{12} + 2} \right) v_{12} \qquad \text{......} \ (3,7)$$

where p_{12} is the specific polarisation of the solution.

It then follows from (3,5),(3,6) and (3,7) that:

$$\infty p_2 = \frac{3 a v_1}{(\varepsilon_1 + 2)^2} + (v_1 + \beta) \left(\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} \right) \qquad \text{......} \ (3,8)$$

where ∞p_2 is the specific polarisation of the solute at infinite dilution.

The specific refraction may be calculated from:

$$r_2 = \frac{3 \nu v_1}{(n_1^2 + 2)^2} + (v_1 + \beta) \left(\frac{n_1^2 - 1}{n_1^2 + 2} \right) \qquad \text{......} \ (3,9)$$

which is analogous to equation (3,8) with ε replaced by n^2 and a by ν. Where ν is the gradient of the plot of n_{12}^2 against w_2.

The dipole moment can then be calculated from equation (3,4).

From the slope (a) of the graph of dielectric permittivity against weight fraction and the slope β of the graph of specific volume against weight fraction the dipole moment of each compound was determined using equations (3,4) and (3,8). The specific refraction was obtained from tables of bond refractions[33].

It was not possible to prepare sufficiently concentrated solutions of the anilides to obtain reliable refractive index measurements. To obtain a consistent set of conditions the calculations of the dipole moments of the esters and imidates were made using bond refraction tables. To test the validity of the R_D values obtained for ethyl benzimidate the molar refraction was calculated from a series of refractive index measurements. The value obtained agreed sufficiently well with the value obtained from tables such that there was no significant difference in the value of the dipole moment obtained from each value.

The dipole moments calculated by this method are given in Table 3.

Table 2

Polarisation Data of some Esters and Imidates Dissolved in Benzene at 25°C

Ethyl benzoate

w_2	ε_x	v	
0.0066253	2.2910	1.14408	$R_D = 42.150$
0.0071910	2.2924	1.14395	
0.0089212	2.2976	1.14372	$P_0 = 79.745$
0.0113259	2.3059	1.14323	
0.0135708	2.3108	1.14281	$\mu = 1.975$ D
0.0170811	2.3208	1.14204	

Ethyl-para-toluate

w_2	ε_x	v	
0.0032640	2.2818	1.14442	$R_D = 50.398$
0.0052891	2.2895	1.14419	
0.0079678	2.2977	1.14355	$P_0 = 99.25$
0.0125658	2.3113	1.14284	
0.0162897	2.3228	1.14237	$\mu = 2.20$ D

Table 2 (continued)

Ethyl-ortho-toluate

w_2	ε_x	v	
0.0028841	2.2786	1.14471	R_D = 50.398
0.0069211	2.2859	1.14406	
0.0097641	2.2916	1.14357	P_O = 60.29
0.0104497	2.2939	1.14344	
0.0140689	2.3016	1.14291	μ = 1.72 D
0.0170431	2.3067	1.14237	

Ethyl-para-chloro-benzoate

w_2	ε_x	v	
0.0035601	2.2809	1.14407	R_D = 46.984
0.0086589	2.2935	1.14238	
0.0092507	2.2951	1.14185	P_O = 84.011
0.0118778	2.3013	1.14147	
0.0152427	2.3091	1.14059	μ = 2.03 D
0.0159561	2.3123	1.14027	

Ethyl-ortho-chloro-benzoate

w_2	ε_x	v	
0.0047952	2.2917	1.14338	R_D = 46.984
0.0059613	2.2952	1.14305	
0.0073709	2.3002	1.14271	P_O = 132.58
0.0092384	2.3075	1.14210	
0.0114041	2.3159	1.14146	μ = 2.55 D
0.0143129	2.3272	1.14043	

Imidate Study Benzene 25°C

Ethyl benzimidate

w_2	ε_x	v	
0.003399	2.2777	1.14408	R_D = 43.05
0.006675	2.2843	1.14327	
0.008225	2.2861	1.14338	P_O = 47.28
0.011955	2.2925	-	
0.012010	2.2921	1.14277	μ = 1.52 D
0.014240	2.2960	1.14228	

Table 2 (continued)

Ethyl-para-toluimidate

w_2	ε_x	v
0.0039457	2.2784	1.14469
0.0052560	2.2852	1.14447
0.0067701	2.2874	1.14422
0.0081151	2.2912	1.14400
0.0108931	2.2978	1.14362
0.0146590	2.3066	1.14310

$R_D = 48.998$

$P_0 = 71.42$

$\mu = 1.87$ D

Ethyl-meta-toluimidate

w_2	ε_x	v
0.003029	2.2774	-
0.003539	2.2780	1.14418
0.006990	2.2841	1.14406
0.009559	2.2895	1.14339
0.012982	2.2922	1.14314
0.014316	2.2950	1.14298

$R_D = 48.998$

$P_0 = 53.39$

$\mu = 1.62$ D

Ethyl-para-chloro-benzimidate

w_2	ε_x	v
0.004423	2.2786	1.14388
0.006301	2.2811	1.14322
0.007555	2.2829	1.14301
0.010488	2.2867	1.14212
0.012821	2.2899	1.14133
0.014730	2.2927	1.14081

$R_D = 53.184$

$P_0 = 32.74$

$\mu = 1.27$ D

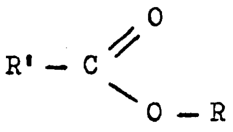
Table 3

Dipole Moments of some Imidates and Related Esters

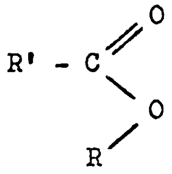
Compound	Dipole Moment/D
Ethyl benzimidate	1.52
Ethyl-meta-toluimidate	1.62
Ethyl-para-toluimidate	1.87
Ethyl-para-chloro-benzimidate	1.27
Ethyl benzoate	1.975
Ethyl-ortho-toluate	1.72
Ethyl-meta-toluate	2.02
Ethyl-para-toluate	2.20
Ethyl-ortho-chloro-benzoate	2.55
Ethyl-para-chloro-benzoate	2.03

Esters

The structure of most carboxylic esters has been found to be closer to trans-planar than to cis-planar[34,35].

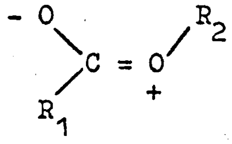


trans-planar



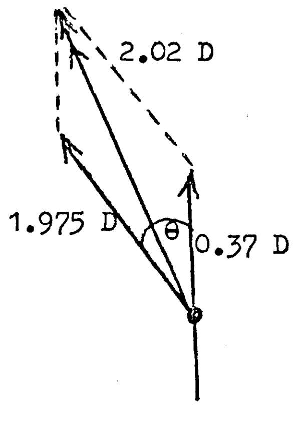
cis-planar

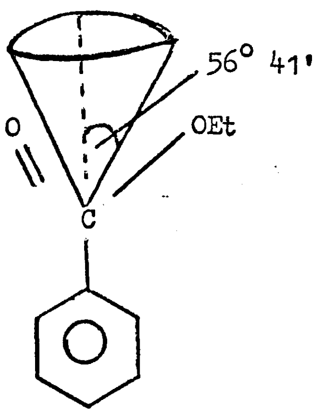
The dipole moments of ethyl and amyl formates; methyl, ethyl and amyl acetates in the vapour phase have been found[36] to be independent of temperature, over a wide range of temperature. The measured moments are quite different from the moments calculated assuming free rotation about the(C — O)bond, so it is most probable that the molecules exist in the trans form over the range of temperature used. Marsden and Sutton[35] suggested that one possible explanation was that resonance occurs involving structure I.



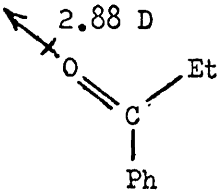
(I)

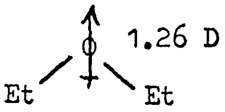
In order to obtain an indication of the direction of the resultant moment some assumptions have to be made. The dipole moment of ethyl-para-toluate (2.20 D) can be considered as the vector sum of the moments of ethyl benzoate and toluene, (1.975 and 0.37 D respectively). Applying the cosine rule to these three moments the dipole moment of ethyl benzoate is found to be directed at 56°41' to the $C_{aliphatic}-C_{aromatic}$ bond.





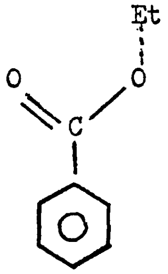
It is not possible using these data to uniquely determine the position of this vector. The moment of ethyl benzoate can be considered as the resultant of the moments of phenyl ethyl ketone[37] 2.88 D and diethyl ether[37] 1.26 D measured under the same conditions.



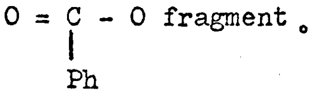


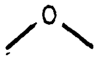
The moments are assumed to be directed as shown above. Applying the cosine rule to these three moments the resultant ethyl benzoate moment 1.975 D is obtained if the angle between the phenyl ethyl ketone moment and that of diethyl ether is 145.5°. This places the ethyl group 34.5° out of plane. This value agrees well with the angle of 30° found by Le Fèvre and Sundaram[38] obtained from Kerr Constant studies of ethyl benzoate.

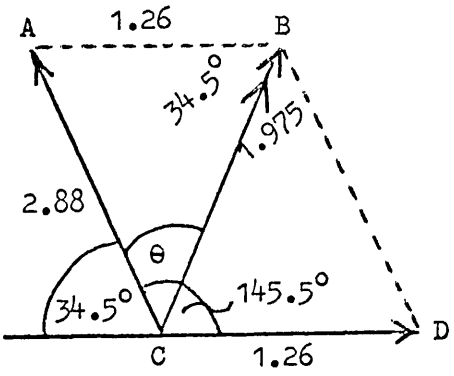
The structure of ethyl benzoate is thus drawn:



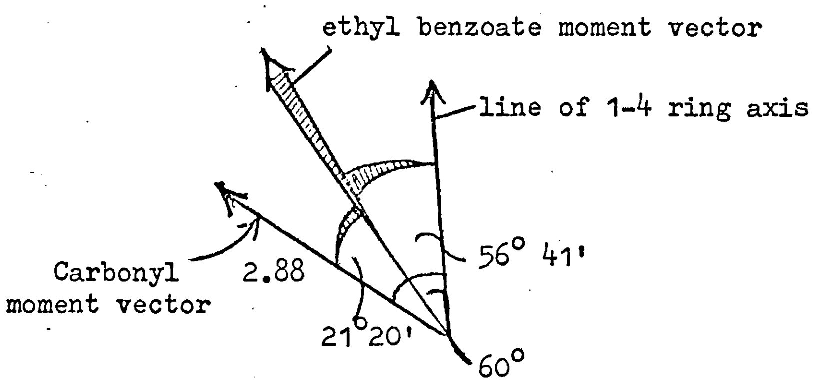
the (O-Et) bond making an angle of 34.5° to the plane containing the


$\underset{\mathrm{Ph}}{\mathrm{O=C}}\mathrm{-O}$ fragment.

The C = O, and  $\overset{\mathrm{O}}{\wedge}\mathrm{Et}$ vectors whose resultant is 1.975 D may be drawn as follows, where AC represents the C = O group moment and CD the O - Et group moment, CB is the resultant.

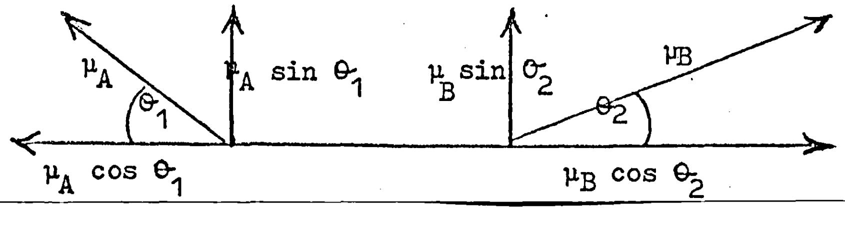


Using the cosine rule on triangle ABC the angle θ between the carbonyl vector 2.88 and the benzoate vector 1.975 is found to be $21^\circ 20'$. The ethyl benzoate vector has been found to be at $56^\circ 41'$ to the 1-4 axis of the ring; it is now found to be also $21^\circ 20'$ to the carbonyl vector. This is summarised:

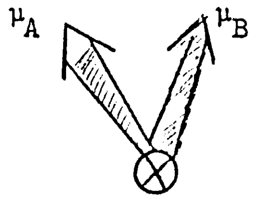


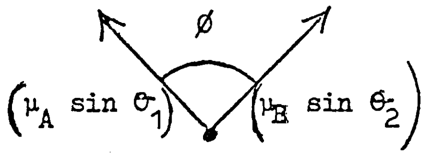
Thus the ethyl benzoate vector is approximately along the carbonyl direction. In order to investigate the possibility of free rotation the following procedure was adopted.

In the general case, consider two moments μ_A and μ_B at angle $\theta 1$ and $\theta 2$ respectively to a line joining them.



Assuming $\mu_B > \mu_A$ whatever the disposition of these two vectors out of plane when viewed from the left,





the horizontal component is $\mu_B \cos \theta_2 - \mu_A \cos \theta_1$. The vertical components generally are $\mu_A \sin \theta_1$ and $\mu_B \sin \theta_2$ at an angle ϕ to each other. These can be resolved into two components.

$\mu_B \sin \theta_2 \cos \phi/_2 + \mu_A \sin \theta_1 \cos \phi/_2$ vertically

and $\mu_B \sin \theta_2 \sin \phi/_2 - \mu_A \sin \theta_1 \sin \phi/_2$ horizontally

For the general angle ϕ the resultant is given by

$$\mu^2 = (\mu_B \sin \theta_2 \cos \phi/_2 + \mu_A \sin \theta_1 \cos \phi/_2)^2 + (\mu_B \sin \theta_2 \sin \phi/_2 - \mu_A \sin \theta_2 \sin \phi/_2)^2$$

replacing $\mu_B \sin \theta_2$ by α

and $\mu_A \sin \theta_1$ by β.

$$\mu^2 = (\alpha + \beta)^2 \cos^2 \phi/_2 + (\alpha - \beta)^2 \sin^2 \phi/_2 .$$

With free rotation all values of ϕ from 0° to 180° are equally possible. The measured term, the orientation polarisation is proportional to μ^2. The observed moment will be the root mean square (r.m.s.) value of the moments for all values of ϕ from 0° to 180°.

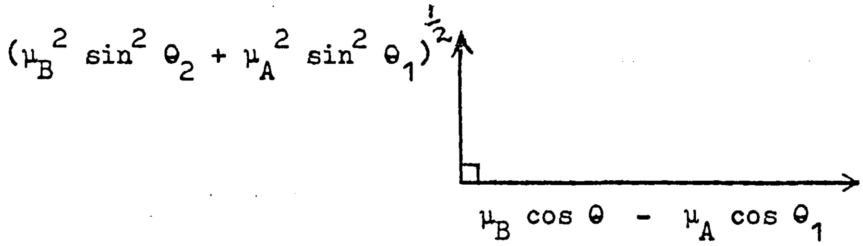
$$\mu^2_{\text{r.m.s.}} = \frac{1}{\pi}\int_0^\pi \mu^2 \, d\phi$$

$$\mu^2_{\text{r.m.s.}} = \frac{1}{\pi}\int_0^\pi [(\alpha+\beta)^2 \cos^2 \phi/_2 + (\alpha-\beta)^2 \sin^2 \phi/_2] d\phi$$

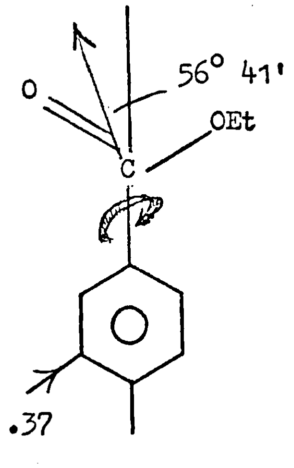
$$\mu^2_{\text{r.m.s.}} = \frac{1}{\pi}[\pi(\alpha-\beta)^2 + 2\alpha\beta\pi]$$

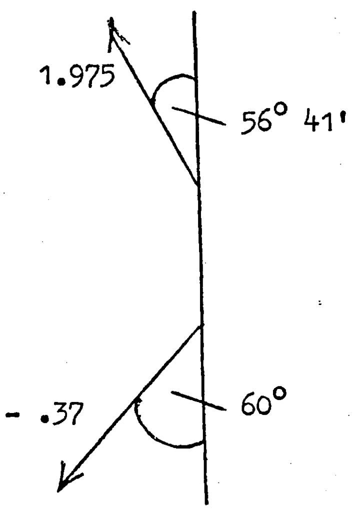
$$\mu^2_{\text{r.m.s.}} = \alpha^2 + \beta^2$$

The moment of this general case can be found from the resultant of the r.m.s. moment and the horizontal component at right angles to it.



The measured moment of ethyl-m-toluate was 2.02 D. If the aromatic group is rotating with respect to the ester group the moment will be the free rotation value obtained from the moments of ethyl benzoate 1.975 D and toluene 0.37 D.





Thus the horizontal component, μ_H, is

$$\mu_H = 1.975 \cos 56^\circ\ 41' + 0.37 \cos 60^\circ$$

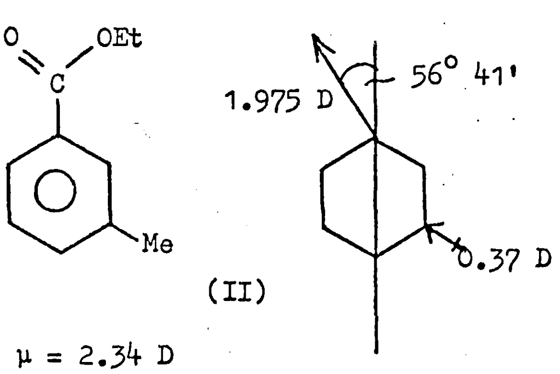
and $\mu_{r.m.s.} = (1.975^2 \sin^2 56^\circ\ 41' + 0.37^2 \sin^2 60^\circ)^{\frac{1}{2}}$

Therefore

$$\mu_{resultant} = (1.975 \cos 56^\circ 41' + 0.37 \cos 60^\circ)^2 + 1.975^2 \sin^2 56^\circ 41' + 0.37^2 \sin^2 60^\circ)^{\frac{1}{2}}$$

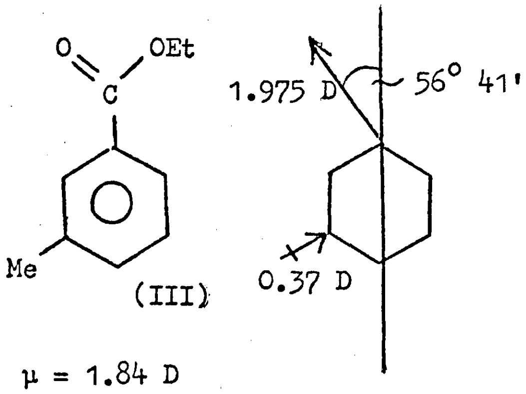
$$= 2.1\ \text{D}.$$

The moments of structures II and III were calculated assuming that the ethyl benzoate vector was in the plane of the molecule and at an angle of 56° 41' to the left of the $C_{aromatic}$-$C_{aliphatic}$ axis, and that the contribution from the $(\emptyset\text{-CH}_3)$ group was 0.37 D, along the $(\text{C} - \text{CH}_3)$ bond, as drawn. The values of the calculated dipole moments are shown in the diagrams.



(II)

$\mu = 2.34$ D



(III)

$\mu = 1.84$ D

The dipole moment of an equal mixture of II and III is given by the mean of the orientation polarisations $P_0(m)$ where:

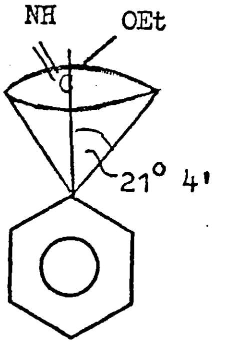
$$\mu_{(II,III)} = 0.012812\ (P_0(m) \times 298)^{\frac{1}{2}}$$

and this gives $\mu_{(II,III)} = 2.10$ D.

This is the same as the free rotation value and therefore the dipole moment study does not unambiguously determine the structure.

Imidates

When the cosine rule is applied to the dipole moments of ethyl-para-toluimidate (1.87 D), ethyl benzimidate (1.52 D) and toluene (0.37 D), measured under the same conditions[37], and if the dipole moment of the first compound is considered as the resultant of the other two, the ethyl benzimidate moment is calculated to be at 21° 4' to the $C_{aliphatic}$-$C_{aromatic}$ axis.

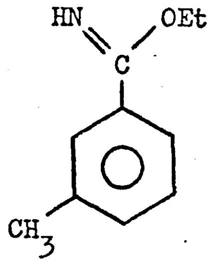


The position on the cone (swept out by a line at an angle of 21° 4') is determined by the orientation of the (-OEt) group.

Using the previously derived method for the determination of the resultant moment of two freely rotating vectors, it is found that for free rotation of the aromatic ring, with respect to the imidate vector, the calculated moment of ethyl-m-toluimidate is 1.72 D. The experimentally determined value is 1.62 D.

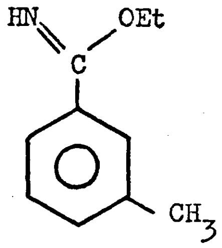
The dipole moments of the following structures were calculated:

Structure IV



1.51 D

Structure V



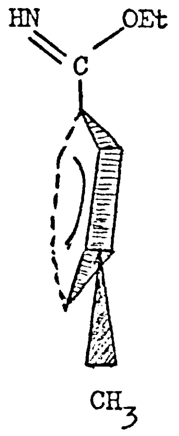
1.66 D

Structure VI

An equal mixture
of forms IV and V.

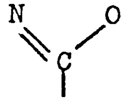
1.60 D

Structure VII



μ calculated = 1.72 D

(ring 90° to plane

containing 

These were all calculated on the basis of the ethyl benzimidate vector being in the plane of the ring and directed at 21° 4' to the $(C_{aliphatic}-C_{aromatic})$ bond. As was the case with ethyl-m-toluate it is not possible to unambiguously determine the structure of ethyl-m-toluimidate.

Before considering ethyl-p-chlorobenzimidate it is necessary to investigate the moment of ethyl-p-chlorobenzoate. When the cosine rule is applied to the ethyl benzoate vector (1.975 D at 56° 41' to the 1,4 axis of the phenyl ring) and a vector x representing the p-chlorophenyl group moment the negative end of which is at the chlorine atom, the value of x from the quadratic equation is calculated to be + 0.11 D or - 2.06 D.

The measured moment of chlorobenzene is 1.59 D the negative end being at the chlorine end of the 1,4 axis. The value of + 0.11 D is then consistent with a mesomeric moment of 1.48 D the negative end of which is at the COOEt end of the phenyl ring.

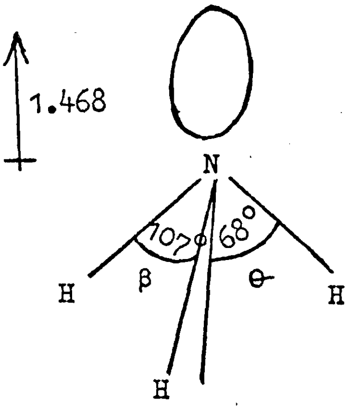
Smith[39] states that when a meta-directing group (e.g. Cl) is substituted in the position para to an o, p-directing group the resonance structures become much more important than with either substituent separately. This is reflected in an increase in the mesomeric moment.

A similar calculation applied to ethyl-p-chlorobenzimidate gives values of + 0.28 D or - 2.57 D for the p-chlorophenyl group moment. The first value is consistent with a mesomeric moment of 1.31 D, the negative end being towards the (HN = COEt) group on the phenyl ring. This is comparable with the corresponding ester value.

The use of bond moments to elucidate the structure of imidates is complicated by the large uncertainty in the value of the (C = N), (N - H) and nitrogen lone pair moments.

For the (N — H) group a value of 1.3 D has been used by Smith[39] and Hughes[7]. This value has been calculated from the dipole moment of ammonia[40].

Ammonia has a resultant moment of 1.468 D as shown below.



The angle θ has been calculated from:

$$\sin\theta = \frac{2\sin {}^{\beta}/_{2}}{\sqrt{3}}$$

and $1.468 = 3\mu_{(N-H)} \cos 68^\circ$

which gives $\mu_{(N-H)} = 1.3$ D.

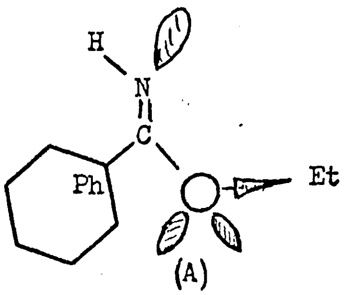
Thus the value of 1.3 D for the (N - H) bond contains a contribution from the lone pair. The lone pair in ammonia is in an approximately sp^3 hybridised orbital. In the imidates the lone pair is in an sp^2 hybridised orbital and the value of its moment will be different from that in ammonia.

In view of this, the better approach is to use group moments. The calculations on ethyl benzoate were found to be consistent with the OEt group being 34.5° out of plane. Similar results were obtained by Le Fèvre[38] using Kerr constant data. Stereochemically the $(\mathrm{C} = \overset{\bullet}{\underset{\bullet}{\mathrm{O}}}\!:)$ and $(\mathrm{C} = \overset{\diagup\mathrm{H}}{\underset{\bullet}{\mathrm{N}}}\bullet\ )$ groups are very similar.

It is reasonable to assume that in ethyl benzimidate the OEt group is similarly disposed as in ethyl benzoate.

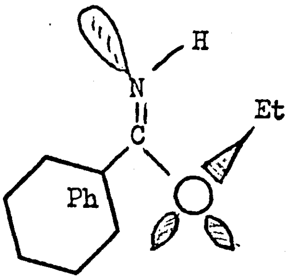
Using a value of x for the moment of the (C = N - H) group along the C = N direction, values are obtained of 2.23 D towards N or 0.16 D towards C. The former value is the more likely.

The (C = NH) group on this basis can be represented by a vector of 2.23 D along the C = N direction. It is still not possible, however, to calculate values of the N - H and N: bond moments, and hence distinguish between A and B.



(A)

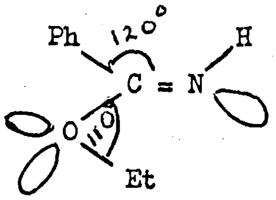
and



(B)

The structure of the N-phenyl benzimidates is probably similar to that of A on the grounds that the O-aryl N-phenyl benzimidates undergo the Chapman rearrangement.

Ethyl benzimidate is prepared by the addition of ethanol to benzonitrile in the presence of HCl. It is effectively addition of ethanol to a (C ≡ N) bond. Additions to acetylene are generally considered to proceed most readily in the trans- sense[41]. Using the supposition that the (N-Ph) bond is trans- to the (C-O) in the N-aryl aryl arylimidates to aid the Chapman rearrangement[22] it is to be assumed that the (N-H) in the ethyl benzimidates is trans- to the (C-O) giving a structure similar to that found for ethyl benzoates.



2. Infrared Study

The spectra of the imidates and N-aroyl diarylamines are presented in Tables 26 - 60 in the Appendix.

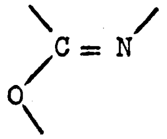
The spectra obtained were analysed in terms of three modes of vibration: ring modes, skeletal modes and localised-group vibrations.

Ring modes

These are absorptions arising from vibrations essentially localised within the benzene ring. X-sensitive modes are also discussed under this heading. These are modes in which the vibration of a bond joining a substituent to a benzene ring is sufficiently close in energy to a ring mode and is coupled with that mode. Where the substituent is part of the imidate skeleton the X-sensitive mode is discussed under the skeletal mode section.

Skeletal modes

These are absorptions due to vibrations of the imidate skeleton:



Localised vibrations

Discussed under this section are vibrations of bonds such as (C=O) and (C=N) where the force constant is large compared with other force constants of bonds in the molecules, the vibrations are then to a first approximation localised within these double bonds.

(a) Normal modes of vibration of aromatic ring systems

Benzene

Benzene is classified by its symmetry elements under point group D_{6h}. Being a 12 atom (non-linear) molecule it will have 30 normal vibrations. The form of the displacement vectors describing these can be found by a normal coordinate analysis of the system as was done, for example, by Wilson[42].

The normal modes have been drawn by several authors. Wilson[42] and Herzberg[17] draw only 20; 10 are singly degenerate and 10 doubly degenerate. Only one of each of the latter pairs have been drawn by these authors. Pitzer and Scott[43] draw all 30 and label them by Wilson's notation[42] (Fig. 2, page 69). The normal vibrations may then be classified according to their symmetry properties as follows:

(Wilson's numbering and Mulliken Symbols)

a_{1g}; 1,2 : a_{2g}; 3 : b_{2g}; 4,5 :

e_{2g}; 6a,6b,7a,7b,8a,8b,9a,9b : e_{1g}; 10a,10b :

a_{2u}; 11 : b_{1u}; 12,13 : b_{2u}; 14,15 :

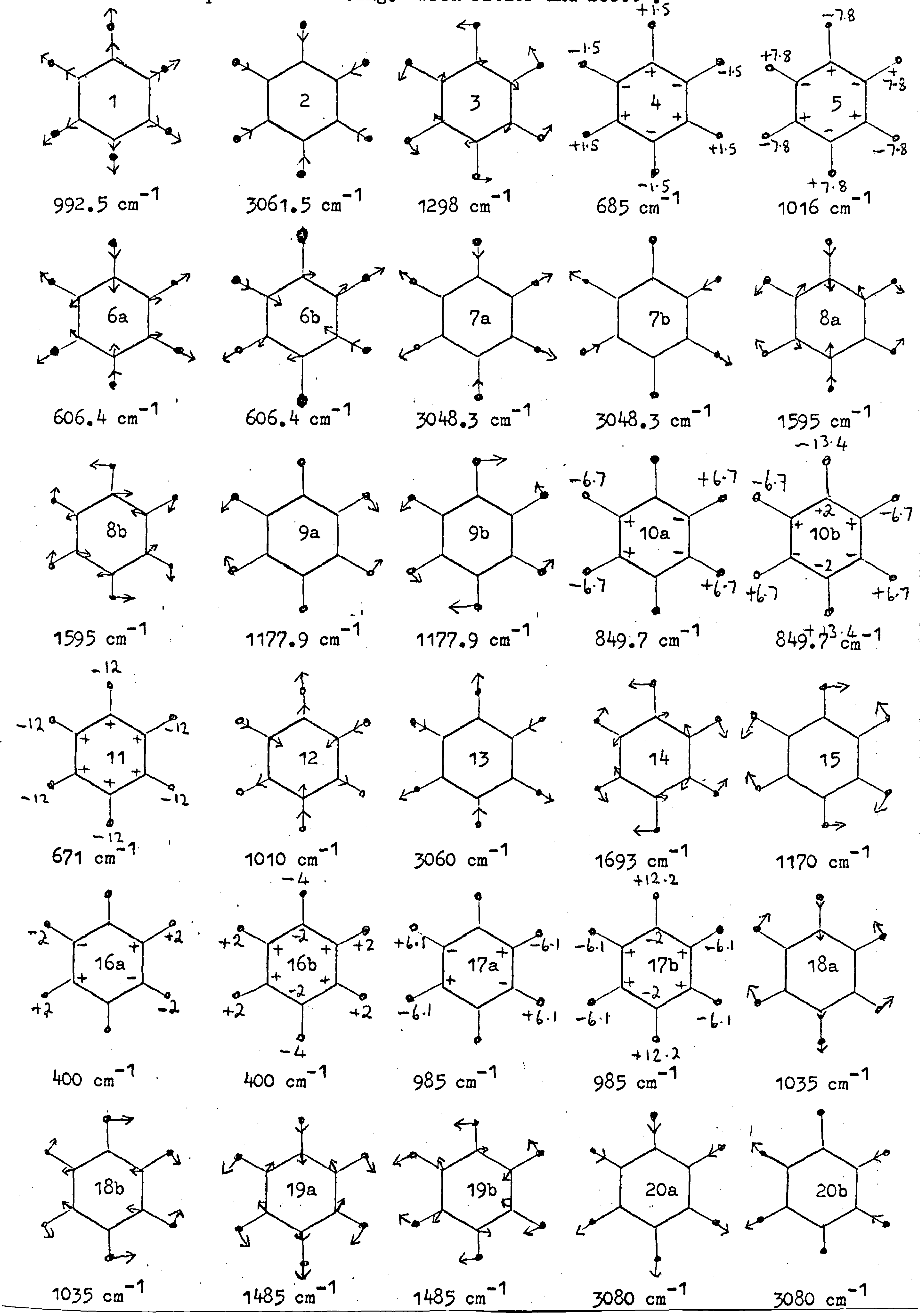
e_{2u}; 16a,16b,17a,17b : e_{1u}; 18a,18b,19a,19b,20a,20b.

The a_{2u} and e_{1u} modes are infrared active. The a_{1g}, e_{1g}, e_{2g} modes are Raman active. There are two polarised Raman shifts which correspond to the totally symmetric vibrations i.e. a_{1g}.

a_{2g}, b_{2g}, b_{1u}, b_{2u} and e_{2u} are spectrally inactive.

Fig. 2

The wavenumber and normal modes of vibration of benzene Wilson's labelling. + and - refer to motions perpendicular to the plane of the ring. From Pitzer and Scott[43]



992.5 cm^{-1}
3061.5 cm^{-1}
1298 cm^{-1}
685 cm^{-1}
1016 cm^{-1}

606.4 cm^{-1}
606.4 cm^{-1}
3048.3 cm^{-1}
3048.3 cm^{-1}
1595 cm^{-1}

1595 cm^{-1}
1177.9 cm^{-1}
1177.9 cm^{-1}
849.7 cm^{-1}
849.7 cm^{-1}

671 cm^{-1}
1010 cm^{-1}
3060 cm^{-1}
1693 cm^{-1}
1170 cm^{-1}

400 cm^{-1}
400 cm^{-1}
985 cm^{-1}
985 cm^{-1}
1035 cm^{-1}

1035 cm^{-1}
1485 cm^{-1}
1485 cm^{-1}
3080 cm^{-1}
3080 cm^{-1}

When the displacement vectors of the normal modes of benzene are examined it is found that they can be further classified into grouped types of vibrations:

C-H stretching modes [ν(C-H)]	2, 7a, 7b, 13, 20a, 20b.
C-C stretching modes [ν(C-C)]	8a, 8b, 14, 19a, 19b
C-H in plane deformations [β(C-H)]	3, 9a, 9b, 15, 18a, 18b
C-H out of plane deformations [γ(C-H)]	10a, 10b, 17a, 17b, 5, 11
C-C deformations [δ(C-C)]	1, 4, 6a, 16a, 16b, 12

ν(C-H) modes

The ν(C-H) modes are easy to separate as the ν(C-H) absorption occurs at a sufficiently high wavenumber ($\bar{\nu} > 3000$) to allow them to be distinguished from other modes absorbing at lower wavenumbers. Katritzky *et.al*[44] investigated the spectra of a number of substituted benzenes, which was reviewed[45] with concurrent work on pyridines.

ν(C-C) modes

It was found[45] that substituting the ring in the mono-, ortho-, meta- and para- position had little effect on the ν(C-C) modes which could be considered as localised in the ring skeleton and classed as characteristic modes. They were found to absorb near 1600, 1580, 1490, 1450 cm^{-1}. The effects of substituents on the intensity of these bands were correlated with the mesomeric moment of the substituent.

The vibrations of benzene form the basis for the study of the modes of vibration of the monosubstituted and ortho-, meta- and para-disubstituted benzene rings in the molecules studied.

β(C-H) modes

Substitution of one or more of the hydrogen atoms of the benzene ring by a heavier atom X will in some cases remove some of the β(C-H) motion from certain modes. The form of such modes should then approximate to the β(C-H) motion of the remaining (C-H) bonds. In-plane motion of a carbon atom originally bonded to hydrogen before such substitution should introduce some (C-X) motion into the mode produced.

Modes 3, 18a and 18b involve movements of the carbon skeleton whereas modes 9a and 9b are pure β(C-H) with negligible movement of the carbon.

Para-substitution results in mode 18b having much less β(C-H) motion. The form of this mode becomes mostly β(C-X).

Mono- and para-substitutions should have little effect on the form of mode 9a which does not involve movement of the (C-H) bonds on the 1,4 axis. This mode is responsible for an absorption at 1177 cm^{-1} in benzene and is unlikely to be perturbed greatly by mono- or para-substitution.

Modes 3, 9a, 15 and 18b involve some β(C-H) of hydrogen atoms on the 1,4 axis. Substitution should alter the form of these modes. Actual coupling between these deformations and that of β(C-X) should be extremely small because of the large difference in energy of these modes and that of β(C-X). Mode 18a involves slight stretching of the bonds on the 1,4 axis. Substitution by X in either of these positions should introduce some ν(C-X) motion.

Ortho- and meta-substitution should introduce some β(C-X) motion into modes 3, 18a, 18b, 9a, 9b and 15.

The β(C-H) modes drawn by Katritzky[45] are the recognisable effects of removing β(C-H) deformations on substituting X for hydrogen which would replace the β(C-H) mode by β(C-X) which being of lower energy do not participate in these modes.

γ(C-H) modes

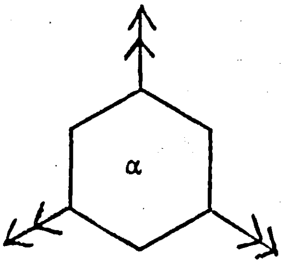
Modes 10a and 17a do not involve motion of any of the atoms on the 1,4 axis so it will be unlikely that mono- or para-substitution will affect the form of these modes.

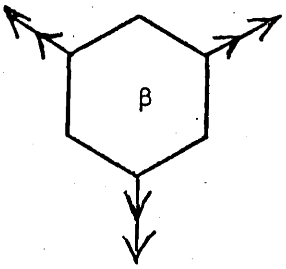
Ortho- and meta-substitution involves replacement of hydrogen atoms which are moving out of phase with their attached carbon atoms. Such substitution by heavier atoms will alter the form of these modes.

10b, 17b, 11 and 5 all involve movements of the hydrogen atoms out of phase with the motion of the attached carbon atoms. Substitution is expected to alter these modes.

Ring modes

Modes 1, 6a, 6b and 12 are in-plane skeletal deformations. Modes 4, 16a, 16b are out of plane deformations. Modes 1 and 12 involve the same C-H motion at position 1. When mono-substituted they should both be affected similarly. In the monosubstituted compound C_6H_5X these modes are of symmetry species a_1. They absorb at a similar wavenumber in benzene and so in C_6H_5X they should couple strongly. Addition and abstraction of these modes gives:





ν(C-X) is also of symmetry species a_1 under the operations of C_{2v} on C_6H_5X. This ν(C-X) stretch could couple strongly with α giving 2 modes. Mode β involves no motion of atoms in position 1 and would be unaffected. On this basis Whiffen[46] draws 3 modes p, q and r. Mode p involves no ν(C-X) motion, q and r involve extensive ν(C-X) motion and are X-sensitive. Mode p is unlikely to be altered by substitution in the 3 position since no motion of this (C-H) bond is involved. Mode p should become X-sensitive by substitution in either the 2 or 4 positions as some ν(C-X) will be involved.

Modes 6a and 6b

Mode 6a involves stretching of the (C-H) bonds and is therefore expected to become X-sensitive on substitution due to involvement of some (C-X) stretching motion.

Mode 6b does not involve any stretching motion on the 1,4 axis. Substitution on this axis should introduce some slight (C-X) deformation as this mode involves some in-plane deformation of the carbon atoms on the 1,4 axis.

Ortho- and meta- substitution should introduce some (C-X) stretching so that this mode is expected to become X sensitive on such substitution.

Modes 16a and 16b

Mode 16a involves no motion of the (C-H) bonds on the 1,4 axis and so mono- and para-substitution are unlikely to alter the form of this vibration. This mode involves in-phase, out of plane motion of the (C-H) bonds in the 2,3,5 and 6 positions and is expected to be altered on ortho- or meta-disubstitution. Mode 16b again involves in-phase motions of the hydrogen atoms with the attached carbon atoms. Substitution will introduce some (C-X) deformation.

Mode 4

This mode involves in-phase motion of each hydrogen with its attached carbon atom. The motion of the hydrogen atoms is slight and the mode is described as an out on plane ring deformation. On substitution some (C-X), deformation motion is involved.

Monosubstituted aromatic compounds; C_6H_5X

The reduction in symmetry from D_{6h} of benzene to C_{2v}, with subsequent loss of the centre of symmetry allows vibrations which were previously only allowed to be infrared or Raman active, to become active in both spectra.

As has been mentioned earlier mono-substitution has little effect on the ν(C-C) modes.

The β(C-H) modes will be altered because the number of adjacent (C-H) bonds has changed. This will similarly affect the γ(C-H) modes. Of the skeletal modes of the benzene nucleus, some will remain unaltered while others will become X sensitive.

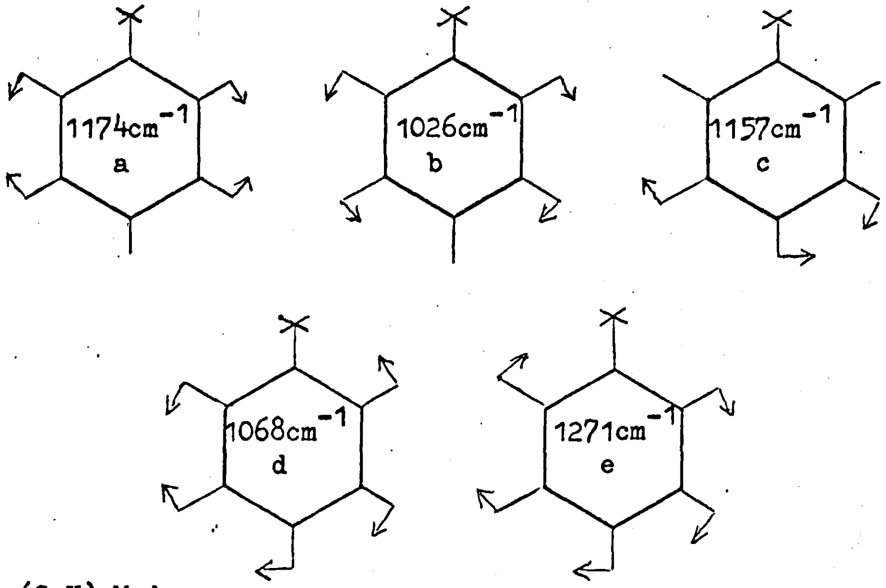
Whiffen and Randle[46] draw the normal modes for monosubstituted benzene rings and assign them to absorptions in the spectra of mono-halogen substituted benzenes.

As many of the compounds in this study contain monosubstituted rings, a pictorial representation of the normal modes is given in Fig. 3, with the position of absorption for chlorobenzene indicated.

Fig. 3

The normal vibrations of monosubstituted benzenes. Labelling due to Whiffen and Randle[46].

β(C-H) Modes



γ(C-H) Modes

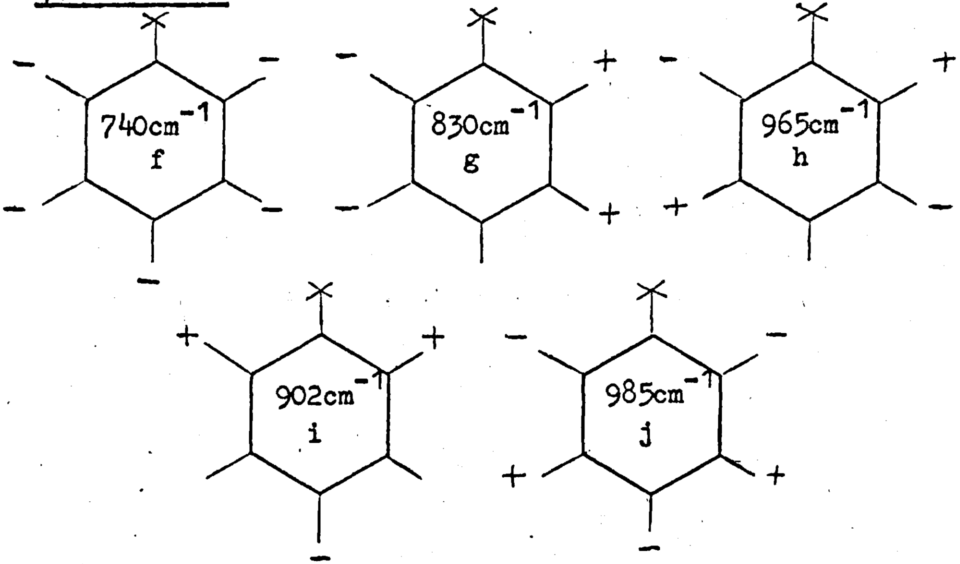


Fig. 3 (continued)

Ring Stretching Modes

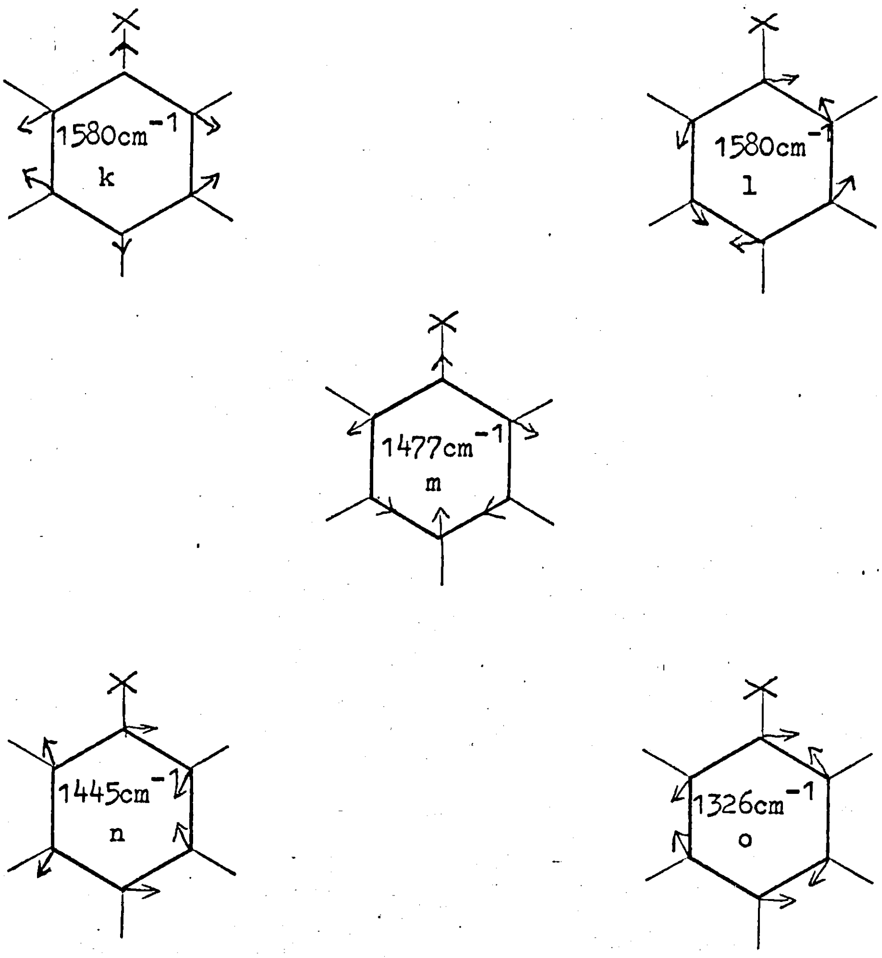
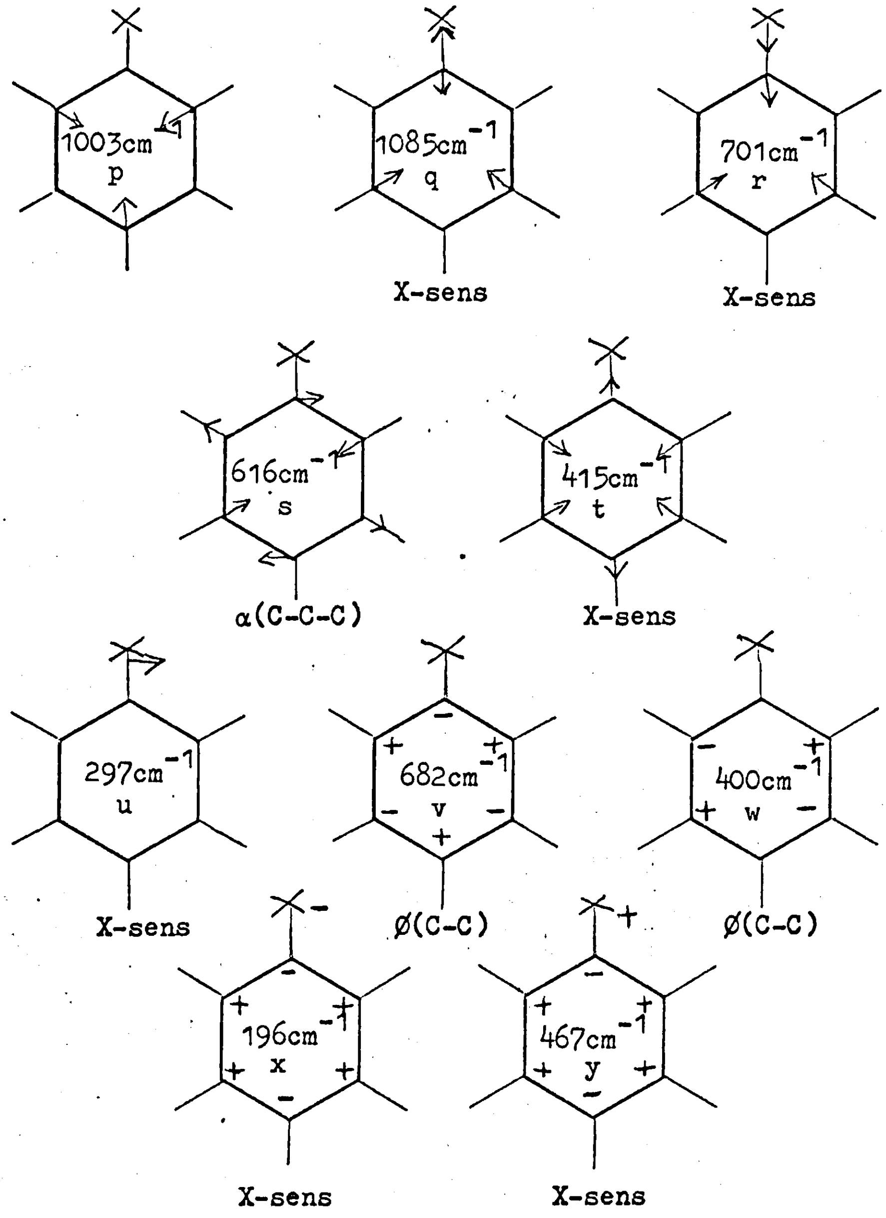


Fig. 3 (continued)

Ring Deformation Modes



Vibrations of the same symmetry, especially when the intrinsic frequencies are similar, can couple together. When the symmetry operations of point group C_{2v} are applied to the stretching and in-and-out-of-plane bending modes of (C-X) in C_6H_5X it is found that:

ν(C-X) is of species a_1

β(C-X) is of species b_1

γ(C-X) is of species b_2

Should the intrinsic frequencies of these modes be similar to any of those in benzene of the same symmetry extensive coupling is expected. This has been found by Green and Harrison[116] for the γ(NO_2) and γ(C-H) modes in nitrobenzene, benzoic acid and in the benzoate ion.

The ν(C-Cl) is expected to occur near 700 cm^{-1} by analogy with aliphatic (C-Cl) stretching modes. The β(C-Cl) will be of much lower wavenumber and γ(C-Cl) of even lower wavenumber.

<u>β(C-H) modes</u>

Katritzky[45] quotes ranges of wavenumber for the absorption of the Whiffen and Randle modes:

e 1240 ± 8 cm^{-1}; a 1177 ± 6; c 1156 ± 5; d 1073 ± 4; b 1027 ± 3

<u>γ(C-H) modes</u>

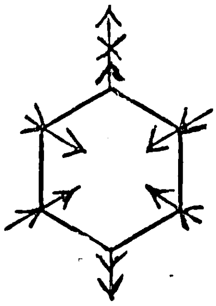
Two of the γ(C-H) modes are of a_2 symmetry which does not allow absorption of infrared radiation. Substitution of these modes by a heavy atom X would not introduce any (C-X) motion and so they should be unaltered from the benzene modes from which they are derived. Of the b_2 modes one is assigned by Whiffen and Randle[46] to an absorption near 970 cm^{-1}. Another (the umbrella mode derived from mode 11 of benzene) is assigned to the strong infrared absorption usually found close to 750 cm^{-1}. With the exception of the mode derived from mode 11 of benzene these are weak absorptions. The umbrella mode has been classed as a group frequency characteristic of monosubstituted benzenes by Bellamy[47].

Ring vibrations

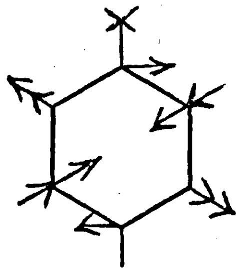
The modes derived from 1 and 12 of benzene are expected to couple and together with the ν(C-X) produce three normal modes:

p in which there is no ν(C-X) motion and q and r which are sensitive to the nature of X.

The 6a and 6b modes of benzene give rise to a Raman active shift at 606 cm^{-1}. On monosubstitution this doubly degenerate mode is 'resolved' into two infrared active bands 6a and 6b.



6a

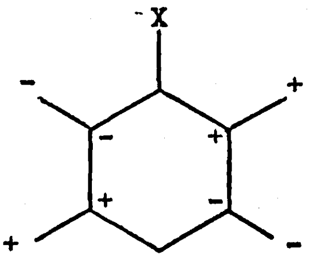


6b

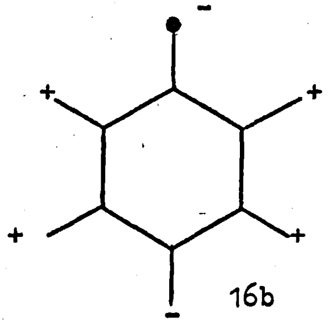
6a involves stretching of the (C-X) bond and so will become X sensitive. Mode 6b involves mostly (C-C) in plane bending although some β(C-X) is involved, the β(C-X) absorptions are much lower than ν(C-X) and are unlikely to couple with this mode. McWhinnie and Poller[48] examined the spectra of several monosubstituted compounds and found mode 6b to absorb in the region 621 - 602 cm^{-1}.

The degenerate modes 16a and 16b of benzene are similarly resolved into two species on monosubstitution.

Monosubstitution gives a Raman active mode 16a and an infrared active mode 16b.



16a



16b

16b is a X-sensitive mode involving γ(C-X) although 16b is found over a large range of wavenumbers (McWhinnie and Poller quote the range 550 - 418 cm^{-1}) it is a relatively strong absorption and can usually be distinguished from other ring modes. These authors found a linear relationship between wavenumber of the absorption and the reciprocal of the reduced mass of X in the compounds studied.

Theyfound the assignment of the X-sensitive mode 6a difficult because of the wide range of absorptions associated with this mode, 580 - 190 cm^{-1}.

Monosubstituted Benzimidates

1. Ethyl benzimidate (Table 26, Appendix)

The β(C-H) modes were readily assigned by comparison with the assignment given for ethyl benzoate[49], the previous assignment of ethyl benzimidate[7] and the assignment of these modes in simple monosubstituted benzenes.

2. N-phenyl ethyl benzimidate (Table 31, Appendix)

The β(C-H) modes were assigned by analogy with the corresponding modes in ethyl benzimidate.

3. N-phenyl phenyl benzimidate (Table 32, Appendix)

The β(C-H) modes were assigned by comparing the spectrum with that of the rearranged compound N-benzoyl diphenylamine (Table 33). The 1000-1100 cm^{-1} region of the spectrum of this latter compound was not complicated by the presence of a υ(C-O) absorption. The β(C-H) absorption in both compounds were of similar wavenumber.

The γ(C-H) modes in these compounds were not so readily assigned. In order to aid the assignment the spectrum of ethyl benzoate(Table 25) was re-investigated. The strong absorption at 710 cm^{-1} in the spectrum of ethyl benzoate has been assigned to several different modes of vibration by different workers. A similar absorption has been observed in the spectra of methyl, propyl and butyl benzoates[50]. A similar band occurs near 760 cm^{-1} in the spectra of some para-chlorobenzoates and is thought to be due to the same type of vibration as occurs at 710 cm^{-1} in the ethyl benzoate spectrum[50,51]. It is assigned to an out-of-plane deformation of the (O-C=O) group. Lebas[52] in accordance with her work on PhCHO, $PhCOCH_3$ and PhCOCl and with the work of Lorenzelli and Moller[53] assigns this absorption to an in-plane deformation of the (O-C=O) group mainly involving the (C=O) group. For methyl benzoate the γ(C=O) mode is assigned to an absorption at 237 cm^{-1}. However in acetone the δ(C=O) mode has been assigned[54] to an absorption at 530 cm^{-1}, in acetophenone to an absorption at 585 cm^{-1} and in benzophenone[55] to an absorption at 639 cm^{-1}.

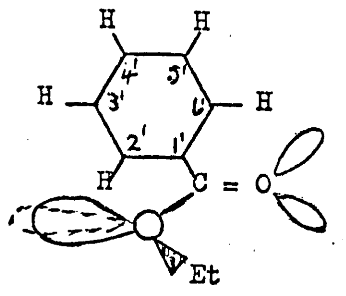
The absorption at 710 cm^{-1} would appear to be too high for a (C=O) deformation. Chattopadhyay[49] has assigned the 710 cm^{-1} absorption in ethyl benzoate to the γ(C-H) umbrella mode derived from mode 11 of benzene. This would seem a more reasonable assignment. The umbrella mode (ν_{11}) in monosubstituted benzenes is usually found in the 750 cm^{-1} region[46]. In para-substituted benzenes this mode is assigned to absorptions around 800 cm^{-1}. If this mode is found at 710 cm^{-1} in ethyl benzoate it is to be expected that the corresponding mode in ethyl para-substituted benzoates would be found near 760 cm^{-1}. Chattopadhyay gave no discussion of the low value of wavenumber of this mode in ethyl benzoate.

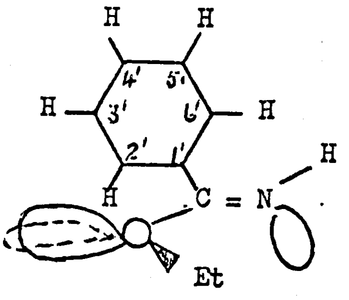
In ethyl benzimidate there is a strong absorption near 698 cm^{-1} which has been assigned by Hughes[7] to the ring mode derived from mode 4 of benzene. However, the spectrum of ethyl para-chlorobenzimidate has an absorption near 740 cm^{-1}, similar to that in ethyl para-chlorobenzoate, which would be consistent with the behaviour of the umbrella mode 11. The 698 cm^{-1} band in ethyl benzimidate is thus assigned to a γ(C-H) mode.

There is no corresponding Raman shift. Jones and Sandorfy[56] noted that monosubstituted benzenes exhibit strong infrared absorption in the 730 cm^{-1} region but that the corresponding Raman shift is absent. The reason for the low value of this mode in ethyl benzoate and ethyl benzimidate is discussed below.

The $>C{=}O$ and $>C{=}N^{\diagup H}$ moieties of ethyl benzoate and ethyl benzimidate can be described in the terms of molecular orbitals involving σ-bonds between the carbon and oxygen and between the carbon and nitrogen atoms involving sp^2 hybridised orbitals on the O, N and C atoms. The double bond is then formed by overlap of the p orbitals and this leaves the lone pairs, in both cases, in sp^2 hybridised orbitals.

The structure of ethyl benzoate and ethyl benzimidate (assuming the (N-H) is cis to the (Ph-C) bond in the latter compound) is shown below.





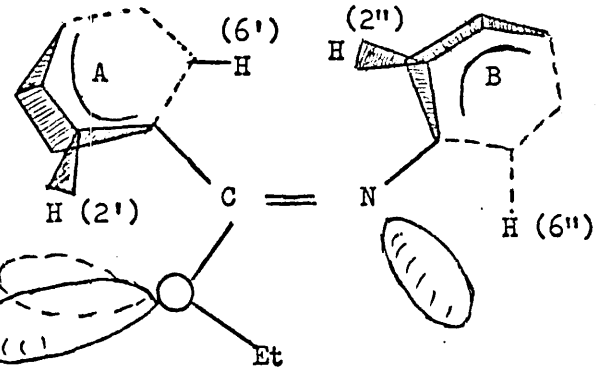
Dipole moment studies on ethyl benzoate (p. 57) and[38] indicate that the ethyl group is out of the plane containing the (O=C-O) group. This has the effect of orientating one of the ethoxy lone pairs nearer to the 2' hydrogen. H$_{2'}$ would be equidistant from both lone pairs if the molecules were planar. The hydrogen atoms on the 2' and 6' positions of ethyl benzoate are in the field of the lone pair of the ethoxy group and the lone pairs on the oxygen of the carbonyl group. There will, in both cases be lone pair-bonding pair repulsions between the (C-H) bonds and the oxygen lone pair. Any motion involving (C-H) out of plane deformation might then be expected to occur at a lower wavenumber than usually observed. The umbrella mode (ν_{11}) usually absorbs near 750 cm^{-1} but is assigned now to an absorption at 710 cm^{-1} for the reasons given above.

The 2' proton in ethyl benzimidate is in an environment similar to that in ethyl benzoate and the (C-H) and lone pairs are expected to repel each other. The 6' proton is in the field of the (N-H) bond and the bonding pair-bonding pair repulsion is expected to be smaller[57] than the lone pair-bonding pair repulsion of ethyl benzoate. The repulsion on the 2' proton could be relieved slightly by closing the (Ph-C=N) angle but this would push the 6' proton near the field of the double bond between C and N. This may account for the even lower wavenumber in the imidate. In acetophenone the umbrella (ν_{11}) mode is found in the expected position. The repulsion between the lone pair and the ortho-(C-H) bond is probably relieved by closing the (CH_3 - C - Ph) angle, without introducing other repulsions.

In ethyl benzimidate there is another broad band in the γ(C-H) region, this is at 830 cm^{-1}. The considerable broadening of this band is ascribed to this absorption having some γ(N-H) character. A similar mode in para-benzoquinone di-imine[58] is assigned to a band at 850 cm^{-1} .

In the spectrum of ethyl benzoate two absorptions were noted near 939 and 875 cm^{-1} which were not recorded by Chattopadhyay[49]. The first is assigned to a γ(C-H) mode the second to a ν_s(C-O-C) mode.

In the 700 - 800 cm^{-1} region of the spectrum of N-phenyl ethyl benzimidate there are two major absorptions at 770 cm^{-1} and 730 cm^{-1}. Due to the size of the phenyl rings the configuration of the molecule could not be one in which all the groups are in one plane. The rings will undoubtedly be out of plane but there will be a tendency to approach as close to planarity with the (C=N) bond to allow maximum overlap of the π electron systems. One possible ~~configuration~~ conformation is as in (VIII).

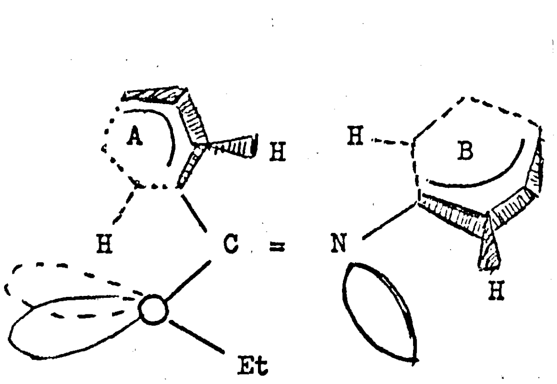


(VIII)

For 'ring A' (assuming the ring is not tilted more than 60° out of plane) the 2' proton should be repelled downwards by the ethoxy lone pair. Proton 6' should be similarly repelled downwards by the aromatic π cloud of ring B.

But for 'ring B' the 2" proton should be repelled upwards by the aromatic π cloud of ring A. Proton 6" should be repelled downwards by the nitrogen lone pair.

The same relative difference of repulsions is found in the ~~configuration~~ conformation (IX).

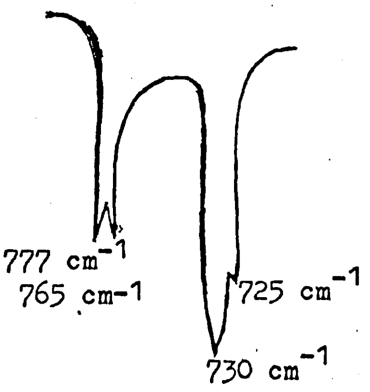


(IX)

In this compound one will expect two different umbrella modes for the two monosubstituted rings. The region of absorption from 780 - 720 cm^{-1} is shown in Fig. 4.

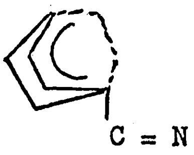
Fig. 4

The 720 - 780 cm^{-1} region of the spectrum of N-phenyl ethyl benzimidate

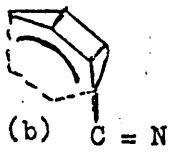


The first order splitting, giving bands at about 770 and 730 cm^{-1} is because of the two different rings as described earlier.

The second order splitting would be consistent with tilting of the ethyl group slightly out of plane and so introducing two possible magnitudes of lone pair-bonding pair repulsion on the carbon ring ortho-proton ; one for each conformer.



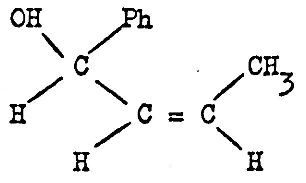
(a) as in (VIII)



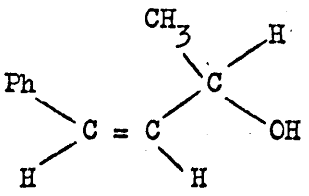
(b) as in (IX)

The small splitting could alternatively be the result of differing orientations of the O-Et group. The assignments for the in-plane and out-of-plane (C-H) deformations are shown in Table 4. The complete assignments for the molecules ethyl benzoate, ethyl benzimidate and N-phenyl ethyl benzimidate are shown in Tables 25, 26 and 31 respectively.

The γ(C-H) region of the N-aryl aryl arylimidates is too complicated to allow ready assignment of each absorption. The γ(C-H) modes are most likely split by steric and electronic interactions. This effect has been reported for the cis forms of phenyl propenyl carbinol and styryl methyl carbinol[87] which are very similar sterically.



cis phenyl propenyl carbinol



cis styryl methyl carbinol

The trans isomers exhibited only one out of plane mode near 750 cm^{-1}. The presence of a multiplet in the cis isomers was ascribed to a steric effect of the methyl group on the aromatic ring.

Table 4

The β(C-H) and γ(C-H) Modes in some Monosubstituted Compounds

The β(C-H) Modes

Compound	Position of Absorption/cm^{-1}					
Ethyl benzoate		1175		1070	1028	
Ethyl benzimidate		1174.5		obscured	1031	
N-phenyl ethyl benzimidate		1160		1070	1029	
N-phenyl phenyl benzimidate	1180	1172	1165	1072	1025	1018
N-benzoyl diphenylamine	1180	1170		1075	1028	

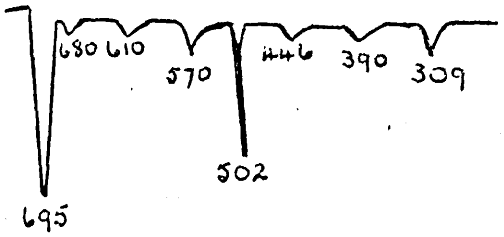
The γ(C-H) Modes

Compound	Position of Absorption/cm^{-1}								
Ethyl benzoate	992	970	939	835					712
Ethyl benzimidate	994		929.5	828					698
N-phenyl ethyl benzimidate			920	905	778	768		735	725
N-phenyl phenyl benzimidate			928	825	770		755	738	
N-benzoyl diphenylamine		960		852	770		755		725

The absorption bands observed in the region 700 - 300 cm^{-1} are expected to arise from ring deformation modes and some other skeletal deformation modes.

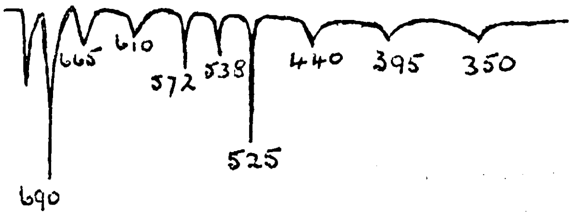
The assignments given below are made by analogy with assigments made by McWhinnie and Poller[48].

Phenyl benzoate (solid state)



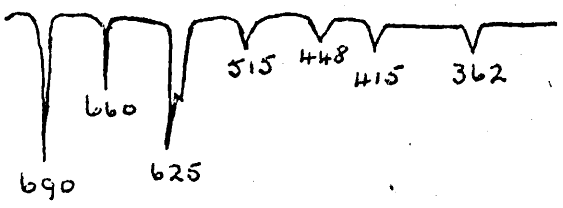
$\bar{\nu}$/cm^{-1}	assignment[48]
610	α(C-C-C) 6b
570	r CO_2
502	(Ph-O) 16b
454 - 438	(Ph-C) 16b
396	X-sens 6a?
309	δ OCO

N-phenyl phenyl benzimidate (solid state)



$\bar{\nu}$/cm^{-1}	assignment
690	ϕ(C-C) (4)
665	δ(CCN)?
610	α(C-C-C) (6b)
572	r CON ??
538	
525	(Ph-O) (16b)
440	(Ph-C) (16b)
395	X-sens (6a)

N-benzoyl diphenylamine



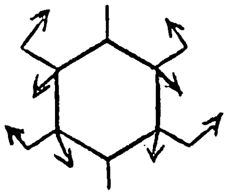
ν/cm^{-1}	assignment
690	ϕ(C-C) (4)
660	δ CCO
625	α C-C-C (6b)
515	Ph-N (16b)*
448	Ph-C (16b)
415	X-sens (6a)

* By analogy with the 16b mode in Ph-NHMe and PhCONHPh at 509 and 508 cm^{-1} respectively[48].

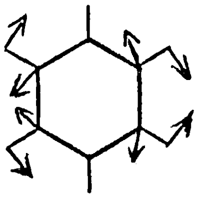
Disubstituted Ring Systems

Para-disubstitution

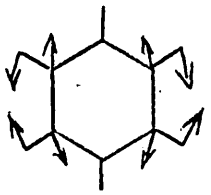
The assignment of the β(C-H) modes due to para-disubstitution in the N-aryl aryl arylimidate system was made by comparison with earlier work carried out on simple para-substituted benzenes. Below are shown the expected displacements of the ring[59,45] and their expected region of absorption in cm^{-1}



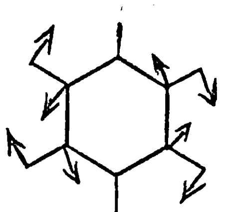
1013 ± 5



1111 ± 7

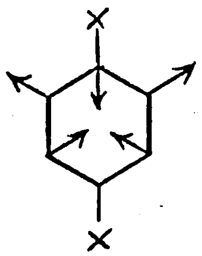


1175 ± 6



1258 ± 11

The assignment of the β(C-H) modes due to para-disubstitution in the N-aryl aryl arylimidates spectra was complicated by the presence of two monosubstituted rings in the compounds. Thus there is always present in the spectra both mono and para-substitution patterns. However, in the chloro-substituted imidates the assignment of the lowest member was simplified because of the intensity of the absorption. The increased intensity is because in this mode there is a contribution from the ν(C-Cl) mode, which involves a large dipole change. Whiffen and Randle[60] noted that a band in the 1011 cm^{-1} region of para-substituted benzenes was substituent dependent and they suggest that it has some ν(C-X) character. The assignments are shown in Table 5. The band expected near 1111 cm^{-1} occurs in the same region as an X-sensitive mode of the type.



This is expected in the 1090 cm^{-1} region[61], it is a mode which involves considerable ring motion and movement of the substituent atom. If both para substituents are the same only one absorption is expected in this region for this type of mode, whereas two absorptions may occur if the substituents are different.

In this study the band near 1090 cm^{-1} may contain a contribution from the X-sensitive mode and have some β(C-H) character. In the tolyl compound there is only one intense band in this region at 1080 cm^{-1} and this probably is due to β(C-H) and a skeletal mode. Similar problems occur with the bands expected near 1175 and 1258 cm^{-1}. The former occur in the region of monosubstituted β(C-H) modes. In the simple benzimidates there is only one benzene ring and the absorption bands occur at 1169 cm^{-1} in ethyl p-chlorobenzimidate and 1170 cm^{-1} in ethyl p-toluimidate. In the other members one band is assigned to two modes, one from the mono rings and one from the para ring, both being of β(C-H) type. The remaining β(C-H) mode is assigned as shown in Table 5.

Table 5

Wavenumber of the Absorption Bands, corresponding to β(C-H) Modes of the p-disubstituted Rings

Compound	Position of Absorption/cm^{-1}			
Ethyl-p-chlorobenzimidate	1017	1095	1169	1304
Ethyl-p-toluimidate	1023	1080	1170	1288 ?
N-phenyl-p-chlorophenyl benzimidate	1015	1085	1165	1285
N-p-chloro phenyl phenyl benzimidate	1012	1075	1170	1295
N-phenyl phenyl-p-chlorobenzimidate	1015	1080	1168	1285
N-benzoyl-p-chlorodiphenylamine	1018	1075	1180	1285
N-p-chlorobenzoyl diphenylamine	1018	1075	1178	1290

It should, however, be noted that it is very difficult to know whether the bands arise from vibrations in the mono or disubstituted rings.

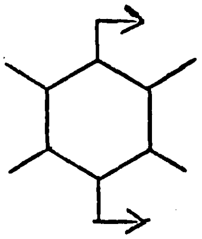
From the disubstituted benzene ring four modes corresponding to the out of plane motion of the (C-H) bonds are expected. These should occur in the 800 - 950 cm^{-1} region. On examining the spectra there appears to be very little change in this region on p-substitution. There were no obvious correlations. Again it was difficult to estimate which bands were due to which ring.

The X-sensitive modes were assigned by comparison with earlier studies on substituted benzenes[62,63]. In the compounds studied the assignments of the X-sensitive and ring modes below 700 cm^{-1} was complicated by the presence of three rings attached to the skeleton by three different types of atom.

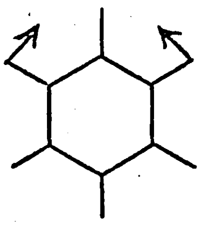
Meta-disubstitution

As in the case of para-disubstitution there will be considerable overlap of the ring modes of the meta ring and the mono ring.

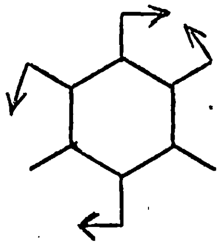
The in plane (C-H) bending modes[45] are depicted as follows with their expected region of absorption in cm^{-1}.



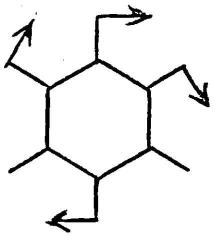
1076 ± 7



1096 ± 7



1157 ± 5



1278 ± 12

In the case of N-aryl aryl arylimidates and the N-aroyl diarylamines the β(C-H) modes of the meta and mono rings were undistinguishable. The assignments for the simpler meta benzimidates and related esters are shown in Table 6.

Table 6

β(C-H) of the meta-substituted ring/cm^{-1}

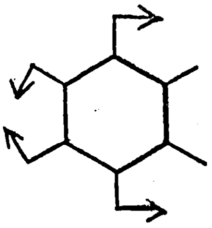
Ethyl-m-chlorobenzimidate	1273	1178	1095	1072
Ethyl-m-toluimidate	1286	1174	1095	1072
Ethyl-m-chlorobenzoate	1282	1178	1087	1075
Ethyl-m-toluate	1303	1176	1109	1085

The out-of-plane (C-H) deformations are assigned as shown in the tables without need for further comment.

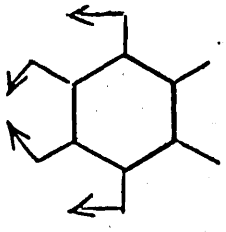
The ring modes and the X-sensitive modes behave as expected, e.g. the modes similar to p and v in monosubstituted benzenes are expected to be unaffected by meta substitution. The modes q, r and s, however, are expected to change.

Ortho-disubstitution

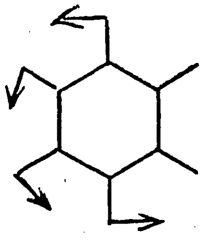
The four in plane (C-H) deformation modes expected [88,79] for ortho-substituted benzene rings are shown below with expected wavenumber range[45] of the absorptions.



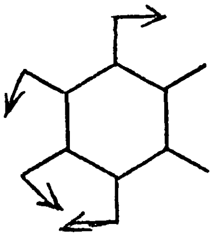
1160 ± 4



1033 ± 11



1269 ± 17



1125 ± 14

Again it is difficult to distinguish bands due to the ortho-disubstituted ring in the N-aryl aryl arylimidate from bands due to the two monosubstituted rings. However, the above β(C-H) modes due to ortho-disubstitution are assigned as in Table 7.

Table 7

β(C-H) modes of the ortho-disubstituted ring/cm^{-1}

N-phenyl phenyl-o-chlorobenzimidate	1280	1162	1030
N-o-chlorophenyl phenyl benzimidate	1285 1275	1165	1030
N-phenyl-o-chlorophenyl benzimidate	1285	1160^{+}	1030
N-phenyl phenyl-o-toluimidate	1295	1162	1045 1035
N-o-tolyl phenyl benzimidate	1280	1165	1025
N-phenyl-o-tolyl benzimidate	1285	1155^{+}	1025
N-benzoyl-o-chloro diphenylamine	1290	1160^{+}	1030
N-o-chlorobenzoyl diphenylamine	1275	1160	1038

+ solid state value

As with para and meta-disubstitution it was not possible to unambiguously assign the γ(C-H) modes due to ortho-disubstitution. Where it was possible to assign X-sensitive modes these were assigned with reference to earlier work on ortho-disubstituted benzenes[79,63].

It was again not possible to assign ring modes below 700 cm^{-1} due to the complexity of having three rings each attached to a different type of atom.

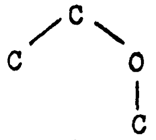
(b) Skeletal modes of vibration

In the study of the skeletal modes of the imidates no help is obtained from symmetry considerations. The highest symmetry likely is

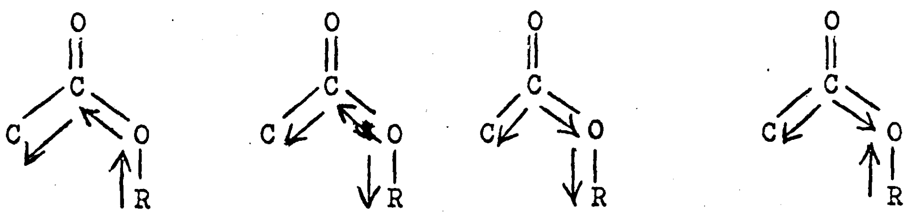
C_s and in many cases the imidates are probably non-planar. In order to assign the skeletal modes, some simpler molecules with similar skeletons are discussed. It is knownthat, when a molecule contains adjacent bonds of similar force constant mixing of the vibrational modes occurs. Instead of say two discrete independent vibrational modes one gets an in phase and out of phase motion of the two bonds.

Skeletal modes in the ester systems

When the following grouping is considered:

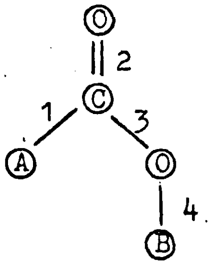


if all the masses attached to the atoms are similar then there is considerable mixing of the modes[17]. Nolin and Jones[64] assigned methyl acetate and described the skeletal modes in terms of a ν_{as}(C-C(=O)-O) similar to that in acetone and a ν_{as}(C-O-C) stretching mode, similar to that in ether. Jones and Sandorfy[56] draw four skeletal modes for this type of ester.



This constitutes a complete mixing of modes and are essentially symmetric and anti symmetric stretches of the (C-C-O) and (C-O-C) units. However, these cannot be a true representation as four stretching modes of vibration are derived for three bonds.

The extent of coupling in the system depends on many factors, mass effects and force constants.



When the force constant of bond 2 is very different from those of bonds 1 and 3 there will only be slight coupling, resulting in slight perturbation of the vibrations of bonds 1 and 3.

If bonds 3 and 4 have similar force constants it is to be expected that they will couple extensively and approximate to roughly anti-symmetric and symmetric combinations. Should mass B be greater than the carbon mass, the two vibrations of bonds 3 and 4 will have different amplitudes and the extent of coupling in the normal mode would decrease. The coupling between vibrations of bonds 1 and 3 will be again decided by the nearness of the force constants and by the mass of A relative to that of oxygen as well as the extent to which 3 coupled with 4.

In phenyl benzoate, mass A and mass B are so much larger than the mass of carbon or oxygen that the vibrations of bonds 1 and 4 are probably largely localised in these bonds.

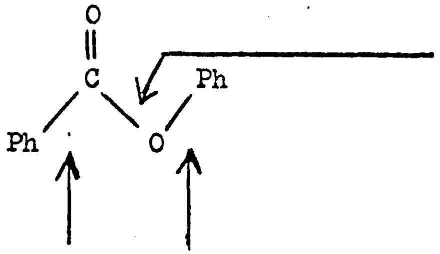
In methyl acetate the masses are all very similar so the system is expected to be extensively coupled.

Ethyl benzoate represents an intermediate stage, the vibration of bond 1 is expected to be largely localised in the bond, vibrations of bonds 3 and 4 are expected to be of similar amplitude and extensive coupling is therefore expected.

Ethyl benzimidate is a similar system to ethyl benzoate and the vibrations are expected to be similar to those in ethyl benzoate.

Expected amplitudes of vibration for the skeletal modes of some esters

Phenyl benzoate

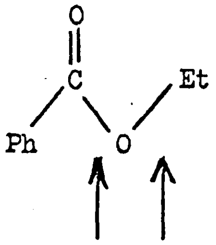


larger amplitude due to 'light' C and O atoms.

small amplitude due to heavy masses (Ph = 77)

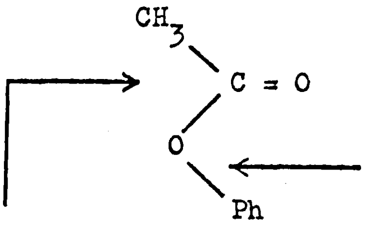
The ν(C-O) mode is expected to be similar to the ν(C-O) mode in methanol but is here perturbed by the ν(C=O) and ν(Ph-O) and ν(Ph-C) modes.

Ethyl benzoate



similar amplitudes
coupling expected to give
anti-symmetric ether type mode
~ 1100 cm^{-1}

Phenyl acetate



amplitude much lower
due to heavier Ph mass.

amplitudes of
$\nu(CH_3\text{-}C)$
$\nu(C\text{-}O)$
expected to be similar
resulting in coupling to
an overall acetone type
anti symmetric combination

The actual assignment of these modes is discussed below.

Skeletal Modes in Related Compounds

ν(Ph-C)

The absorption at 1261 cm^{-1} in the spectrum of acetophenone was assigned by Lebas[65] to a ν(Ph-C) mode by comparison with similar absorptions in benzaldehyde at 1200 cm^{-1} and in benzoyl chloride at 1202 cm^{-1}. The elevation in wavenumber being ascribed to coupling with neighbouring $\nu(C\text{-}CH_3)$ mode which was not possible with the other two compounds. In benzaldehyde the adjacent stretching vibration would be a ν(C-H) which is of much higher wavenumber than ν(Ph-C). In benzoyl chloride the adjacent stretch would be a ν(C-Cl) mode of much lower wavenumber.

In acetophenone, benzaldehyde and benzoyl chloride the ν(C=O) occurs at 1689, 1709 and 1774 cm^{-1} respectively, and the ν(Ph-C) at 1261, 1202 and 1200 cm^{-1} respectively. There is undoubtedly some coupling of ν(C=O) and ν(Ph-C).

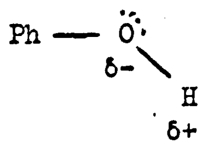
Benzaldehyde and acetophenone would be expected to have similar electron density at the carbon carrying the carbonyl bond; benzaldehyde by the difference in electronegativity of C and H, acetophenone by the inductive effect of the (CH_3) group. In benzoyl chloride the carbon carrying the carbonyl bond is itself bonded to the electron withdrawing Cl atom. The ν(C=O) absorption has increased to a value comparable to that in acetone.

ν(Ph-O)

In phenol an absorption at 1256 cm^{-1} has been assigned to an X-sensitive vibration involving ν(Ph-O)[66,67]. Mecke and Rossmy[68] showed that there is no coupling of this mode with the (O-H) bend but that the ν(Ph-O) was coupled with a ring vibration. The spectrum of anisole has been assigned by Owen and Hester[69]. Absorptions at 1246 cm^{-1} and 1039 cm^{-1} have been assigned as stretching modes of the group (Ph-O) and ($O-CH_3$) respectively. The spectrum of phenyl acetate was assigned by Lee and Wilmshurst[70], the absorption at 1194 cm^{-1} being assigned to an X-sensitive mode involving ν(Ph-O). The (C-C-O) acetate fragment was then involved in a ν_{as} mode giving rise to an absorption at 1210 cm^{-1}.

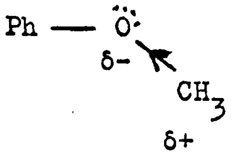
When the respective molecules are drawn and the various inductive effects marked, the range of wavenumbers from 1256 to 1198 cm^{-1} for the ν(Ph-O) mode is consistent with electronic changes in the (Ph-O) bond.

Phenol



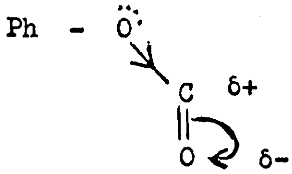
"ν(Ph-O)"
1256 cm^{-1}

Anisole



1246 cm^{-1}

Phenyl acetate

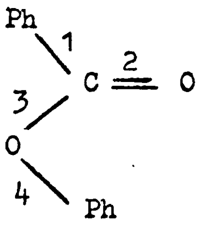


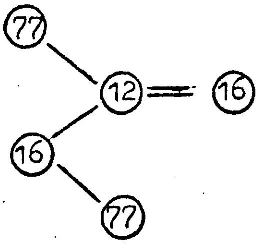
1198 cm^{-1}

There are two approaches to the method of studying the skeletal modes of the esters and imidates. One can either consider fragments of the molecule and assign by comparison with simple molecules or one can consider the system as a whole. The approach which is most relevant depends on the complexity of the system. Use of the first approach is illustrated for some esters.

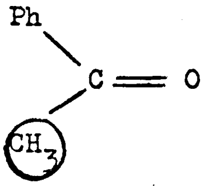
(a) Phenyl benzoate

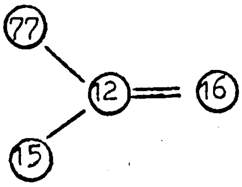
In phenyl benzoate the masses involved are:





It can be seen that the fragment containing bonds 1, 2 and 3 is formally similar to acetophenone.



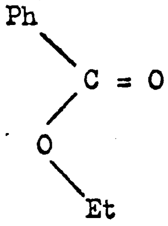


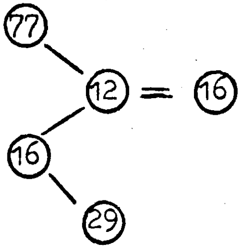
The absorption at 1265 cm^{-1} in the spectrum of phenyl benzoate is assigned as being predominantly a ν(Ph-C) mode by analogy with the assignment of acetophenone[65,71]. The absorption at 1200 cm^{-1} is assigned to an X-sensitive mode which is mainly ν(Ph-O).

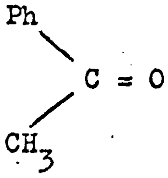
The absorption at 1065 cm^{-1} is assigned to a ν(C-O) mode. The spectrum of methanol has a similar absorption at 1035 cm^{-1} described as ν(C-O) on the basis of the calculated potential energy distribution among the normal coordinates by Tanaka Kuratani and Migushima[72] They show that this is essentially a purely ν(C-O) mode. In ethanol a similar absorption is found at 1053 cm^{-1}, the difference in wavenumber most probably being the result of coupling with adjacent ν(C-C) modes.

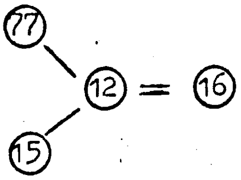
(b) Ethyl benzoate

Consider the masses involved, the system is similar to acetophenone and diethyl ether,

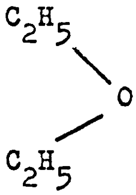


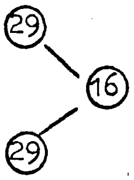






and

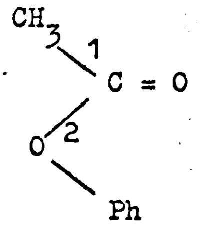


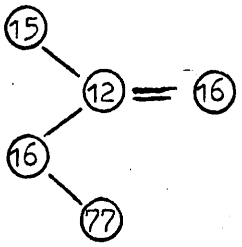


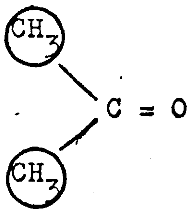
The partial assignment of ethyl benzoate given by Lebas[65] in a study of esters[73] describes the absorption at 1270 cm^{-1} as being similar to that in acetophenone at 1261 cm^{-1} which was described as principally a ν(Ph-C) mode. The spectrum of diethyl ether has absorptions at 1120 and 846 cm^{-1} assigned by Weiser et. al[74] to an anti-symmetric (C-O-C) stretch and symmetric (C-O-C) stretch respectively, the ν_s(C-O-C) vibration being coupled with adjacent ν(C-C) mode. A band at 1108 cm^{-1} is found in the spectrum of ethyl benzoate (Table 25, Appendix) and is assigned as being essentially a ν_{as}(C-O-C) mode.

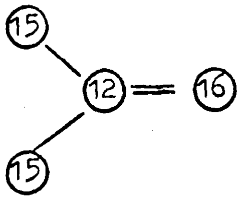
(c) Phenyl acetate

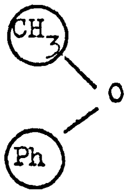
In the spectrum of phenyl acetate there are strong absorptions at 1210 cm^{-1} and 1194 cm^{-1}. These were assigned by Lee and Wilmshurst[70] to the ν(C-O) mode of the acetate group and an X-sensitive mode respectively. Considering the masses and bonding in phenyl acetate the system contains fragments similar to acetone and anisole.

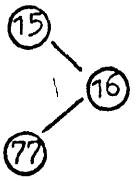










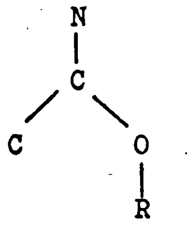


The spectrum of acetone has been assigned by Overend and Dellepiane[54], an absorption at 1215.5 cm^{-1} being assigned to ν_{as}(C-C-C) and the band at 786.5 cm^{-1} to ν_{s}(C-C-C).

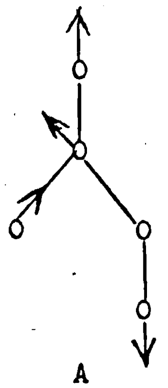
The absorption at 1210 cm^{-1} in phenyl acetate could be described as ν_{as}(C-C-O) and that at 1194 cm^{-1} as an X-sensitive benzene mode containing considerable (Ph-O) stretch.

Skeletal Modes in the Imidate Systems

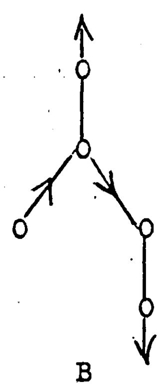
Prichard[8,9] in his study of simple aliphatic imidates described the skeletal modes in terms of a five particle system. This is the alternative approach.



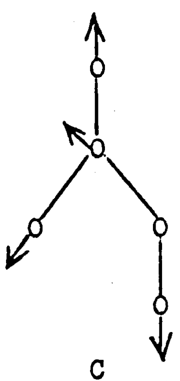
This can be considered as two coupled three particle systems each having associated with it a pseudo symmetric and pseudo anti symmetric vibration which would lead to the following mixed modes:


A

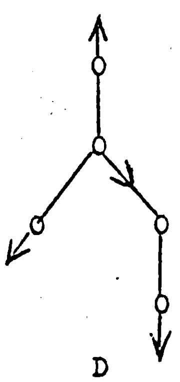
(1314 cm^{-1})


B

(1086 cm^{-1})


C

(1009 cm^{-1})


D

(906 cm^{-1})

The wavenumbers shown are for the assignment of methyl trichloroacetimidate[8].

Hughes[7] prepared a large number of aliphatic imidates and assigned the skeletal vibrations in terms of these modes.

The approach of Prichard and Hughes is probably more appropriate for relatively light systems where mechanical coupling is extensive. Thus the esters listed in Table 9 can be treated in a similar manner to the imidates given in Table 8, i.e. the skeletal modes, A, B, C and D can be recognised in both esters and imidates. However, it will be seen that this approach is not appropriate for the N-aryl aryl arylimidates.

Table 8

Skeletal Modes in some ethyl benzimidates

Compound (ν C=N ~ 1640 cm^{-1}) Mode:	A	B	C	D
Ethyl benzimidate	1329 cm^{-1}	1075 cm^{-1}	1016 cm^{-1}	873 cm^{-1} [7]
Ethyl-p-chlorobenzimidate	1330	1080	1017(+βCH)	877.5
Ethyl-p-toluimidate	1332.5	1080	1015	877.5
Ethyl-m-chlorobenzimidate	1325	1080	1021	881
Ethyl-m-toluimidate	1329	1080	1024	909

Due to the formal similarity of the ester structure to the imidate system it was decided to examine the spectra of the analogous esters for similar bands.

Table 9

Skeletal modes in some ethyl benzoates

Compound (ν C=O ~1720 cm^{-1}) Mode:	A	B	C	D
Ethyl benzoate	1270 cm^{-1}	1108 cm^{-1}	1020 cm^{-1}	850 cm^{-1}
Ethyl-p-chlorobenzoate	1272	1100	1015	850
Ethyl-p-toluate	1275	1105	1020	840
Ethyl-m-chlorobenzoate	1260	1134	1024.5	897
Ethyl-m-toluate	1282.5	1120 (sh)	1029	900

Effect on these modes of changing the (C=N) group for the (C=O) group.

The skeletal mode A involving some coupling with the ν(C=N) mode has shifted to a lower wavenumber when the (C=N) group is replaced by (C=O) which absorbs at a higher wavenumber.

The skeletal mode B has moved to slightly higher wavenumber in the esters.

Mode C, described as mainly ν(C-C) without such contribution from ν(C=N) has remained unaltered by changing from (C=N) to (C=O).

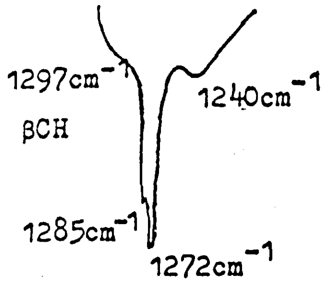
Mode D involving some ν(C=N) has decreased in wavenumber for para-substituents and increases on meta substitution.

The 1270 cm^{-1} band in these compounds (shown in Fig. 5) is discussed below.

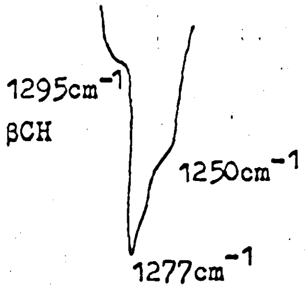
Fig. 5

The 1270 cm^{-1} band in the series of esters studied

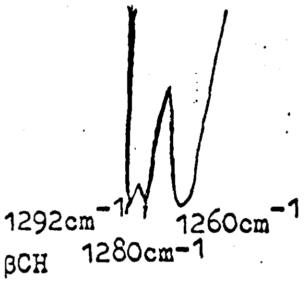
Ethyl-p-chlorobenzoate



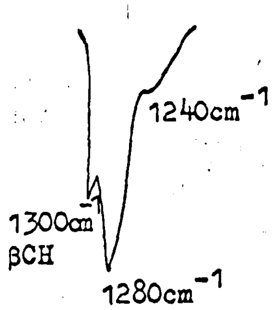
Ethyl-p-toluate



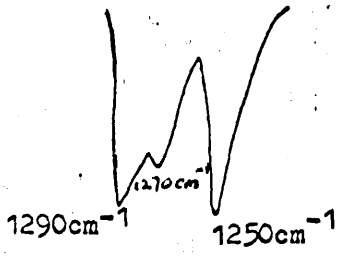
Ethyl-m-chlorobenzoate



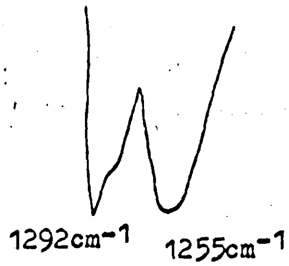
Ethyl-m-toluate



Ethyl-o-chlorobenzoate



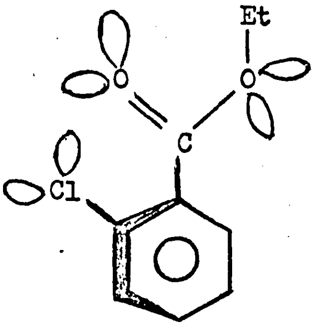
Ethyl-o-toluate



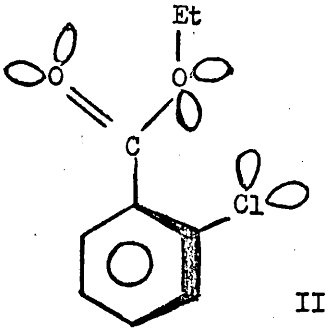
The rates of alkaline hydrolysis of ortho substituted ethyl benzoates have been found to be affected purely by electrical effects of the substituent[75]. Steric effects were not found to be significant. The electrical effects were found to be almost entirely localised field effects.

The alkaline hydrolysis of ethyl ortho benzoate involves attack of OH^- on the +ve end of the C=O dipole. This is at the carbon atom adjacent to the aromatic ring. The electron density at this carbon atom is then decided by the field effect of the ortho substituent.

The ν(Ph-C) absorption of ethyl-o-chlorobenzoate is associated with two absorptions in the infrared spectrum. This is consistant with two conformers of the forms I and II.



I



II

The repulsions between the chlorine lone pairs and the lone pairs on the oxygen atoms should be different in I and II. This would lead to two different angles between the aromatic ring plane and the plane containing the ethyl carboxyl group for forms I and II. This in turn means a difference between forms I and II of the distance between the (Ar-C) dipole and chlorine atom and hence a different magnitude of field effect (dipole dipole interaction)[76].

The corresponding ν(Ph-C) absorption in the meta-chloro compound also shows slight splitting. Again this is consistent with two forms analogous to I and II above. The spectra of both compounds also show splitting of the ν_{as}(C-O-C) mode - this mode would be sensitive to changes in orientation of the chlorine atom to the C-O dipole and changes in electron density at the carbon of the carbonyl group. Both ν(C=O) absorptions are broader than in the ethyl benzoate and ethyl-p-chlorobenzoate spectra.

A field effect of chlorine on the (C=O) dipole has been reported for ortho halogen substituted benzoic acids and methyl benzoates by Brookes, Eglinton and Morman[77] where there is an actual splitting of the carbonyl absorption observed in solution.

The skeletal modes in the spectra of the N-aryl aryl arylimidates are best discussed in terms of the assignment given for the skeletal modes of phenyl benzoate. The two systems are formally similar and the arrangement of the masses on the bonds such that little coupling is expected between the (Ph-C), (C-O) and (O-Ph) stretching vibrations.

All the N-aryl aryl arylimidates show, in their spectra, (Appendix), an absorption near 1050 cm^{-1} assigned by analogy to phenyl benzoate to a $(C_{\textbf{aliphatic}}-O)$ stretch.

All these compounds showed a series of absorptions between 1200 - 1300 cm^{-1}, the slight changes in which are discussed below. The basic pattern of these absorptions was found in each spectrum;

An absorption near 1270 cm^{-1} is assigned to a mode predominantly ν(Ph-C).

An absorption near 1200 cm^{-1} is assigned to an X-sensitive mode involving ν(Ph-O).

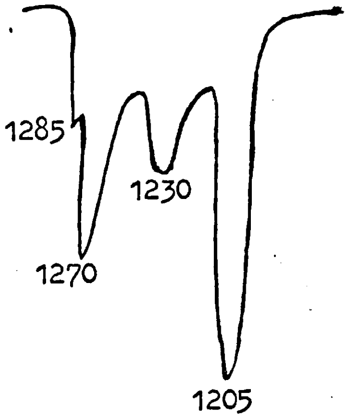
An absorption near 1240 cm^{-1} is assigned to a ν(Ph-N) stretch by analogy with the above absorptions taking account of the mass of nitrogen being intermediate between that of carbon and that of oxygen.

The 1300-1200 cm^{-1} region

The spectrum of N-phenyl phenyl benzimidate in this region is shown in Fig. 6.

Fig. 6.

The absorptions in the 1200-1300 cm^{-1} region of the spectrum of N-phenyl phenyl benzimidate

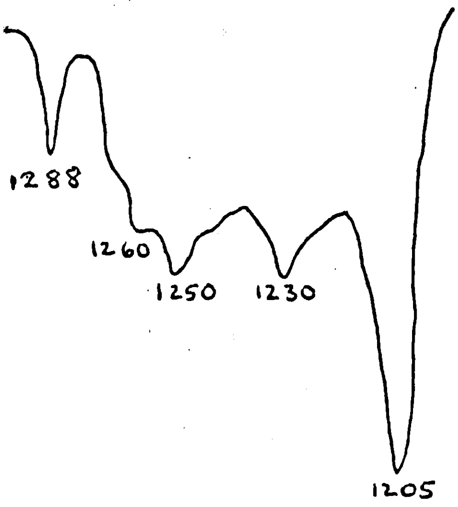


The band at 1270 cm^{-1} is assigned as being predominantly ν(Ph-C), the 1205 cm^{-1} band as predominantly ν(Ph-O) and the 1230 cm^{-1} band is tentatively assigned as a ν(Ph-N) mode.

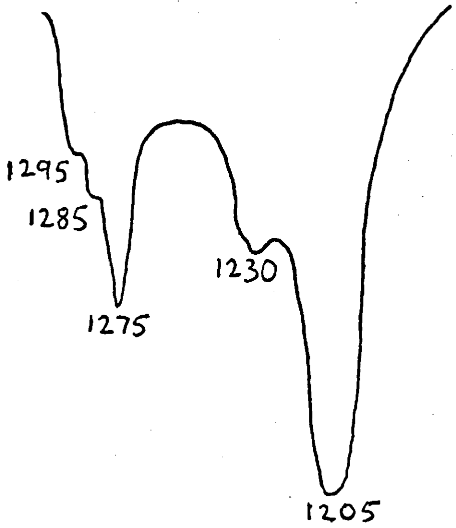
This pattern was unaltered by para-substitution at any of the three sites.

Fig. 7

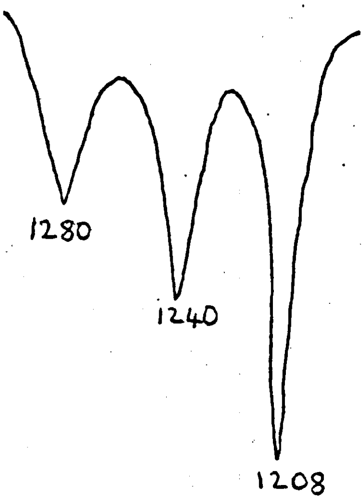
Skeletal region of the meta-substituted compounds



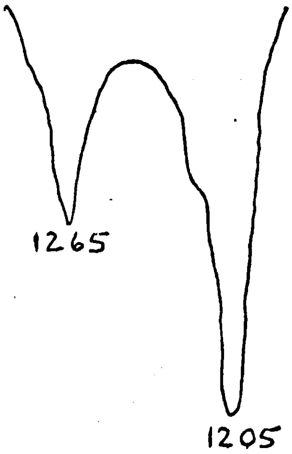
N-phenyl phenyl-m-chlorobenzimidate



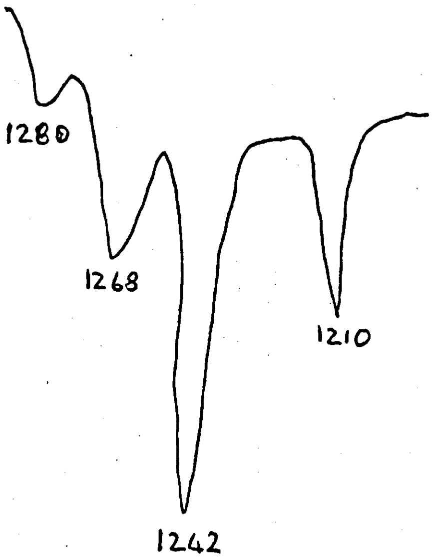
N-phenyl phenyl-m-toluimidate



N-m-tolyl phenyl benzimidate



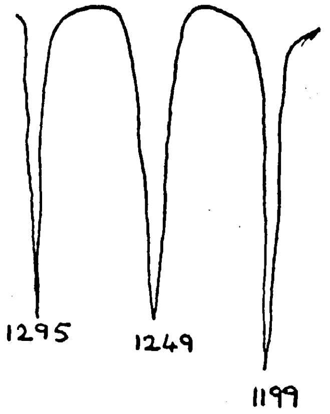
N-phenyl-m-chlorophenyl benzimidate



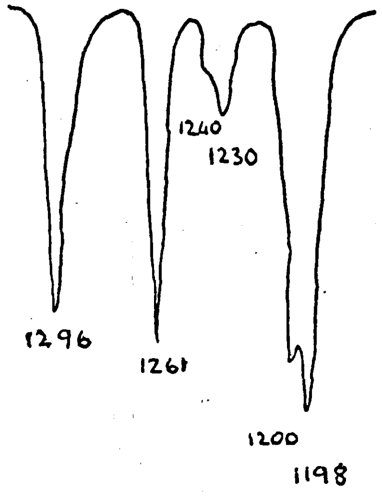
N-phenyl-m-tolyl benzimidate

Fig. 8

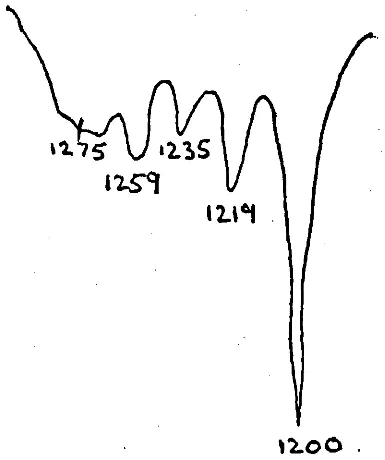
Skeletal region of the ortho-substituted compounds



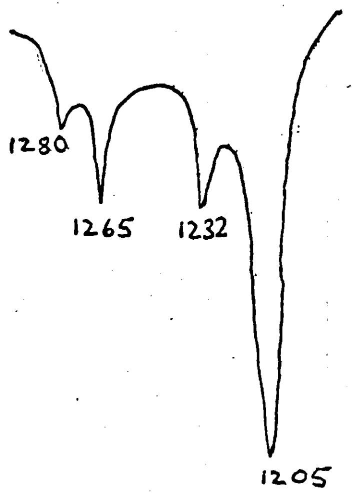
N-phenyl phenyl-o-chlorobenzimidate



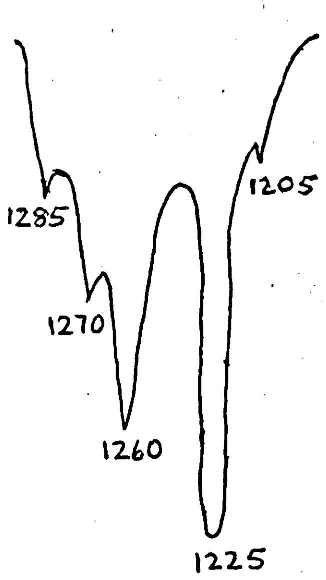
N-phenyl phenyl-o-toluimidate



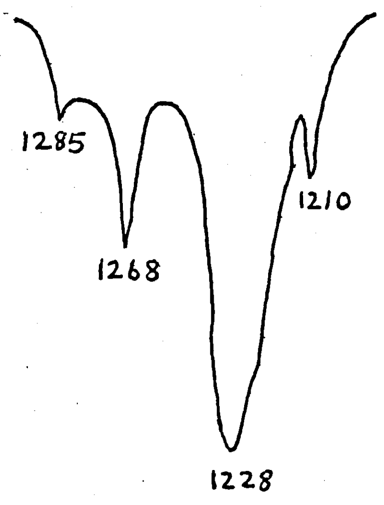
N-o-chlorophenyl phenyl benzimidate



N-o-tolyl phenyl benzimidate



N-phenyl-o-chlorophenyl benzimidate



N-phenyl-o-tolyl benzimidate

It is interesting that substitution of the oxygen ring has an effect on the ν(Ph-O) vibration. This is described as an X-sensitive mode. The highest X-sensitive mode found by Green[62] for p-xylene was 1204 cm^{-1} and for p-chloro toluene 1209 cm^{-1}. Para-substitution would then be expected not to alter the monosubstitution value for this mode of 1200 cm^{-1}.

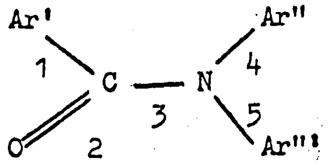
The corresponding modes in m-xylene and m-chloro toluene are given[78] as 1252 cm^{-1} and 1221 cm^{-1} respectively. The observed effect on the 1200 cm^{-1} band is in accordance with this.

The X-sensitive modes of o-xylene and o-chloro toluene are reported[79] as 1222 and 1207 cm^{-1} the similarity is not so marked in this case but the electrical and steric effects of ortho-substitution in this already crowded system are difficult to assess. This X-sensitive mode is for phenol[66,67] derived from mode 7a of benzene (Fig. 2), page 69.

p-disubstitution would introduce in phase ring - substituent stretching. Whereas ortho or meta substitution introduces out of phase motion.

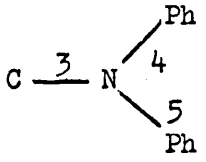
In benzene this 7a mode is identified with an absorption at 3048.3 cm^{-1}. The X-sensitive mode should be principally a ν(Ph-O) vibration. There is probably more coupling with this mode and the other ring vibrations than in the case of ν(Ph-C); this is because this is of the appropriate energy.

Assignment of the skeletal modes of vibration of the N-aroyl diarylamines



In the N-aroyl diarylamines little coupling is to be expected between bonds 1, 3 due to mass and electronic differences. Bond 1 is very similar to that in acetophenone which causes an absorption in the 1260 cm^{-1} region. Bond 3 is similar to an amine type (C-N) bond which is expected to absorb between 1220 and 1020 cm^{-1}. Even less coupling is expected between bond 2 and bonds 1 and 3 due to the larger force constant of the (C=O) bond relative to the (Ph-C) or (C-N) bonds.

Bonds 1,2,3 approximate very nearly to the acetophenone system. A more or less characteristic (C=O) frequency is expected, also an absorption around 1260 cm^{-1} corresponding to principally a (Ph-C) stretch. Bonds 3,4,5 are of interest especially in compounds containing the system;

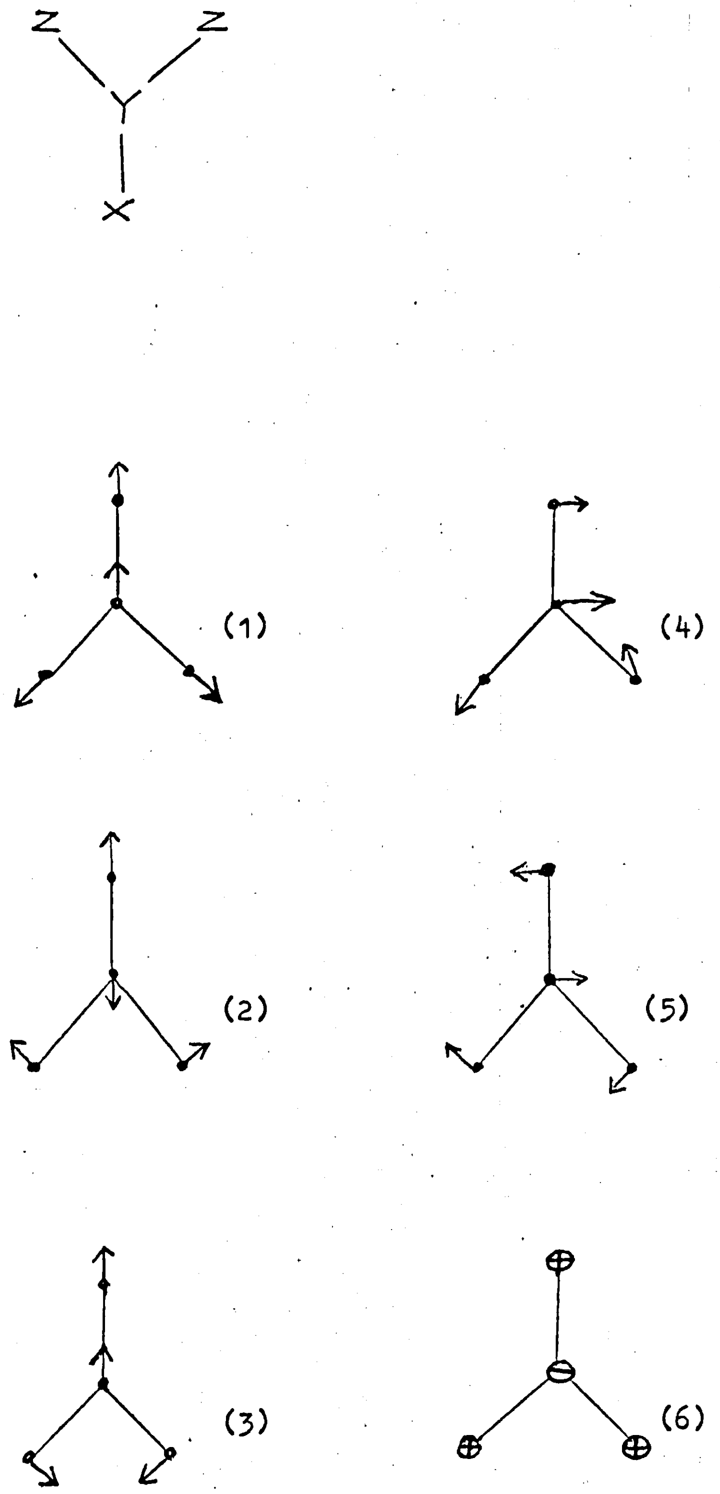


In this case extensive coupling is expected between bonds 4 and 5 to produce an antisymmetric mode and a symmetric mode.

The modes of vibration of an XYZ_2 molecule are shown in Fig. 9[17].

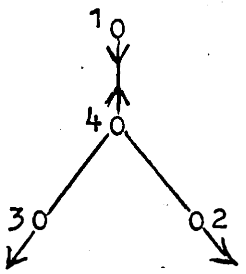
Fig. 9

The modes of vibration of an XYZ_2 molecule



A routine spectrum of diphenylamine was recorded and absorptions between 1200-1400 cm^{-1} observed. A strong absorption was found at 1320 cm^{-1} which is assigned to the antisymmetric mode (4) in Fig. 9. Due to the relative masses of H and Ph little coupling is expected between ν(N-H) and ν(N-Ph) but coupling between β(N-H) and ν(N-Ph) is possible.

A routine spectrum of triphenylamine was recorded. In particular the mode analogous to (4) above is of interest. For the XY_3 molecule all three bonds are participating to a similar extent and mode (4) now[80] becomes:

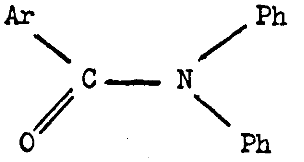


Of particular interest are the motions of bonds (1-4) and (3-4). The overall motion is that of an anti symmetric mode, the motion of bond (2-4) is mixed with this mode. In the spectrum of triphenylamine there is an absorption 1277 cm^{-1} corresponding to that at 1320 cm^{-1} in diphenylamine.

A simple isolated ν(Ph-N) vibration is expected around 1240 cm^{-1}(ν(Ph-O) $\sim$ 1200 cm^{-1}, ν(Ph-C) $\sim$ 1270) coupling of such vibration with a ν_{as}(Ph-N-Ph) in triphenylamine might be expected to lower the wavenumber of the overall mode from that of the pure ν_{as}(Ph-N-Ph). Coupling in diphenylamine of ν_{as}(Ph-N-Ph) with a β(N-H) mode (assigned to an absorption around 1290 cm^{-1} in some imidate systems[7]) might be expected to produce an overall mode of higher wavenumber than a pure ν_{as}(Ph-N-Ph).

The spectra of diphenylamine and triphenylamine are discussed by Ritschl[81]. This author mentioned the difficulty in unambiguously assigning the 1300-1400 cm^{-1} region for these compounds, because of the presence of combination bands, β(C-H) and ring modes.

The 1250-1400 cm^{-1} region of the spectra of compounds of the type



(A)

would be expected to contain an absorption similar to that in acetophenone due to mainly a ν(Ph-C) [probably coupled to some extent with ν(C-N) and ν(C=O)] and a ν_{as}(Ph-N-Ph) mode perturbed by ν(C-N). The absorption due to ν(C-N) is either not apparent due to its intrinsically low intensity or the mode does not exist as a recognisable isolated mode, due to involvement with other normal modes.

The ν(C=O) absorption is of similar wavenumber to that of ν(C=N) in the imidate compounds.

In order to confirm the assignment of the skeletal modes of the N-aroyl diarylamines a further study of similar compounds is required.

(c) Localised Modes of Vibration

ν(N-H)

The ν(N-H) absorption in all the ethyl benzimidates studied was asymmetric in form. The absorption was studied over a range of concentrations of ethyl benzimidate in carbon tetrachloride. At 0.002 mol dm^{-3} the ν(N-H) gave rise to a sharp symmetrical absorption at 3322 cm^{-1}. At 0.2 mol dm^{-3} a series of weak absorptions were observed at 3255, 3200 and 3155 cm^{-1}, these were consistent with overtones of absorptions at 1630 1600 and 1575 cm^{-1} respectively. At 0.5 mol dm^{-3} a shoulder near 3305 cm^{-1}

had appeared making the ν(N-H) absorption asymmetric. At 1 mol dm^{-3} the shoulder was more marked and was beginning to coalesce with the absorption at 3255 cm^{-1}. The broad shoulder in the liquid film is consistent with aggregation of ethyl benzimidate in the liquid state.

ν(C=N)

The ν(C=N) has been observed and assigned for several compounds.

Table 10

The ν(C=N) in some compounds

Compound	Absorption position or wavenumber spread/cm^{-1}	Reference
Imidoyl chloride	1689	99
N-hydroxyl methyl benzimidate	1630	100
Cyclic Imidic esters	1643 - 1670	101
Aromatic Schiff bases e.g. N-**benzylidineaniline**	1613 - 1631	102
Methyl benzimidate	1639	100
Methyl acetimidate	1660	9

Fabian, LeGrand and Poirier[82,83] made a study of the ν(C=N) in several compounds. Their results together with those of the authors in the table above show that the ν(C=N) is a strong broad absorption found between 1600 and 1700 cm^{-1}.

Melendez and Sanchez del Olmo[84] in a study of the effect of substituents on the wavenumber of the ν(C=N) in 17 imines (R-N=CR'R") have found that each phenyl group introduced lowered the ν(C=N) by 20 - 30 cm^{-1}. Baccar et. al.[85] find that the ν(C=N) is similarly lowered 20 cm^{-1} in ethyl benzimidates from the value in phenyl acetimidates.

The ν(C=N) is then well characterised and was readily assigned in all the imidates of this study.

ν(C=N) and ν(C=O) of ethyl benzimidate and ethyl benzoate

Due to the similarity of structure the spectra of ethyl benzimidate and ethyl benzoate were expected to be similar. With the exception of a few absorptions this was found to be true. The ν(C=O) of ethyl benzoate is assigned to a strong absorption around 1720 cm^{-1}, the ν(C=N) of ethyl benzimidate is assigned to a strong absorption near 1635 cm^{-1}. The difference in wavenumber could be the result of changes in force constants due to the use of different molecular orbitals in bond formation, and partly due to the fact that the ν(C=N) in addition to the possible vibrations with which it (and the ν(C=O)) can couple, could couple with the β(N-H) mode (assigned to an absorption near 1290 cm^{-1}).

ν(C=N) and ν(C=O) of N-aryl aryl arylimidates and N-aroyl diarylamines

Both absorptions are observed at similar wavenumber, i.e. near 1670. The higher wavenumber of the ν(C=N) in these imidates compared with the ν(C=N) in the ethyl benzimidates could be due to less delocalisation of the double bond into the aromatic ring due to steric interaction forcing the rings more out of the plane containing the (C=N) group. Also in the N-substituted imidates the possibility of coupling between ν(C=N) and β(N-H) has been removed. The β(N-H) was assigned to an absorption near 1290 cm^{-1}, the ν(Ph-N) introduced in the N-aryl aryl imidates is assigned to an absorption at 1240 cm^{-1}.

Table 11

ν(C=O) in some esters

(1) in liquid phase; (2) in solution. 0.1 mol dm^{-3} in benzene

Compound	ν(C=O)
Ethyl benzoate	1720 cm^{-1} (1)
	1725 cm^{-1} (2)
Ethyl-p-chlorobenzoate	1725 cm^{-1} (1)
	1725 cm^{-1} (2)
Ethyl-o-chlorobenzoate	1725 cm^{-1} (br) (1)
	1738 cm^{-1}, 1725 cm^{-1} (sh) (2)
Ethyl-p-toluate	1727 cm^{-1} (1)
	1725 cm^{-1} (2)
Ethyl-o-toluate	1720 cm^{-1} (br) (1)
	1725 cm^{-1} (2)
Ethyl-m-toluate	1723.5 cm^{-1} (1)
	1725 cm^{-1} (2)

Table 12

ν(C=N) in some analogous imidates (in liquid phase)

Compound	ν(C=N)
Ethyl benzimidate	1640 cm^{-1}
Ethyl-p-chlorobenzimidate	1640 cm^{-1}
Ethyl-p-toluimidate	1639.5 cm^{-1}
Ethyl-m-chlorobenzimidate	1642 cm^{-1}
Ethyl-m-toluimidate	1637 cm^{-1}

With the exception of ortho-substituents the position of the absorption due to ν(C=N) and ν(C=O) is insensitive to substitution of the phenyl ring.

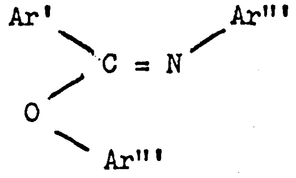


Table 13

ν(C=N) in some aryl aryl arylimidates

Ar'' = Ar''' = Ph	Disc (all br) cm-1	Cyclohexane cm-1 (intensity)			Tetrachloroethylene cm-1 (intensity)		
Ar' = p-chlorophenyl	1655	1672(7)	1662(7)	1655(6)	1662 br(7)		
m-chlorophenyl	1660	1675(6)		1655(5)	1672(6)		1655(6)
o-chlorophenyl	1670	1680(8)			1680(8)		
m-tolyl	1665	1672(7)		1655(6.5)	1670(6)		1655(6)
o-tolyl	1665	1675(10)			1672(10)		
Ar' = Ar'' = Ph							
Ar''' = p-chlorophenyl	1640	1672(7)		1655(7)	1660 br (7)		
o-chlorophenyl	1670	1680(8)	1665(7)	1655sh(6)	1680(8)	1665(7)	1655 sh(6)
p-tolyl	1645	1670(6)		1655(7)	1670(6)		1655(7)
m-tolyl	1660	1675(6)		1658(6)	1665(6)		1655(6)
o-tolyl	1660	1678(7)		1660(6)	1675(7)		1660br sh (6)
Ar' = Ar''' = Ph							
Ar'' = p-chlorophenyl	1665	1670br(6.5)		1655sh(5.5)	1670br(5)		1655sh(4)
m-chlorophenyl	1670	1672(7)		1660(6)	1672(7)		1655brsh(6)
o-chlorophenyl	1665	1680(7.5)		1655shbr(3)	1680(7)br		1655brsh(3)
p-tolyl	1660	1670(7)		1655sh(6)	1670(7)		1655sh(6)
m-tolyl	1670	1670(7)		1655sh(6.5)	1675(8)		1660(8)
o-tolyl	1660	1670(9)		1655sh(7)	1670(10)		1655sh(8)
Ar' = Ar'' = Ar''' = Ph	1660	1675(7)		1658(6)	1670(7.5)		1655(5.5)

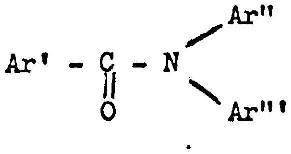


Table 14

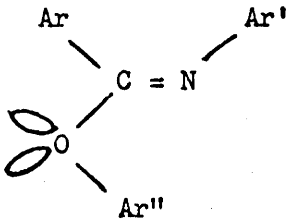
ν(C=O) in some N-aroyl diarylamines

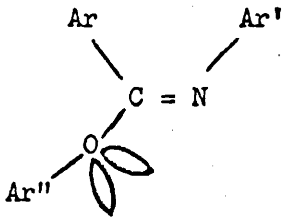
Ar" = Ar"' = Ph	Disc cm^{-1} (intensity)	Cyclohexane cm^{-1} (intensity)	Tetrachloroethylene cm^{-1} (intensity)
Ar' = p-chlorophenyl	1660(10) 1655sh(10)	1677(10)	1672(10)
m-chlorophenyl	1660(10)	1678(10)	1673(10)
o-chlorophenyl	1658(10)	1680(10)	1680(10)
o-tolyl	1650(10)	1678(10)	1672(10)
Ar' = Ar" = Ph			
Ar"' = p-chlorophenyl	1655(10)	1678(10)	1672(10)
m-chlorophenyl	1660(10)	1678(10)	1675(10)
o-chlorophenyl	1670(10) 1655(10)	1680(10)	1678(10)
p-tolyl	1655(10)	1673(10)	1668(10)
m-tolyl	1650(10)[1655(10)]	1675(10)	1670(10)
o-tolyl	1650(10)[1655(sh)]	1672(10)	1670(10)
Ar' = Ar" = Ar"' = Ph	1650(10)	1675(10)	1670(10)

Substitution of the ortho-position of the Ar"' ring by carboxy groups has led to optical activity[109] of the species. It is most likely that the o-chloro and o-tolyl compounds are diastereomeric mixtures.

The ν(C=N) Absorption of N-aryl aryl arylimidates - a temperature study

With the exception of ortho-substituted oxygen and carbon rings the spectra show splitting of the ν(C=N) absorption, around 1670 cm^{-1} in solution. When the oxygen or carbon ring carries an ortho-substituent rotation of the phenol ring attached to oxygen is restricted. The double ν(C=N) absorption is ascribed to some effect of the rotation of the (O-Ph) ring, probably two extreme conformations:





possibly a field effect of the lone pairs on the oxygen.

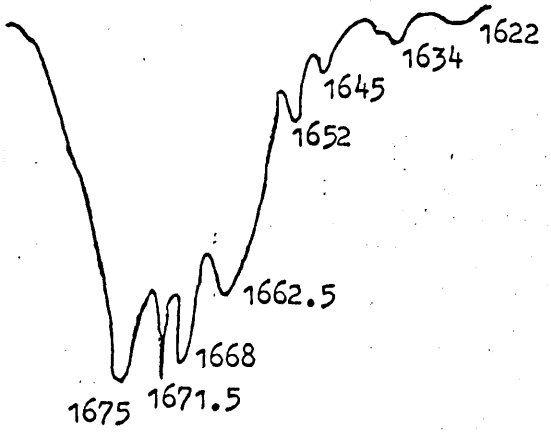
In order to study the cause of the fine structure on the ν(C=N) band, the effect of temperature on the band shape was investigated.

A solution containing 0.09 mol dm^{-3} N-phenyl phenyl benzimidate in tetrachloroethylene was prepared. The spectrum was recorded in the form of a thin film 0.1 mm path length between silver chloride plates in a cell designed to be used over a range of temperatures.

At room temperature the spectrum was recorded on the Beckmann IR9 grating spectrometer over the range 1600 - 1700 cm^{-1}. The operating conditions so chosen to give a resolution better than 0.1 cm^{-1}. The spectrum revealed peaks at 1675, 1671.5, 1668, 1662,5, 1652, 1645, 1634, 1622 cm^{-1} as shown in Fig. 10.

Fig. 10

The fine structure of the ν(C=N) absorption for N-phenyl phenyl benzimidate



The spectrum was also recorded at -20°C, -15°C, -10°C, -5°C, 0°C, room temperature, + 50°C. Varying the temperature over this range had virtually no effect on the spectrum.

The spectrum of N-phenyl phenyl-o-chlorobenzimidate in the region 1190-1300 cm^{-1} showed three strong sharp absorptions at 1199 cm^{-1}, 1248 cm^{-1} and 1295 cm^{-1}. These were assigned, as described previously, as skeletal modes. Unlike the corresponding modes in the other imidates studied the absorptions were sharp. It was thought that the sharpness was due to the chlorine atom preventing most of the freedom of intramolecular rotation in the molecule. This region of the spectrum was examined in the temperature range 25° to 100°C. Over this range of temperature this region of the spectrum was unaltered.

The absorption described as ν(C=N) was also observed over this temperature range and also was unaltered from the spectrum obtained at room temperature.

The analogous methyl-substituted compound was thought not to show such hindrance to intramolecular rotation so the region 1200-1300 cm^{-1} was recorded at varying temperatures between -25°C and +55°C. Again the spectrum was unaffected by temperature over this range.

It would seem most likely that the ortho-chlorine group removed most intramolecular rotational freedom and that the methyl group was also an effective group in removing some of this rotational freedom. It is possible that while the complete rotations of various groups are hindered, a certain amount of oscillation is possible producing broadening of the skeletal absorptions. The ortho-chlorine group is also effective in removing some of this freedom of motion.

3. Nuclear Magnetic Resonance (n.m.r.) Study of Some Arylimidates.

Spectra

The following compounds were dissolved in deuterochloroform and their n.m.r. spectra recorded using the Various HA.60 I.L. operating at 60 MHz. T.M.S. was used as an internal standard.

Table 15

The n.m.r. spectra of some N-aryl aryl arylimidates

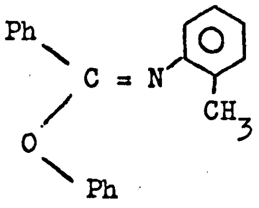
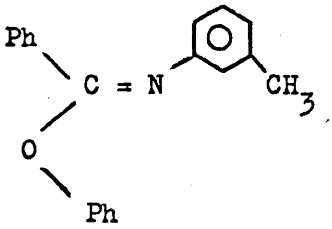
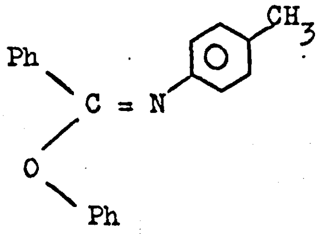
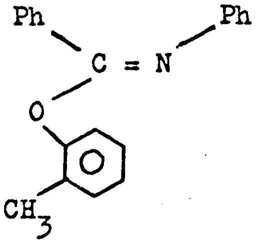
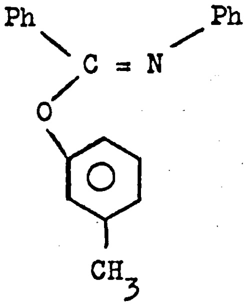
Compound	Principal Absorptions (p.p.m.) T.M.S. value = 0	Integral (No. of protons)	Assignment
	2.175 (130 Hz)	3	CH_3
	7.1 (multiplet)	12	Aromatic H
	7.7 (broad)	2	deshielded ortho protons (carbon ring)
	2.225 (133 Hz)	3	CH_3
	7.1 (multiplet)	12	Aromatic H
	7.7 (broad)	2	deshielded ortho protons (C ring)
	2.225 (133 Hz)	3	CH_3
	7.1 (multiplet)	12	Aromatic H
	7.7 (broad)	2	deshielded ortho protons (C ring)
	2.3 (138 Hz)	3	CH_3
	7.1 (multiplet)	12	Aromatic H
	7.7	2	deshielded ortho protons (C ring)
	2.225 (133 Hz)	3	CH_3
	7.1 (multiplet)	12	Aromatic H
	7.7	2	deshielded ortho protons (C ring)

Table 15 (continued)

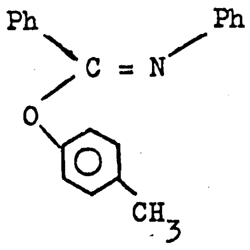
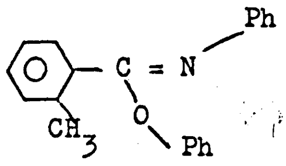
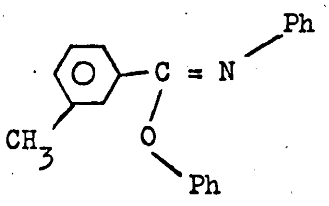
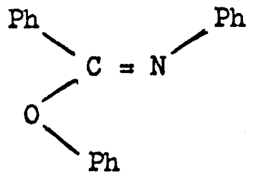
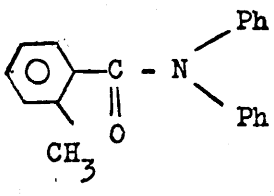
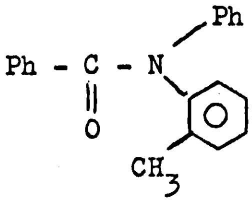
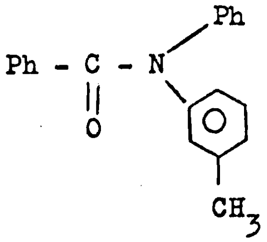
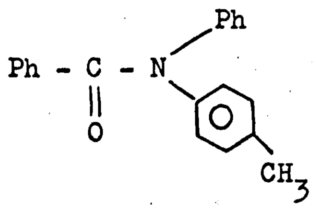
Compound	Principal Absorptions (p.p.m.)	Integral (No. of protons)	Assignment
	2.225 (133 Hz)	3	CH_3
	7.1 (multiplet)	12	Aromatic H
	7.7	2	deshielded ortho protons (C ring)
	2.4 (144 Hz)	3	CH_3
	7.1 (multiplet)	14	Aromatic H
	2.275 (136 Hz)	3	CH_3
	7.1 (multiplet)	12	Aromatic H
	7.7	2	C ring ortho H
	7.1 (multiplet)	-	Aromatic H
	7.7 (broad)	-	C ring ortho H
	2.4 (146 Hz)	3	CH_3
	7.1 multiplet	14	Aromatic H

Table 15 (continued)

Compound	Principal Absorptions (p.p.m.)	Integral (No. of protons)	Assignment
	2.3 (137 Hz)	3	CH_3
	7.1 (multiplet)	12	Aromatic H
	7.4 (broad multiplet)	2	Ortho protons C ring.
	2.3 (136 Hz)	3	CH_3
	7.1 (multiplet)	12	Aromatic H
	7.4 (broad multiplet)	2	Ortho H C ring
	2.3 (137 Hz)	3	CH_3
	7.1 (multiplet)	12	Aromatic H
	7.4 (broad multiplet)	2	Ortho H C ring

It was hoped that the n.m.r. spectra might show up any differences between the three aromatic rings. The aromatic multiplet obtained for each compound was centred around 7.1 p.p.m. and most likely the ring patterns overlap. The tolyl compounds gave rise to a resonance due to the CH_3 group near 2.2 p.p.m. (relative to T.M.S used as an internal standard). A small broad peak was found near 7.7 p.p.m. for all compounds except N-phenyl phenyl-o-toluimidate. In the spectrum of this compound the CH_3 proton resonance was at a noticeably different frequency from those of the other tolyl compounds. This resonance at 2.4 p.p.m. was consistent with deshielding due to electron withdrawal from the ring by the (C=N) group. The CH_3 proton resonance position in the spectrum of N-o-toluoyl diphenylamine was also different from those of other tolyl compounds.

It is not possible to draw any definite conclusions from this however as these results are also consistent with the anisotropic effect of the (C=O) and (C=N) groups[86]. Thus it is not possible using this technique to decide whether the aromatic ring plane is in the same plane as the (C=N) or (C=O) moieties.

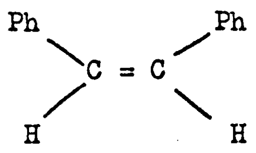
It was hoped that perhaps a study of the ultra violet spectra of the compounds might give any evidence as to whether there were any electronic interaction between the carbon ring and the double bond in the compounds.

4. Ultra Violet Study of the N-aryl aryl imidates

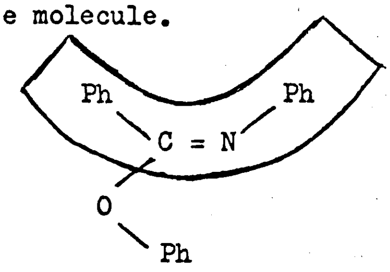
The ultra violet spectra of the N-aryl aryl arylimidates in solution in n-hexane were recorded over the range 30,000 - 50,000 cm^{-1}; the hexane used was Spectrosol hexane fraction and was used without further purification. Solutions of 1×10^{-4} mol dm^{-3} imidate in this solvent were prepared and measurements were made in 1 cm quartz cells using the Unicam SP.800 spectrophotometer. n-Hexane was used in the reference beam.

The ultra violet results are presented (Table 16) with the exception of a strong band around 47,000 cm^{-1} found for each compound as this absorption was near the region of the spectrum where n-hexane itself starts absorbing.

The ultra violet spectra of cis and trans-stilbene form a useful basis for the discussion of the ultra violet spectra of the N-aryl aryl arylimidates. The cis form of stilbene is structurally similar to part of the N-phenyl phenyl benzimidate molecule.



cis-stilbene

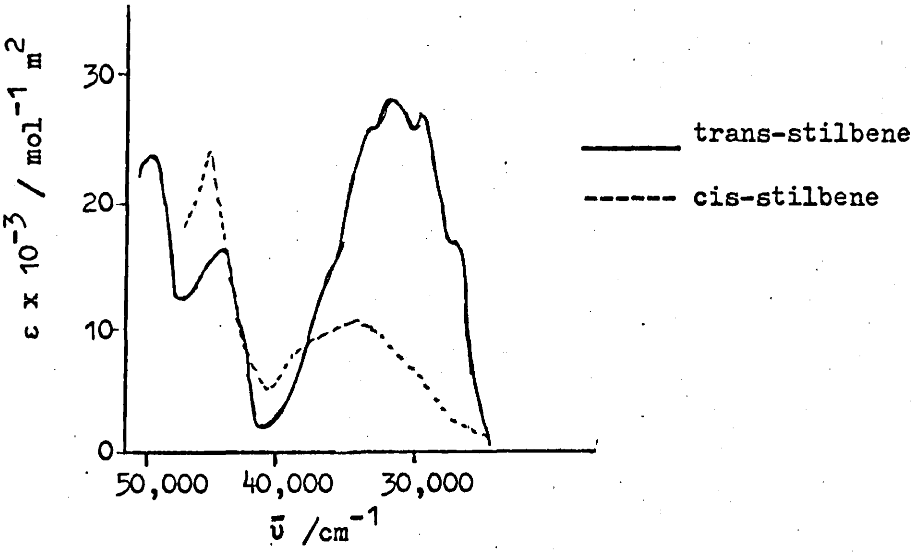


N-phenyl phenyl benzimidate

The differences in the ultra violet spectra of cis and trans-stilbene are shown below in Fig. 11.

Fig. 11

Spectra of cis and trans-stilbene[114]

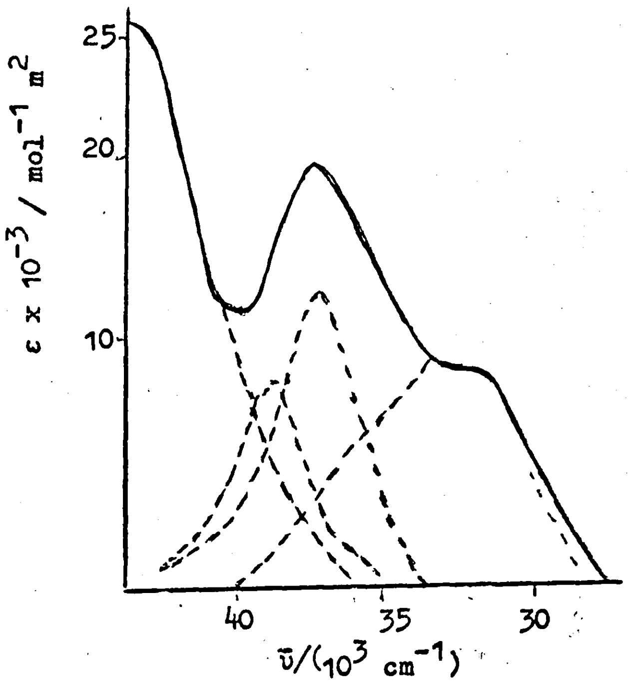


The reduced intensity of the longer wavelength band in cis-stilbene is related to steric crowding in the cis-isomer[115].

The spectrum of trans-benzalaniline (Fig. 12) is similar to that of trans-stilbene. The molecules are related by one carbon atom of the latter being replaced by nitrogen in the former.

Fig. 12

Spectrum of benzalaniline[115]



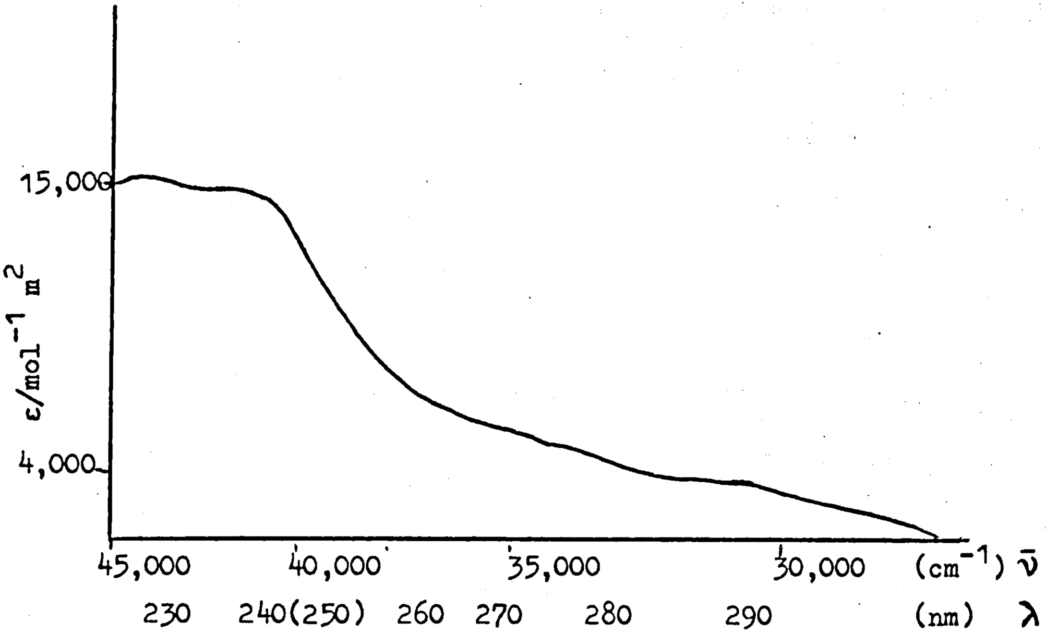
The dotted lines (Fig. 12) indicate the resolved bands[115].

By analogy with cis-stilbene, it is to be expected that a cis-arrangement of two phenyl rings on a (C=N) would produce a reduction in intensity of the longer wavelength band.

The ultra violet spectrum of N-phenyl phenyl benzimidate (Fig. 13) is similar to that of cis-stilbene and this most probably represents a cis-arrangement of phenyl rings on the (C=N) group.

Fig. 13

The ultra violet spectrum of N-phenyl phenyl benzimidate



The ultra violet spectrum of benzene consist of three major bands at 54,350 cm^{-1}, 49,020 cm^{-1} and 39,060 cm^{-1}. Delocalisation of the π-electrons over the ring and (C=C) bond in styrene result in an absorption at 34,761 cm^{-1}. The longer wavelength absorption in the spectrum of N-phenyl phenyl benzimidate is thus tentatively described as the result of some interaction between the π-electrons of the (C=N) bond and the aromatic ring on the carbon of the (C=N) bond.

Substitution of the benzene nucleus by alkyl groups causes a shift to longer wavelength of the 39,060 cm^{-1} benzene band e.g. the corresponding band in toluene is at 38,310 cm^{-1}. The alkyl substitution of the parent N-phenyl phenyl benzimidate produced only a slight effect on intensity and wavelength of the longer wavelength bands. Meta-substitution of the carbon ring caused the shorter wavelength band to increase markedly in intensity. Substitution of the benzene nucleus by halogen atoms caused both the 49,020 cm^{-1} and 39,060 cm^{-1} bands to move to longer wavelength.

When the phenyl group attached to the carbon of the (C=N) group is substituted by chlorine in the ortho-position the long wavelength band in the parent compound near 32,500 cm^{-1} shifts to near 37,500 cm^{-1}. This band, by analogy with the stilbenes and styrene, has been associated with interaction of the π-electrons of the C ring and the (C=N) bond. The effect observed in the ultra violet spectrum on ortho-chlorine substitution is consistent with lowering of this electronic interaction, caused by tilting of the C ring further away from the plane of the (C=N) compound.

Para-chlorine substitution of the C ring causes a shift of the band which is near 42,500 cm^{-1} in the parent compound to a value near 40,000 cm^{-1}. An observed shift in this direction is expected when there is interaction between the (C=N) group and the chlorine attached to the ring, taking place via the π-cloud of the ring.

The absorption associated with the (C=N) bond is expected near 52,630 cm^{-1} by analogy with this absorption in acetoxime. This was too near the cut-off point of the solvent to be observed.

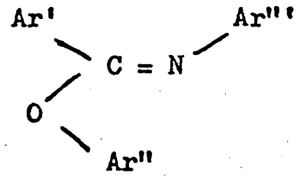


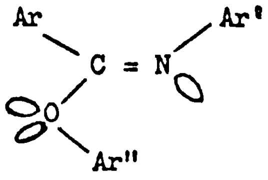
Table 16

The ultra violet spectra of some N-aryl aryl arylimidates

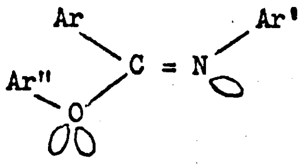
Ar'	Ar''	Ar'''	ν/cm^{-1}	ε/mol^{-1} m^{2}	ν/cm^{-1}	ε/mol^{-1} m^{2}	ε at 37,500 cm^{-1} mol^{-1} m^{2}
Ph	Ph	Ph	45,000	1.5×10^{3}	42,500	1.5×10^{3}	6.0×10^{2}
Ph	p-ClC_6H_4	Ph	43,500	2.2×10^{3}			5.0×10^{2}
Ph	p-$CH_3C_6H_4$	Ph	44,000	1.75×10^{3}	42,500 sh	1.6×10^{3}	6.5×10^{2}
Ph	m-ClC_6H_4	Ph	46,000	1.9×10^{3}	42,500 sh	1.6×10^{3}	6.0×10^{2}
Ph	o-ClC_6H_4	Ph	43,500	1.8×10^{3}			4.0×10^{2}
Ph	o-$CH_3C_6H_4$	Ph	43,500	1.7×10^{3}			5.0×10^{2}
Ph	Ph	p-ClC_6H_4	42,500	1.8×10^{3}			8.0×10^{2}
Ph	Ph	p-$CH_3C_6H_4$	44,500	1.6×10^{3}	42,500	1.6×10^{3}	5.0×10^{2}
Ph	Ph	m-$CH_3C_6H_4$	45,000	1.55×10^{3}	42,500	1.55×10^{3}	3.2×10^{2}
Ph	Ph	o-ChC_6H_4	42,500	1.65×10^{3}			1.5×10^{2}
Ph	Ph	o-$CH_3C_6H_4$	42,500	1.65×10^{3}			2.0×10^{2}
p-ClC_6H_4	Ph	Ph	44,500	1.5×10^{3}	40,000	1.55×10^{3}	8.5×10^{2}
m-ClC_6H_4	Ph	Ph	42,500	1.45×10^{3}			5.0×10^{2}
m-$CH_3C_6H_4$	Ph	Ph	42,500	1.55×10^{3}			7.0×10^{2}
o-ClC_6H_4	Ph	Ph	broad tail from		47,500 cm^{-1}		3.5×10^{2}
o-$CH_3C_6H_4$	Ph	Ph	45,000	1.5×10^{3}			4.0×10^{2}

5. CONCLUSIONS

From the work carried out on the N-aryl aryl arylimidates it appears that the two aryl groups on the (C=O) group are in a cis configuration. The orientation of the (O-Ar) group is less certain but it is most probably in oscillation between two extreme conformations:

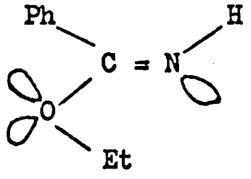


and



Much of this internal rotational freedom appears to be lost when the aromatic ring on the carbon atom is substituted in the ortho- position by a chlorine atom, because the skeletal modes in this compound are sharper than those observed with any of the other imidate compounds of this type.

The structure of the simpler arylimidates, (the ethyl benzimidate compounds) was not so certain. It is highly probable that the structure is of the form:



but this is only by analogy with the ethyl benzoate structure and after consideration of the mechanism for the addition of ethanol to (C≡C) bonds. Large uncertainties in the bond and group moments required, preclude any definite structural calculations using the data obtained from the dipole moment studies.

The skeletal modes of the simpler ethyl arylimidates were found to be extensively coupled as was expected. The best description of these modes was found to be in terms of the four normal vibrations described by Prichard and Hughes[7,8,9].

In the N-aryl aryl arylimidates the skeletal modes were found to be more highly localised in the (Ar-C), (Ar-N), (C=N) and (Ar-O) bonds; the coupling between these modes being much smaller than in the ethyl arylimidates. Of the skeletal modes only the ν(Ar-O) was found to behave as a X-sensitive mode.

The spectra of the N-aryl aryl arylimidates and their products of rearrangement (the N-aroyl diarylamines) are very similar but the skeletal modes are sufficiently different to give an indication as to whether the rearrangement has proceeded. The ν(Ph-O) absorption near 1200 cm^{-1} is not to be observed in the skeletal region of the N-aroyl diarylamine spectra.

Although the assignment given ethyl benzimidate by Hughes[7] adequately described most of the absorptions, it was felt that the absorption near 698 cm^{-1} should be reassigned as a γ(C-H) mode derived from mode 11 of benzene. This compared with a similar absorption near 710 cm^{-1} in ethyl benzoate. The low wavenumber of this absorption, expected near 750 cm^{-1}, could be the result of steric repulsions making the ground state nearer in energy to the excited state. Hughes had assigned the 698 cm^{-1} band to a ring mode from mode 4 of benzene. Bogolomov[118] and Schmid[119] have found that there is very strong coupling between modes 11 and 4 of benzene in toluene and halobenzenes. Huguchi <u>et. al.</u>[120] have studied these bands from the point of view of intensity sharing and find that the sums of the intensities of the two bands can be considered as corresponding approximately to the 'original' γ(C-H) mode. Thus it could be, that the mode 4 has acquired most of the intensity of the two modes such that mode 11 is not observed. However, the γ(C-H) mode 11 of the para-substituted imidates is also 50 cm^{-1} lower than expected. Since the γ(C-H) mode 11 in the spectra of the esters and imidates studied is lower than normally observed in mono- and para-substituted compounds it is thought consistent with the steric effect postulated.

CHAPTER IV

ACETANILIDE STUDY

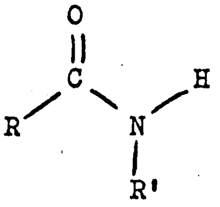
Dipole Moment Study

Infrared Study

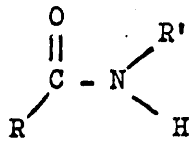
Ultra Violet Study

Anilide Structure

For some considerable time work has been carried out to determine the structure of amides. Thompson and co-workers made several important statements on the structure. Thompson stated that amides exist predominantly in the ketonic form[110] with cis-trans isomerism about a partial double bond between C and N.



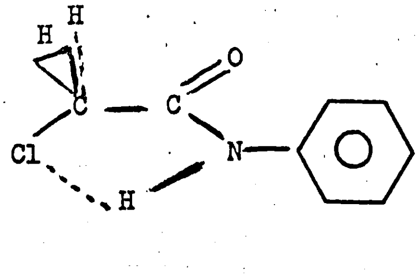
cis



trans

The existence of cis-trans isomerism was challenged by Nyquist[111,112,113] who attributed the two (N-H) absorptions, attributed by Thompson to cis-trans isomerism, to an overtone of the ν(C=O) in Fermi resonance with the ν(N-H).

Nyquist found that for acetanilides (and acetamides) chlorinated in the 2-position there was a shift of ν(N-H) to a lower wavenumber (and hence energy) on mono-halogenation, followed by a smaller shift to slightly higher wavenumber on further halogenation in the 2-position. This increase never re-established the ν(N-H) to the value in the parent unhalogenated compound. This phenomenon was ascribed by Nyquist to the formation of an intra-molecular hydrogen bond in the preferred trans-structure.



In a survey of 2 halogenated species, Bellamy and Williams[76] attributed the effect to a dipolar interaction (field effect). This present study was aimed at investigating the effect of substituent on the value of ν(N-H) and ν(C=O) of some 2-substituted acetanilides in order to establish the structure of the compounds and obtain information on the cis-trans isomerism. Nuclear magnetic resonance studies on acetanilide[103,104] indicate the presence of two forms of acetanilide. At a concentration of 0.3 mol dm^{-3} in $CDCl_3$ the ratio of cis/trans was found to be <1:>99[103]. Similarly 0.3 mol dm^{-3} solutions of some 2'-alkyl acetanilides in $CDCl_3$ were found to exhibit a broad n.m.r. signal due to the acetyl protons near τ= 7.9. On cooling this signal sharpened whilst increasing in intensity and at the same time another signal appeared around τ = 8.12. This effect was ascribed to cis-trans-isomerism about the (C-N) bond.

0.3 mol dm^{-3} solutions of some 2',6'-dialkyl acetanilides were found to exhibit two n.m.r. signals at room temperature ascribed to acetyl protons. From the peak heights the ratio of cis:trans isomers were estimated e.g. 2',6'-dimethylacetanilide 26:74 (1:2.8) cis/trans and 2',6'-diethylacetanilide 31:69 (1:2.2) cis/trans.

The isomerism was ascribed to steric hindrance to rotation about the (C-N) bond by interaction between the 2',6'-alkyl groups and the acetyl group. The proportion of cis:trans isomer increased with increase in the size of the alkyl group. From the measurements of the temperature dependence of the n.m.r. spectra the Free Energies of Activation were calculated for the isomerism[103,105].

'In the present study some further spectroscopic analysis was carried out on the anilides (infrared and ultra violet) and a full dipole moment study.

Dipole Moment Study

The dipole moments were measured and the polarisation data is given in Tables 17 and 18 and the calculated dipole moments in Table 19.

Table 17

Polarisation data for solutions of anilides in benzene at 25°C

Acetanilide

w_2	ε_x	υ	
0.0014548	2.28634	1.14444	$R_D = 39.322$
0.0023395	2.29757	1.14435	
0.0034725	2.30794	1.14400	$P_0 = 299.80$
0.0041420	2.32689	1.14380	
0.0051276	2.33231	1.14410	$\mu = 3.83$ D
0.0059162	2.34510		
0.0000000		1.14461	

2-Chloro-acetanilide

w_2	ε_x	υ	
0.0025711	2.27990	1.13721	$R_D = 44.156$
0.0026783	2.28199	1.13707	
0.0032237	2.28310	1.13717	$P_0 = 85.983$
0.0035263	2.28469	1.13694	
0.0046955	2.29017	1.13660	$\mu = 2.35$ D

2,2-Dichloro-acetanilide

w_2	ε_x	υ	
0.0017672	2.27899	1.14456	$R_D = 48.990$
0.0026427	2.28338	1.14413	
0.0029886	2.28566	1.14400	$P_0 = 181.41$
0.0041940	2.29186	1.14337	
0.0048693	2.29670	1.14328	$\mu = 2.98$ D

Table 17 (continued)

2,2,2-Trichloro-acetanilide

w_2	ε_x	υ	
0.0029389	2.28588	1.13645	R_D = 53.824
0.0032437	2.28765	1.13641	
0.0035199	2.28846	1.13663	P_0 = 200.21
0.0041214	2.29164	1.13624	
0.0050589	2.29726	1.13573	μ = 3.2 D

2-Chloro-4'-chloroacetanilide

w_2	ε_x	υ	
0.0024998	2.28332	1.14413	R_D = 48.990
0.0029107	2.28511	1.14385	
0.0032204	2.28721	1.14377	P_0 = 162.28
0.0034916	2.28838	1.14368	
0.0039954	2.29277	1.14346	μ = 2.82 D

2,2-Dichloro-4'-chloroacetanilide

w_2	ε_x	υ	
0.0007015	2.27429	1.14462	R_D = 53.824
0.0012759	2.27887	1.14433	
0.0013809	2.27773	1.14407	P_0 = 135.37
0.0015157	2.27687	1.14462	
0.0019657	2.27878	-	μ = 2.77 D
0.0037515	2.28459	-	

2,2,2-Trichloro-4'-chloroacetanilide

w_2	ε_x	υ	
0.0041442	2.28874	1.14288	R_D = 58.658
0.0043082	2.28975	1.14263	
0.0053234	2.29388	1.14233	P_0 = 241.93
0.0065050	2.29914	1.14163	
0.0084486	2.30672	1.14070	μ = 3.42 D

Table 17 (continued)

2-Chloro-4'-bromoacetanilide

w_2	ε_x	υ
0.0011841	2.27631	
0.0027616	2.28316	
0.0028014	2.28340	
0.0029410	2.28396	
0.0030673	2.28437	
0.0016388		1.14414
0.0031182		1.14318
0.0037052		1.14288
0.0046515		1.14235
0.0054928		1.14190

$R_D = 51.87$

$P_0 = 165.03$

$\mu = 2.84$ D

2,2-Dichloro-4'-bromoacetanilide

w_2	ε_x	υ
0.0012638	2.27585	
0.0030293	2.28200	
0.0046199	2.28675	
0.0059778	2.29280	
0.0015970		1.14391
0.0047240		1.14243
0.0059240		1.14110
0.0000000		1.14461

$R_D = 56.704$

$P_0 = 168.34$

$\mu = 2.79$ D

2,2,2-Trichloro-4'-bromoacetanilide

w_2	ε_x	υ
0.0041289	2.28588	1.14288
0.0070333	2.29708	1.14121
0.0088577	2.30363	1.13989
0.0088893	2.30475	1.13987
0.0092221	2.30353	1.13965
0.010045	2.30744	1,13926
0.011292	2.31125	-

$R_D = 61.538$

$P_0 = 196.75$

$\mu = 3.1$ D

Table 18

Polarisation data for solutions of anilides in dioxan at 25°C

Acetanilide

w_2	ε_x	υ	
0.0046397	2.27693	0.92795	R_D = 39.322
0.0079018	2.32721	0.92533	
0.0101981	2.36289	0.92275	P_0 = 385.39
0.0131389	2.41242	-	
0.0151583	2.46411	-	μ = 4.34 D
0.0168916	2.47339	0.91765	
0.0176979	2.49735	-	

2-Chloroacetanilide

w_2	ε_x	υ	
0.0035154	2.23825	0.97232	R_D = 44.156
0.0037650	2.24294	-	
0.0065086	2.26678	0.97174	P_0 = 249.43
0.0087351	2.29541	0.97182	
0.0100974	2.29815	-	μ = 3.49 D
0.0137994	2.32566	0.97039	

2,2-Dichloroacetanilide

w_2	ε_x	υ	
0.0017003	2.21886	0.97225	R_D = 48.990
0.0018353	2.22110	-	
0.0037572	2.23454	0.97181	P_0 = 234.80
0.0046299	2.24147	0.97158	
0.0046857	2.24230	0.97156	μ = 3.50 D

Table 18 (continued)

2,2,2-Trichloroacetanilide

w_2	ε_x	υ	
0.0045395	2.23808	0.97125	$R_D = 53.824$
0.0048286	2.24516	-	
0.0052914	2.25044	0.97106	$P_0 = 283.21$
0.0083756	2.27286	0.97049	
0.0089255	2.27377	0.97022	$\mu = 3.79$ D
0.0123500	2.30252	0.96933	

2-Chloro-4'-bromoacetanilide

w_2	ε_x	υ	
0.0037821	2.23583	0.97124	$R_D = 51.870$
0.0045402	2.24107	0.97135	
0.0050059	2.24381	0.97102	$P_0 = 301.12$
0.0058173	2.25342	-	
0.0068692	2.25904	0.97053	$\mu = 3.84$ D
0.009047	2.27500	0.96959	

2,2-Dichloro-4'-bromoacetanilide

w_2	ε_x	υ	
0.0027151	2.22543	0.97190	$R_D = 56.704$
0.0058127	2.24300	-	
0.0061913	2.24590	0.97014	$P_0 = 264.13$
0.0067680	2.24802	0.97033	
0.0090683	2.26166	0.96952	$\mu = 3.64$ D
0.0104400	2.27055	0.96883	

Table 18 (continued)

2,2,2-Trichloro-4'-bromoacetanilide

w_2	ε_x	υ
0.0032542	2.22734	0.97178
0.0046709	2.23361	0.97135
0.0063949	2.24222	-
0.0066877	2.24508	0.97108
0.0072702	2.24648	0.97011
0.0080281	2.25124	0.97001

$R_D = 61.538$

$P_0 = 260.05$

$\mu = 3.65$ D

The results of the dipole moment study of 2-chlorinated anilides are given below.

Table 19

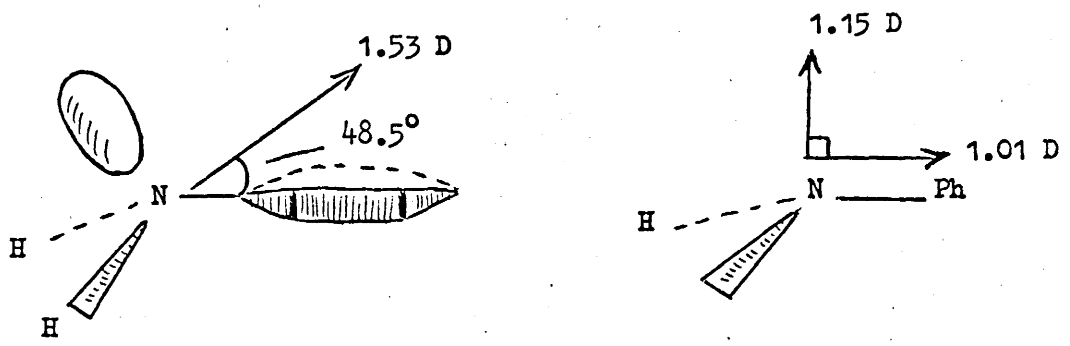
Calculated dipole moments of some 2-chlorinated anilides/Debye

Compound	Solvent	
	Benzene	Dioxan
Acetanilide	3.81	3.96
2-Chloroacetanilide	2.36	3.49
2,2-Dichloroacetanilide	2.93	3.38
2,2,2-Trichloroacetanilide	3.21	3.79
2-Chloro-4'-chloroacetanilide	2.87	
2,2-Dichloro-4'-chloroacetanilide	2.77	
2,2,2-Trichloro-4'-chloroacetanilide	3.42	
2-Chloro-4'-bromoacetanilide	2.86	3.84
2,2-Dichloro-4'-bromoacetanilide	2.84	3.64
2,2,2-Trichloro-4'-bromoacetanilide	3.09	3.65

Smith[106] has shown that the dipole moment of aniline can be represented by a vector of magnitude 1.53 D directed as shown in Fig. 14 and that this vector can be resolved into a component at right angles to the (N-Ph) bond of 1.15 D and one along the (N-Ph) bond of 1.01 D also shown in Fig. 14.

Fig. 14

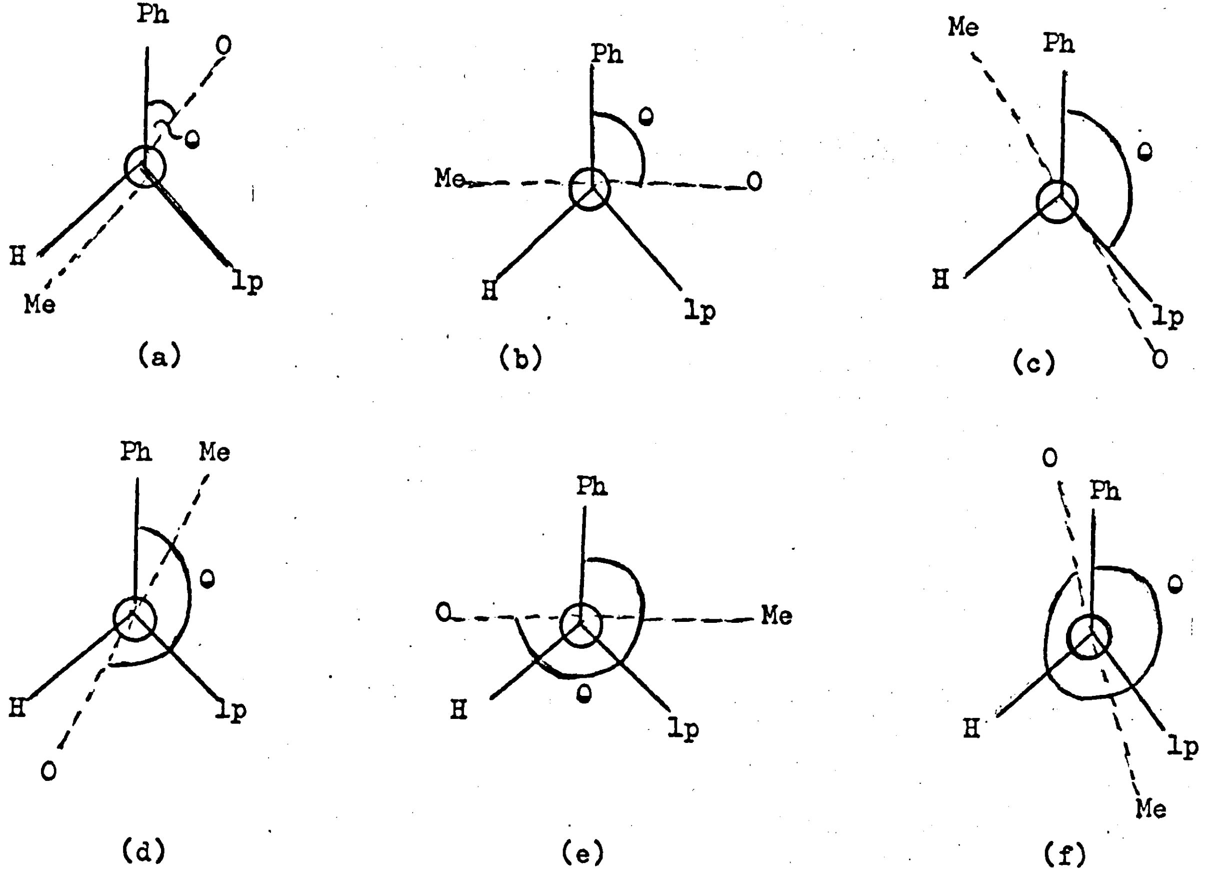
Representations of the dipole moment of aniline



Alternatively the aniline moment can be resolved into a component along the (N-Ph) bond of 1.42 D and another at the tetrahedral angle to this vector, along the lone pair orbital, of magnitude 1.22 D.

The dipole moment of acetanilide may then be represented[107] as the vector sum of the moment of aniline and that of acetone, i.e. 2.78 D directed along the (C=O) direction. The bonds about nitrogen are assumed to be disposed at the tetrahedral angle, and the (N-$C_{aliphatic}$ – O) bond angle is assumed to be 120°.

On this model[107], calculations were made for varying angle Θ between the plane containing the methyl and carbonyl groups and the plane containing the phenyl group, bisecting the angle between the hydrogen and the lone pair. In Newman Projection (a) to (f) are shown below:



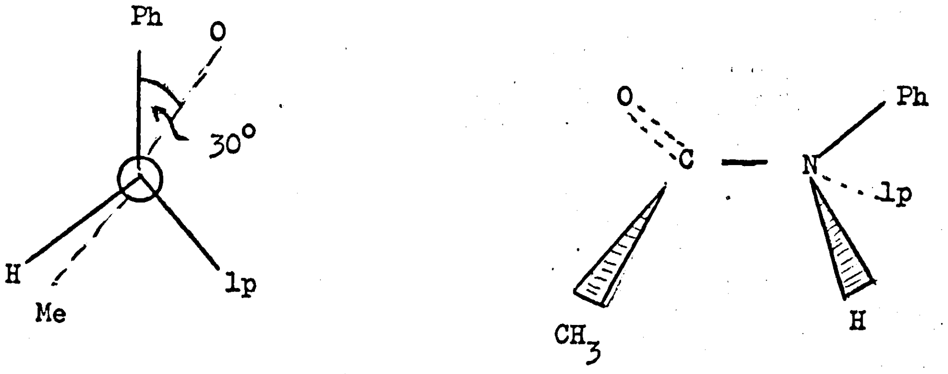
(a) (b) (c)

(d) (e) (f)

The best agreement with the experimentally measured value of 3.65 D was obtained for an angle θ of about 30°. This structure is represented in Fig. 15.

Fig. 15

The structure of acetanilide found to give best agreement with calculations.



This model is, however, insensitive to small changes of angle between the groups (Table 20).

Table 20

The variation of dipole moments of acetanilide with θ

$\theta/^\circ$	μ/D
0	3.36
30	3.63
38	3.67
60	3.69
90	3.52

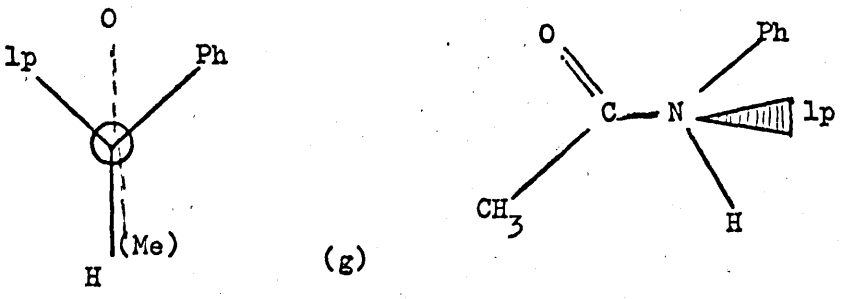
The (N-H) bond is however certainly trans to the (C=O) bond although the (C=O) and (N-H) bonds are not exactly in the same plane.

When p-chloroacetanilide is treated similarly i.e. represented by the vector sum of aniline, chlorobenzene and acetone moments, poor agreement was obtained.

It was decided to use Smith's model and extend it to calculate the dipole moments of the substituted anilides. In view of the large number of conformations possible for substituted anilides it was decided to calculate the dipole moment initially for a trans (C=O), (N-H) planar structure (g) Fig. 16 and then for other conformations, each time rotating the -(NHPh) group through 120° around the (C-N) axis.

Fig. 16

The planar trans (N-H), (C=O) structure for acetanilide



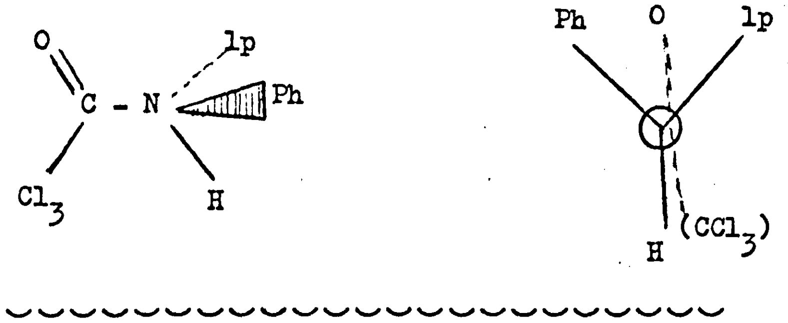
Examination of Table 20 reveals that the model is insensitive to small changes of angle between 30 - 90°. Calculating moments for the conformations described above will, however, decide whether the structure is transoid or cisoid.

Bond angles around nitrogen are assumed tetrahedral whereas those around the carbon carrying the carbonyl oxygen are assumed trigonal. The structure (g) for acetanilide shown in Fig. 16 gives a calculated moment of 3.69 D. The C-Cl bond moment varies with its environment e.g., $CHCl_3$ $\mu = 1.22$ D, CH_3Cl $\mu = 1.70$ D, chlorobenzene $\mu = 1.58$ D[37]. The dipole moment of each of these compounds should be resultant of a (C-Cl) and a (C-H) bond moment. To take account of the environment the bond moments of the relevant chloro-methane derivatives were used to calculated the dipole moments of the 2-substituted anilides.

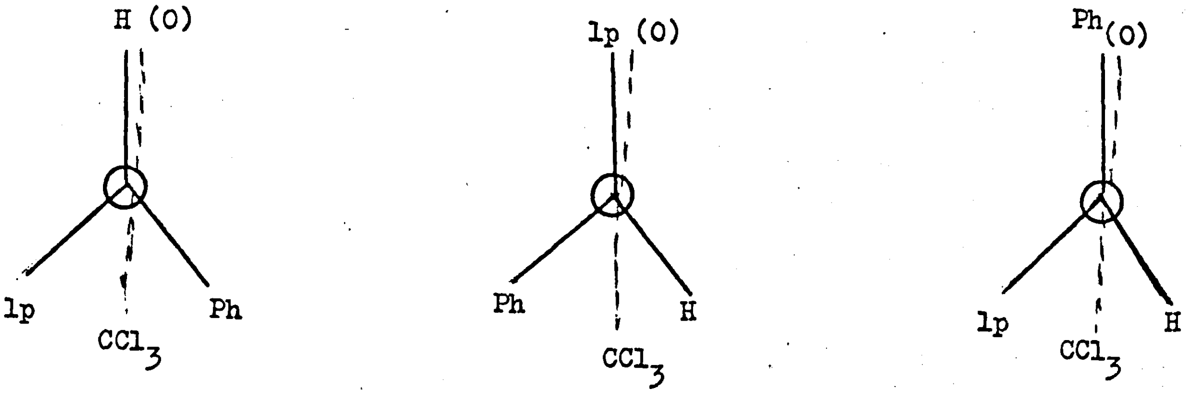
Using the model for acetanilide and the moment of chloroform[37] 1.22 D (benzene at 25°C) as the ($C\text{-}Cl_3$) group moment, the structure of 2,2,2-trichloroacetanilide giving the best agreement with the measured moment of 3.2 D was (a) shown below in Fig. 17.

Fig. 17

Various conformations of 2,2,2-trichloroacetanilide and their calculated dipole moments



(a) 2.83 D



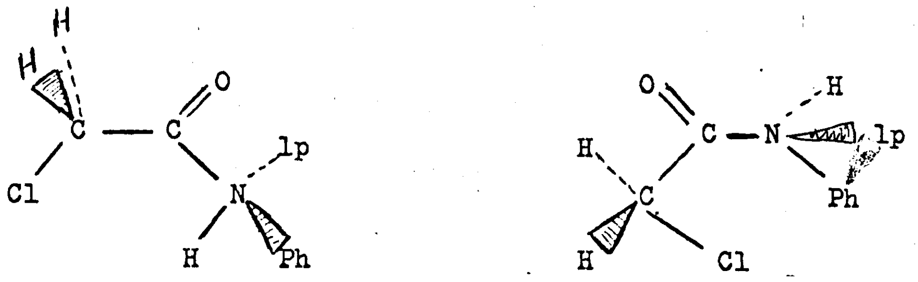
(b) 1.3 D (c) 2.1 D (d) 2.6 D

It is clear that ~~configuration~~ conformation (a) best represents the structure of the molecule, i.e. on trichloro-substitution of the CH_3 group of acetanilide the (C=O) and (N-H) bonds remain trans to each other.

Using the chloromethane moment[37] 1.70 D (benzene at 25°C) directed along the (C-Cl) bond and the model for acetanilide described, the structure of 2-chloroacetanilide giving the best agreement with the measured moment of 2.36 D was (a) shown below in Fig. 18.

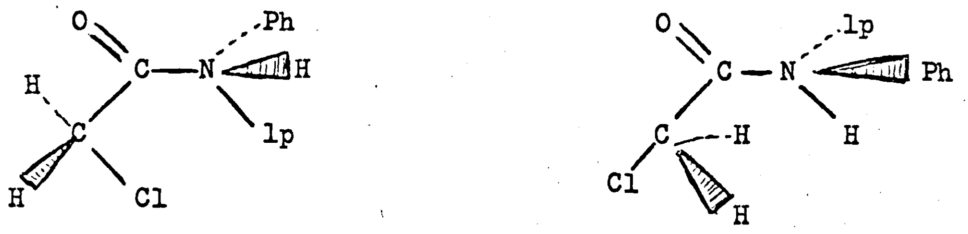
Fig. 18

Various conformations of 2-chloroacetanilide and their calculated dipole moments



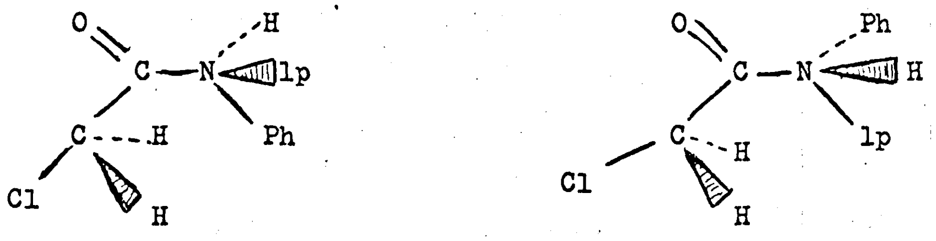
(a) 2.43 D

(b) 1.2 D



(c) 1.5 D

(d) 4.5 D



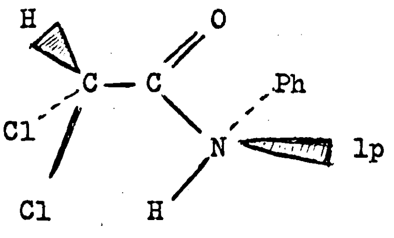
(e) 3.1 D

(f) 3.3 D

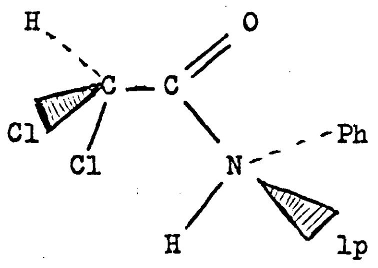
Thus on mono-chloro-substitution of acetanilide the (C=O) and (N-H) bonds remain trans to each other and the (C-Cl) is directed towards the (N-H) bond as shown in structure (a) above.

For the 2,2-dichloroacetanilide compound dipole moments of various conformations were calculated using the dichloromethane moment[37] of 1.55 D (benzene at 25°C)[37] directed along the bisector of the (Cl-C-Cl) bond angle and using the previously described acetanilide model. It was not possible to unambiguously determine the structure of this compound.

The measured moment was 2.93 D. The dipole moment of two possible structures are given below (a) and (b).



(a) 3.18 D



(b) 3.05 D

For an equal mixture of both forms, the dipole moment is given by that derived from the average of the orientation polarisations of these two forms, i.e. 3.11 D. It is necessary to take the average of the orientation polarisations because the specific permittivity ε_{12} of a solution of the two species is given by

$$\varepsilon_{12} = \varepsilon_0 + a_1 w_1 + a_2 w_2$$

ε_0 = specific permittivity of solvent.

w_1 and w_2 are the weight fractions of species 1 and 2 respectively.

a_1 and a_2 are the slopes of the specific permittivity against weight fraction graphs for the species 1 and 2 respectively.

For an equal mixture of 1 and 2 $w_1 = w_2 = w$ and $\varepsilon_{12} = \varepsilon_0 + \left(\frac{a_1 + a_2}{2}\right) w$

The orientation polarisation P_o depends on the average of a_1 and a_2 whereas for a single component it depends only on the 'a' value. The dipole moment μ is given by

$$\mu = 0.012812 \sqrt{P_o \times T}$$

T = temperature (K).

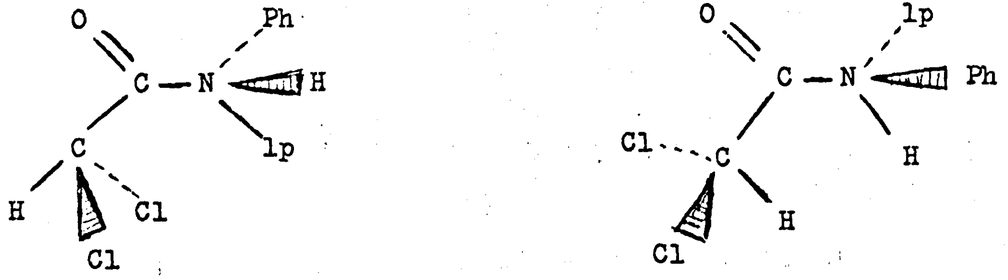
The calculated moments of various conformations of 2,2-dichloroacetanilide are given in Fig. 19.

Fig. 19

The calculated dipole moments of various conformations of 2,2-dichloroacetanilide

(c) 2.25 D

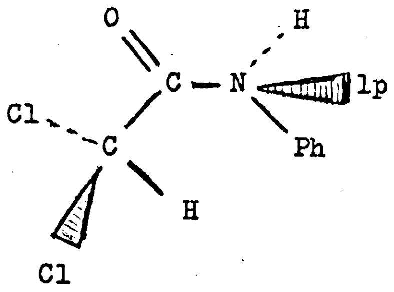
(d) 1.0 D



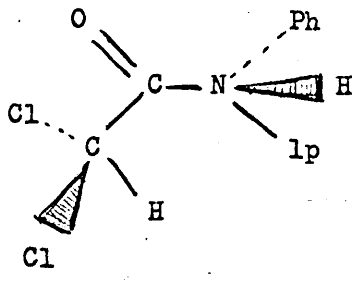
(e) 1.3 D

(f) 4.1 D

Fig. 19 (continued)



(g) 2.7 D



(h) 2.9D

It is obvious that it is impossible to unamiguously determine the structure of this compound. An equal mixture of (a) and (b) or structure (g), or structure (h) all give calculated dipole moments very similar to the experimentally determined value.

Thus to conclude, the dipole moments of the 2-chlorinated anilides are consistent with structures in which the (C=O) and (N-H) bonds are trans to each other and the (C-Cl) bonds are directed towards the H of the (N-H) group.

For 2,2-dichloroacetanilide it was not possible using only the dipole moment to unambiguously determine the overall structure.

It was not possible to find a model to reproduce the dipole moments of the 4'-halogenated anilides. It is most likely that the 4'-halogenation alters the electronic environment of the nitrogen atom.

The results of the study in dioxan indicate the formation of aggregate species and were not analysed further.

Under the same conditions as the 2-halogenated species the dipole moment of acetanilide was measured as 3.81 D (benzene at 25°C). This is a value intermediate between that found by Smith[107] and that by Le Fèvre[108] which were 3.65 D and 4.01 D respectively.

Table 21

Spectroscopic results - anilide study

Compound as 0.002 mol dm^{-3} solutions in CCl$_4$ (unless stated otherwise)	$\tilde{\nu}$ (N-H)/cm^{-1}	$\bar{\nu}$ (C=O)/cm^{-1} broad absorptions centre absorption given
Acetanilide	3448 (s)	1705 (s)
0.02 mol dm^{-3}	3402 (w)	
	3360 (w)	
Acetanilide	3448 (s)	1708 (s)
	~ 3400 (vw)	
2-Chloroacetanilide	3410 (s)	1695 (s)
2,2-Dichloroacetanilide	3417 (s)	1712 (s)
2,2,2-Trichloroacetanilide	3424 (s)	1731 (s)
4'-Chloroacetanilide	3447 (s)	1711 (s)
	3440 (w)	
2-Chloro-4'-chloroacetanilide	3412 (s)	1702 (s)
2,2-Dichloro-4'-chloroacetanilide	3416 (s)	1716 (s)
2,2,2-Trichloro-4'-chloroacetanilide	3424 (s)	1734 (s)
4'-Bromoacetanilide	Not sufficiently soluble	
2-Chloro-4'-bromoacetanilide	3410 (s)	1700 (s)
2,2-Dichloro-4'-bromoacetanilide	3415 (s)	1713 (s)
2,2,2-Trichloro-4'-bromoacetanilide	3422 (s)	1734 (s)
2'6'-Diethylacetanilide	3437 (s)	1693 (s)
	3395 (s)	
2-Chloro-2',6'-diethylacetanilide	3410 (s)	1697 (s)
2,2-Dichloro-2',6'-diethylacetanilide	3414 (s)	1716 (s)
2',6'-Dimethylacetanilide	3437 (s)	1704 (s)
	3393 (s)	1688 (s)
2-Chloro-2',6'-dimethylacetanilide	3409 (s)	1694 (s)
2,2,2-Trimethylacetanilide	3462 (s)	1692 (s)
2,2,2-Trimethyl-4'-chloroacetanilide	3462 (s)	1695 (s)
2,2,2-Trimethyl-2',6'-dimethylacetanilide	3456 (s)	1691 (s)
2-Methylacetanilide	3445 (s)	1705 (s)
	3398 (vw)(b)	

Table 22

Summary of the spectroscopic results for some substituted anilides; ν(N-H) and ν(C=O)

(as 0.002 mol dm^{-3} solutions in CCl_4)

$\tilde{\nu}$ (N-H)/cm^{-1}

	Ph	$-C_6H_4Cl$	$-C_6H_4Br$
CH_3CONH-	3448, 3440 w	3447, 3400 w	-
$ClCH_2CONH-$	3410	3412	3410
$Cl_2CHCONH-$	3417	3416	3415
$Cl_3CCONH-$	3424	3424	3422

$\tilde{\nu}$ (C=O)/cm^{-1}

	Ph	$-C_6H_4Cl$	$-C_6H_4Br$
CH_3CONH-	1708	1711	-
$ClCH_2CONH-$	1695	1702	1700
$Cl_2CHCONH-$	1712	1716	1713
$Cl_3CCONH-$	1731	1737	1734

Table 23

The ratio of various species estimated from peak heights of the ν(N-H) absorption in the infrared for solutions of anilide 0.002 mol dm^{-3} in various mixed solvents

		Ratio	
Compound	Solvent	cis	trans
Acetanilide	carbon tetrachloride	1	13.2
2-Methylacetanilide	" "	1	13.8
2',6'-Dimethylacetanilide	" "	1	1.7
2',6'-Diethylacetanilide	" "	1	1.7

Compound	Solvent	trans	bonded
Acetanilide	carbon tetrachloride		
	" + 2% dioxan	2.3	1
	" + 5% dioxan	1.2	1
	" + 10% dioxan	1	2.8
	" + 15% dioxan	1	3.5

Compound	Solvent	trans	cis	bonded
2',6'-Diethylacetanilide	carbon tetrachloride			
	" + 2% dioxan	2.7	1.6	1
	" + 5% dioxan	1.6	1	1.1
	" + 10% dioxan	1.3	1	2.2
	" + 15% dioxan	1.2	1	2.7

Compound	Solvent	trans	bonded
2-Chloroacetanilide	carbon tetrachloride		
	" + 2% dioxan	16	1
	" + 5% dioxan	7.7	1
	" + 10% dioxan	3.7	1

Compound	Solvent	trans	bonded
2-Chloro-2',6'-diethylacetanilide	carbon tetrachloride		
	" + 2% dioxan	10.5	1
	" + 5% dioxan	4	1
	" + 10% dioxan	2.8	1

Table 23 (continued)

Compound	Solvent	Ratio trans ~~cis~~ : bonded ~~trans~~
Acetanilide	carbon tetrachloride + 10% dioxan	1 : 2.8
2-Chloroacetanilide	" + 10% dioxan	3.7 : 1
2,2-Dichloroacetanilide	" " "	1.7 : 1
2,2,2-Trichloroacetanilide	" " "	2.3 : 1
Acetanilide	carbon tetrachloride + 10% benzene	trans : cis : bonded 13.1 : 1.2 : 1
2-Chloroacetanilide	" " "	trans only
2,2-Dichloroacetanilide	" " "	trans only

The results of the infrared study on acetanilide and some substituted acetanilides are shown in Tables 21, 22, 23. Dipole moment and n.m.r. studies[107, 103] have shown that in solution the trans form of acetanilide predominates. The present dipole moment study of acetanilide substituted by chlorine in the 2-position indicates that these compounds also exist in the trans form in solution. This is to be expected as in the cis form the halogen atom would be close to the phenyl ring where there would be large repulsion between the aromatic electron cloud and that of the lone pairs on the halogen.

When acetanilide is monosubstituted by chlorine in the 2-position the absorption associated with the ν(N-H) moves from the acetanilide value of 3435 cm^{-1} to 3410 cm^{-1} in 2-chloroacetanilide. On disubstitution the ν(N-H) is found at 3417 cm^{-1} and on trisubstitution at 3424 cm^{-1}. The carbonyl absorption decreases by 13 cm^{-1} from the acetanilide value of 1708 cm^{-1} to 1695 cm^{-1} on mono-substitution, increases from this value by

17 cm^{-1} to 1712 cm^{-1} on disubstitution and increases by 19 cm^{-1} to 1731 cm^{-1} on trisubstitution.

The lowering of the wavenumber of the ν(N-H) absorption from the acetanilide value is consistent with interaction between the (C-Cl) and (N-H) bonds which dipole moment studies have shown to be suitably orientated for interaction. The ν(N-H) absorption in all these spectra are sharp absorptions.

The ratio of cis to trans forms (from peak heights) in acetanilide was estimated as 1 : 13.2 for a 0.002 mol dm^{-3} solution in carbon tetrachloride. Similarly the ratio of cis : trans forms in 2-methylacetanilide was estimated as 1 : 13.8 under the same conditions.

The infrared spectrum of 2',6'-dimethylacetanilide has two absorptions ascribed to ν(N-H) the first at 3437 cm^{-1}, the second at 3393 cm^{-1}. Similarly the spectrum of 2',6' diethylacetanilide has corresponding peaks at 3437 and 3395 cm^{-1}. The higher peak in both cases is assigned to the trans-isomer, the lower to the cis-isomer. Examination of the ν(C=O) absorptions reveals broadening and that of 2',6'-dimethylacetanilide is consistent with two overlapping absorptions producing two partially resolved peaks at 1704 and 1688 cm^{-1}.

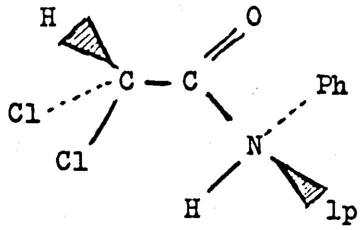
In both 2',6'-dimethyl and 2',6'-diethylacetanilide the ratio of cis : trans-isomer was estimated as 1 : 1.7. This similarity is expected because, due to free rotation in the ethyl groups, the ethyl and methyl groups are of comparable bulk. When the spectrum of a solution of 0.02 mol dm^{-3} of acetanilide was examined a broad peak was observed at 3360 cm^{-1} which was assigned to a bonded species caused by aggregation of solute molecules. The n.m.r. studies were carried out on 0.3 mol dm^{-3} solutions of solute in $CDCl_3$ and it would seem most likely that an intermolecularly bonded species has been observed.

The peak heights of the ν(N-H) bands observed in the spectrum of a solution 0.02 mol dm^{-3} in acetanilide suggest a ratio of 1.2 : 5.7 : 1 cis:trans:bonded species. Thus at a concentration 1/10 of that used for the n.m.r. studies the proportion of bonded species is similar to that of the cis species.

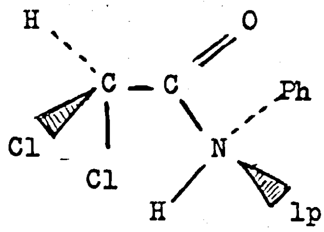
The higher ratio of cis : trans forms found by n.m.r. probably indicates that the species were intermolecularly H-bonded and thus less able to isomerise so readily.

Dipole moment studies on the anilides carried out in dioxan gave results which indicated the presence of aggregate species. To study the aggregation the ν(N-H) region of the spectrum of the anilides was studied using carbon tetrachloride as solvent and also carbon tetrachloride with added dioxan as solvent. The estimated ratios of cis : trans : bonded species are shown in Table 23. In particular, comparison of the ratios for a solvent of carbon tetrachloride + 10% dioxan (Table 23) show that the (N-H) is more readily available for bonding with the solvent, for the anilides which have not been substituted in the 2-position by chlorine than for the 2-chlorine substituted compounds.

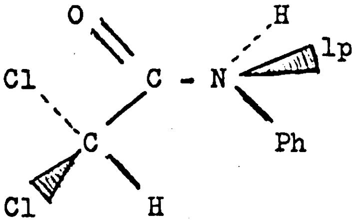
In the series 2-monochloroacetanilide, 2,2-dichloroacetanilide, and 2,2,2-trichloroacetanilide in carbon tetrachloride + 10 dioxan the ratio of trans : bonded species was 3.7 : 1, 1.7 : 1, 2.3 : 1 respectively. Thus in the dichloro- species the(N-H)is more readily available to form the bonded species than for either the mono, or the trichloro-species. The dipole moment study of dichloroacetanilide was not able to unambiguously determine the orientation of the halogen atoms and this result could indicate that the structures (g) or (h) are nearer the correct structure than the (a) and (b) structures in which the halogens were directed towards the (N-H).



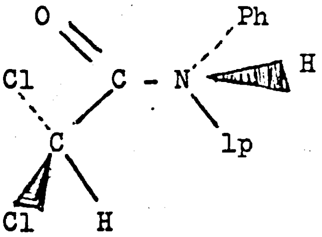
(a)



(b)



(g)



(h)

In a mixed solvent of carbon tetrachloride and 10% benzene there was no evidence for any bonded species for the acetanilides substituted in the 2-position by chlorine.

In all cases as the percentage of dioxan in the solvent was increased so it was apparent that the bonded species became the dominant species.

Mono substitution of the 2',6'-dimethylacetanilide by chlorine in the 2-position resulted in only one ν(N-H) at 3409 cm^{-1}. Similar substitution of 2',6'-diethylacetanilide resulted in a single ν(N-H) at 3410 cm^{-1}. In 2,2-dichloro-2',6'-diethylacetanilide the ν(N-H) was a single absorption at 3414 cm^{-1}. The spectrum of 2,2,2-trimethylacetanilide revealed only one ν(N-H) absorption at 3462 cm^{-1} again assigned to the trans-isomer. On 2',6'-dimethyl substitution of this compound only one ν(N-H) was obtained (unlike 2',6'-dialkyl substitution of acetanilide). This absorption was at 3456 cm^{-1}. The interaction between the tertiary butyl group and the ring in the cis form probably is so large as to prevent isomerism.

Thus it is found that the results of the study of 2-chloro-substitution of anilides reveals that these compounds exist predominantly in the trans form in solution. The wavenumber of the absorption due to the ν(N-H) varies more or less linearly with the group moment of the halo-methyl group Fig.20. This may be fortuitous as only three chlorine substituted species are available for one anilide. There would appear to be no direct evidence for intramolecular hydrogen bonding as there is no noticeable broadening apparent when comparing the ν(N-H) absorption of 2-chloroanilides with that in the parent anilide. It has been shown that intermolecular H-bonding and H-bonding to solvent do take place in suitable conditions. It is thought that the results are consistent with a field effect of the chlorine atom(s) on the (N-H) dipole when the (C=O) and (N-H) dipoles are orientated trans to each other.

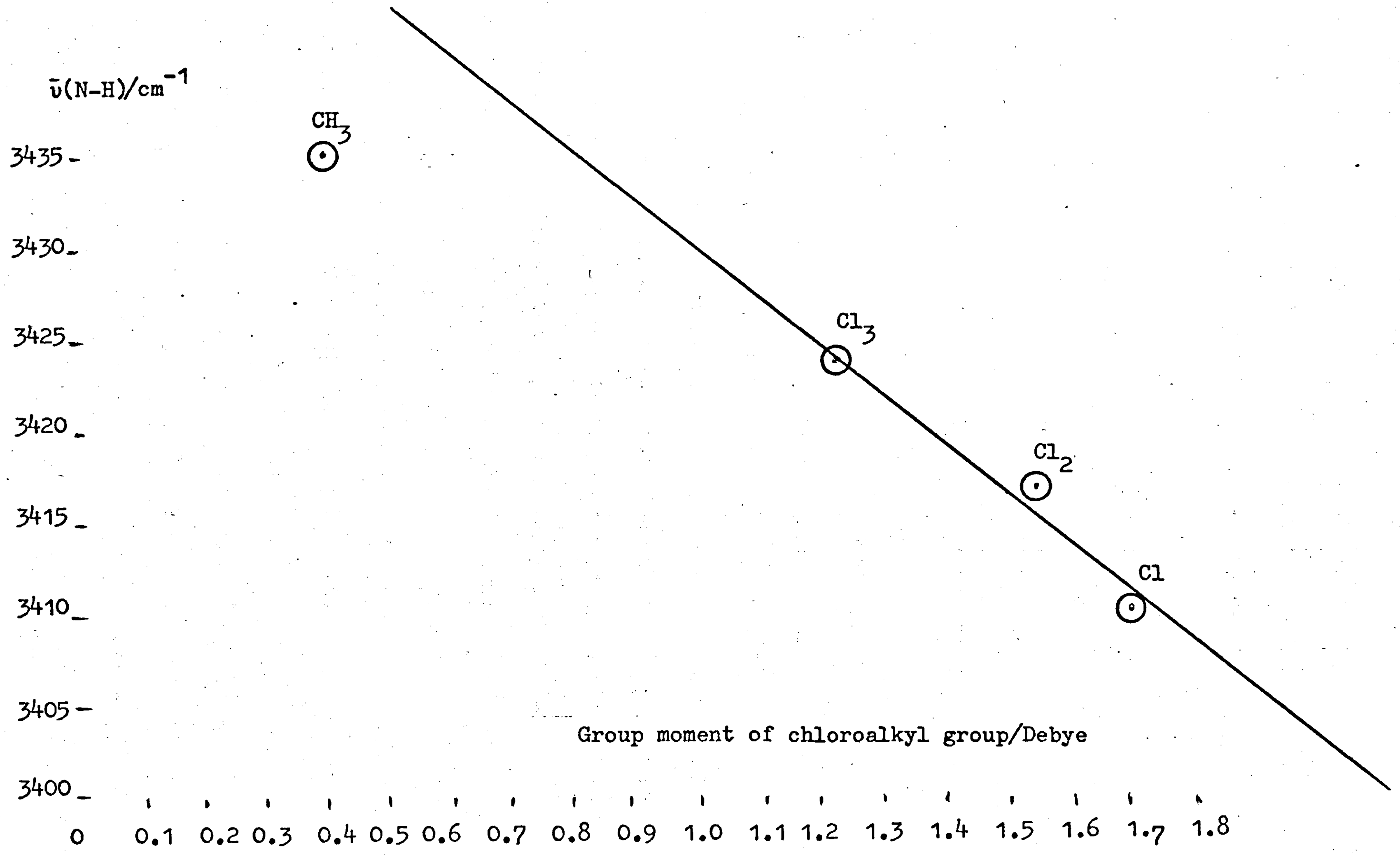
The results of the study of the 2',6'-dialkyl substitution are consistent with a cis-trans-isomerism about the C-N bond, the rotation being sufficiently sterically hindered to permit an observation of the two forms by infrared spectroscopy at room temperature. The difference in the wavenumber of the ν(N-H) absorptions of cis and trans forms is consistent with different orientation of the (C=O) and (N-H) dipoles in the two forms.

Ultra violet spectroscopic study

The ultra violet spectra of some of the anilides were recorded in ethanol at a concentration of 8×10^{-5} mol dm^{-3}. This was unfortunately

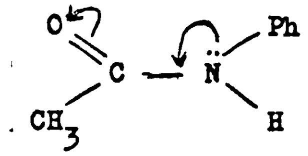
Fig. 20

The $\bar{\nu}$(N-H) plotted against the group moment of the chloroalkyl group in some anilides



the only solvent which would adequately cover the range of wavenumber required and easily dissolved the samples.

Acetanilide is far less reactive towards nitration, halogenation etc., than is aniline. This is attributed to the diminished availability of the nitrogen lone pair electrons to the ring caused by the 'opposing' resonance:



This resonance causes some delocalisation of charge over the (O-C-N) moiety and explained the larger shift to longer wavelength, in para-disubstituted acetanilides, of the 39,060 cm^{-1} benzene band compared with that observed in the spectra of the para-disubstituted anilines[115]. Similar observations were made for acetanilide and aniline[117].

The results of the present study shown in Table 24 indicate a large reduction in the extent of interaction of aromatic orbitals with the rest of the molecule when the ring is substituted in the 2' and 6' positions.

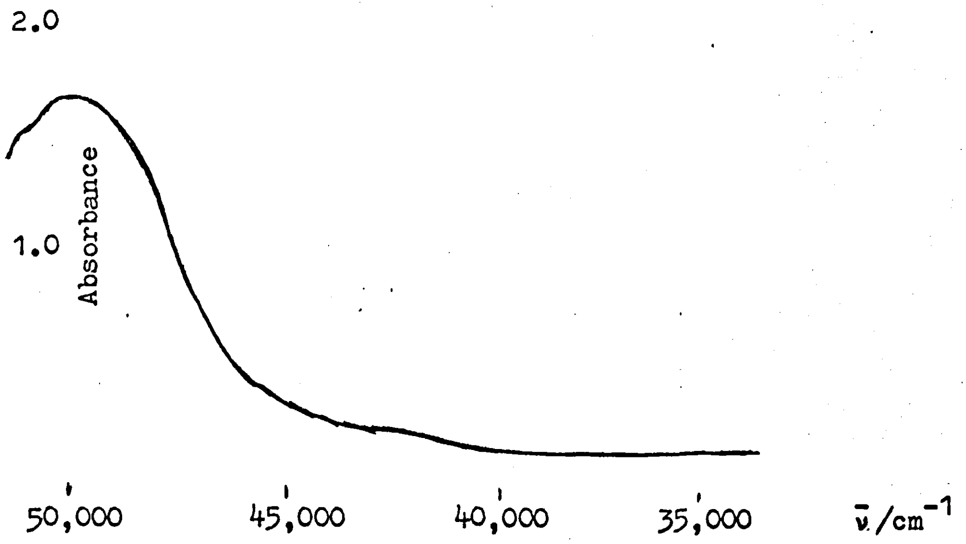
Chlorine substitution of the 2-position causes a reduction in intensity of the band near 40,000 cm^{-1} with the introduction of each chlorine atom. This is probably due to repulsions between the lone pairs on the chlorine atoms and the nitrogen end of the molecule lowering the extent of interaction of the ring electrons with the rest of the molecule.

However, the fact that a solvent which could readily hydrogen bond with the acetanilides has been used, means that the results cannot be taken as more than an indication because the spectra obtained are almost certainly those of a species involving ethanol and acetanilide in interaction with each other.

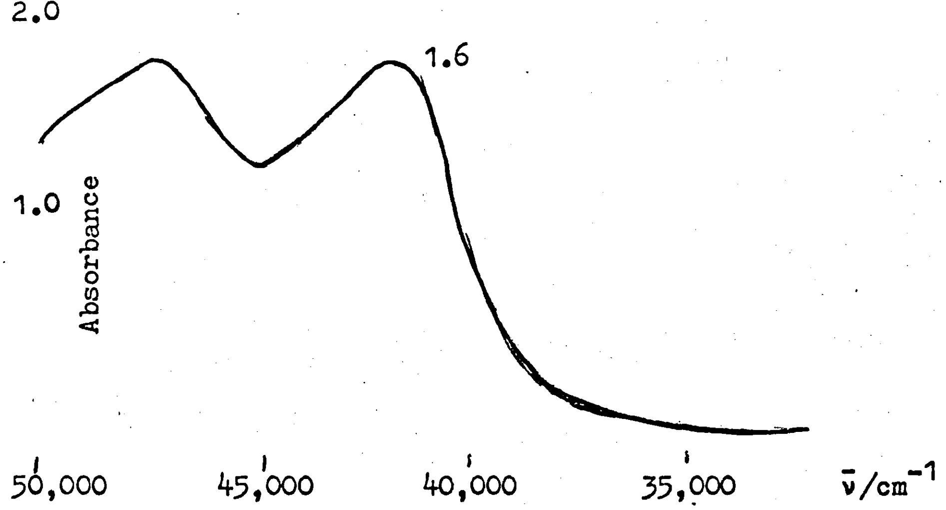
Table 24

The results of the ultra violet studies on anilides

Ethanol



Acetanilide



2-Chlocoacetanilide

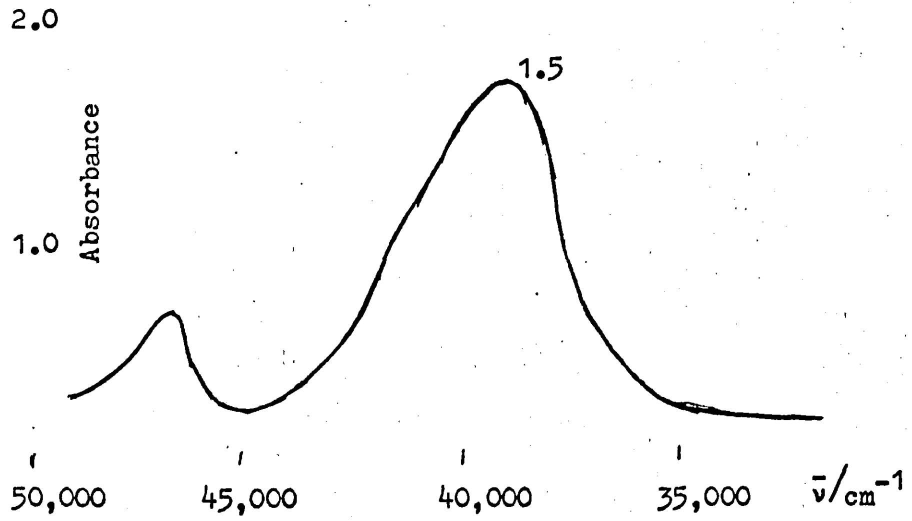
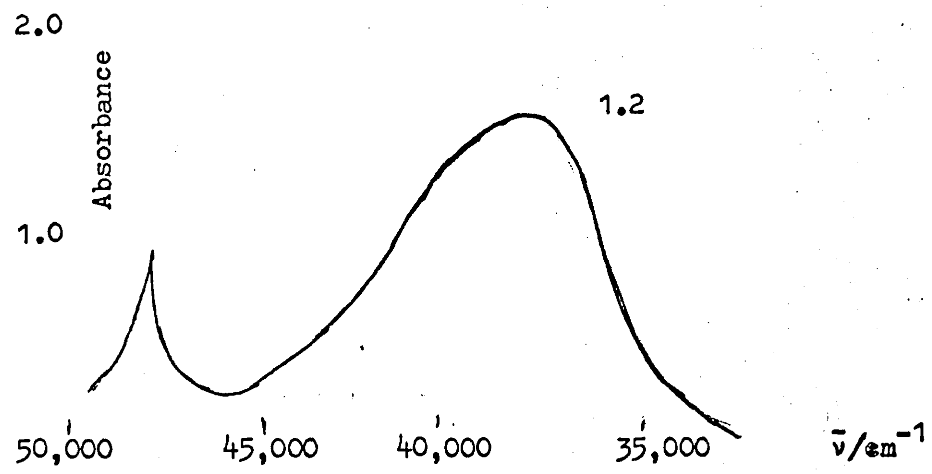
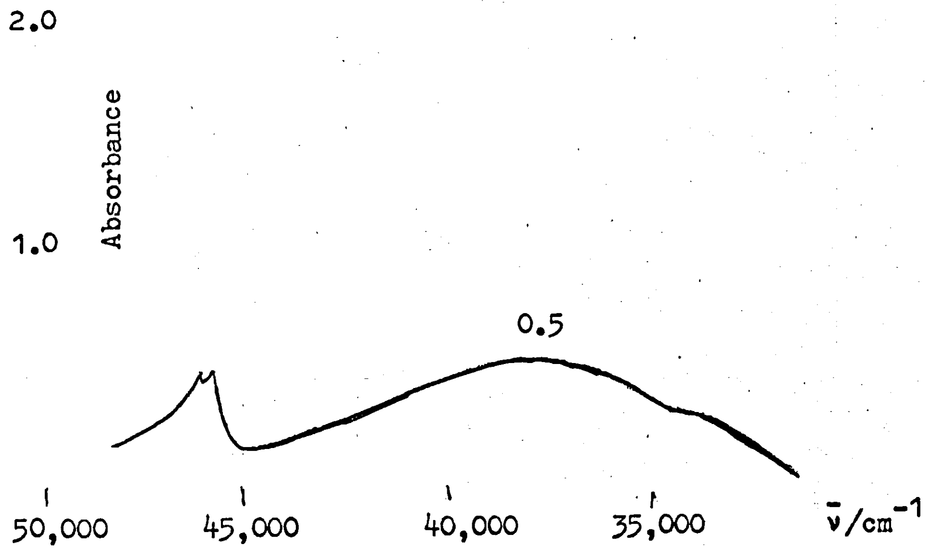


Table 24 (continued)

2,2-Dichloroacetanilide



2,2,2-Trichloroacetanilide



4'-Chloroacetanilide

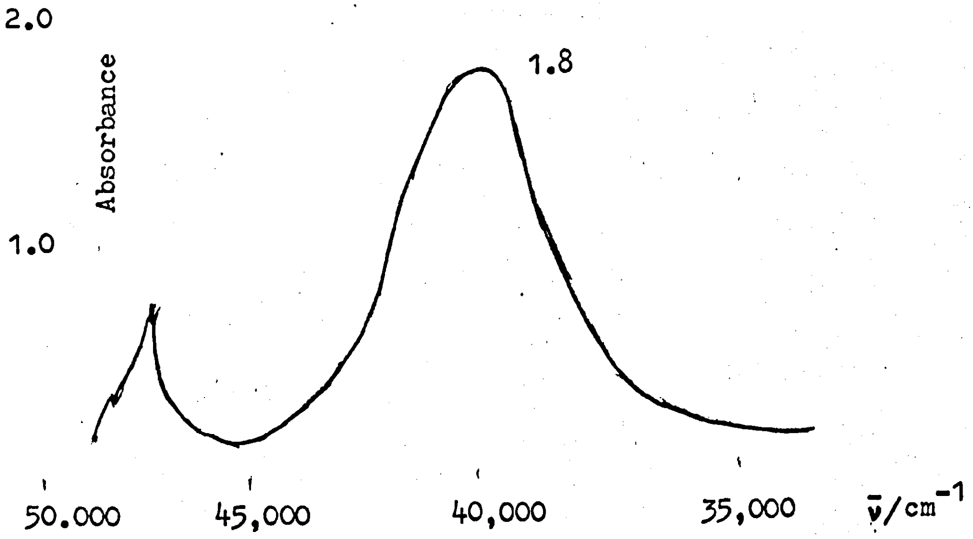
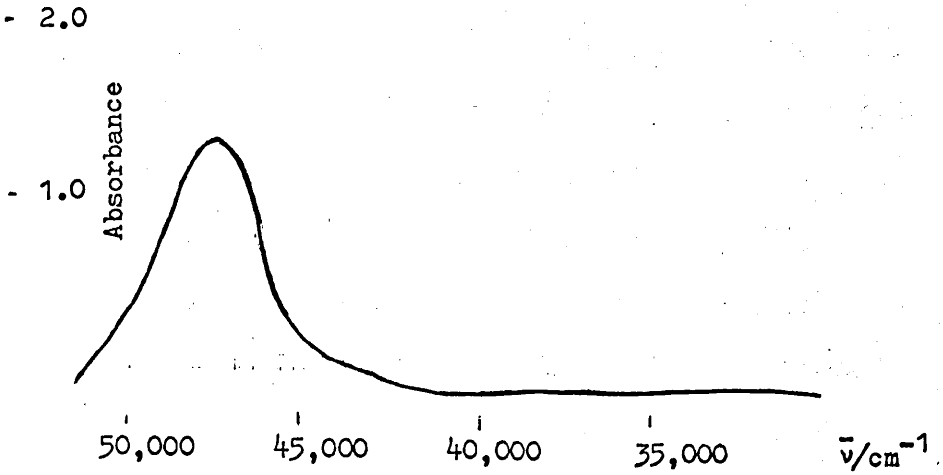
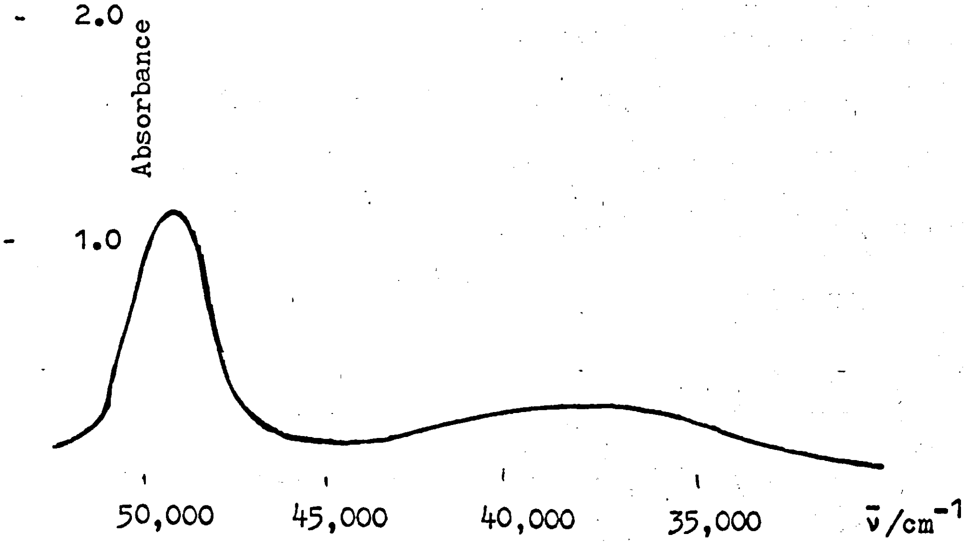


Table 24 (continued)

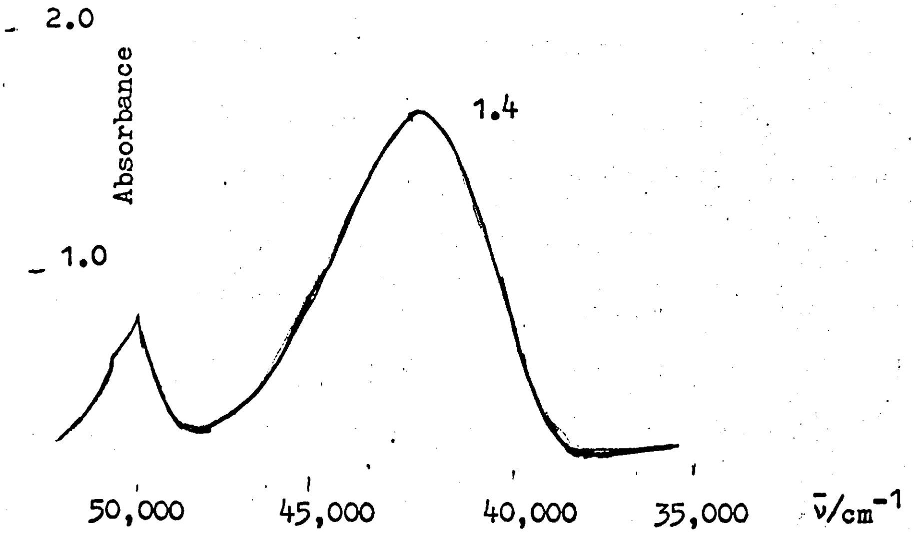
2',6'-Diethylacetanilide



2-Chloro-2',6'-Diethylacetanilide



2,2,2-Trimethylacetanilide



REFERENCES

1. A. Pinner and F. Klein, Ber. 10, 1889, (1877).
2. A. Balog, E. Vargha and I Balazs, Acad. Rep. Populare Romîne Inst. Biochim. Stud 11, Cercetări, Biochem., 1, 97, (1958).
3. A.W. Chapman, J. Chem. Soc., 127, 1992, (1925).
4. A.W. Chapman, J. Chem. Soc., 1743, (1927).
5. A.W. Chapman, J. Chem. Soc., 569, (1929).
6. A.W. Chapman and C.H. Perrott, J. Chem. Soc., 2462, (1930).
7. J.C.Hughes, Thesis The City University, (1972).
8. W.H. Prichard, Thesis University of Wales (1962).
9. W.H. Prichard and W.J. Orville-Thomas, J. Chem. Soc., (A), 1102, (1967).
10. M.M. Jamison and E.E. Turner, J. Chem. Soc., 1646, (1938).
11. D.M. Dennison, Rev. Mod. Phys., 3, 280,(1931)
12. E.B. Wilson, J. Chem. Phys. 7, 1047, (1939), and 9, 76, (1941).
13. E.B. Wilson, J.C. Decius and P.C. Cross, Molecular Vibrations, McGraw Hill (1955).
14. M.V. Volkenstein, M.A. Elyashevitch and B.I. Stepanov, Kolebanya Molekul II, Moscow, 364, (1949).
15. W.T. King and B. Crawford, J. Mol. Spectroscopy, 5, 421, (1961).
16. S. Bratoz and S. Besnainou, J. Chim. Phys. 56, 555, (1959).
17. E.B. Herzberg, Infrared and Raman Spectra, Van Nostrand (1966).
18. E. Teller quoted by W.R. Angus, C.R. Bailey, J.B. Hale, C.K. Ingold, A.H. Leckie, C.G. Raisin, J.W. Thompson and C.L. Wilson, J. Chem. Soc., 978, (1936).
19. O. Redlich, Z. Physik. Chem, B28, 371, (1935).
20. J. C. Decius and E.B. Wilson, J. Chem. Phys. 19, 1409, (1951).
21. D. Mumm, H. Hess and H. Volquartz, Ber. 48, 379, (1915).

22. K.B. Wiberg and B.I. Rowland, J. Amer. Chem. Soc., 77, 2205, (1955).

23. G.M. Bennett, Ann. Reports, 26, 123, (1929).

24. H.M. Relles, J. Org. Chem. 33, 2245,(1968).

25. A.I. Vogel, A Text Book of Practical Organic Chemistry, Longmans, Third Edition, p.167.

26. J.W. Schulenberg and S. Archer, Organic Reactions, Vol.14, John Wiley and Sons (1965).

27. C.S, Gibson and J.D.A. Johnson, J. Chem. Soc., 2743, (1929).

28. C.S. Gibson and J.D.A. Johnson, J. Chem. Soc., 1473, (1929).

29. D.H. Hey and T.M. Moyneham, J. Chem. Soc., 1563, (1959).

30. R. Jaunin and G. Séchaud, Helv. Chim. Acta. 39, 1257, (1956).

31. R.H. de Wolfe and F.B. Augustine, J. Org. Chem. 30(3), 699, (1965).

32. I.F. Halverstadt, and W.D.Kumler, J. Amer. Chem. Soc., 64, 2988 (1942).

33. A.I. Vogel, W.T. Cresswell, G.H. Jeffrey and J. Leicester, J. Chem. Soc., 514, (1952).

34. A. Eucken and L. Meyer, Phys. Z. 30, 397, (1929).

35. R.J.B. Marsden and L.E. Sutton, J. Chem. Soc., 1383, (1936).

36. C.T. Zahn, Phys. Z. 33, 730, (1932).

37. A.L. McClellan, Tables of Experimental Dipole Moments. W.H. Freeman and Co. San Francisco and London (1963).

38. R.J.W. Le Fèvre and A. Sundaram, J. Chem. Soc., 3904, (1962).

39. J.W. Smith, Electric Dipole Moments, Butterworths, London, (1955).

40. J.Moody and J.Thomas, Dipole Moments in Inorganic Chemistry, Edward Arnold Ltd., London, (1971).

41. R.A. Raphael, Acetylenic Compounds, In Organic Synthesis, Butterworth, London, (1955).

42. E.B. Wilson, Phys. Rev. 45, 706, (1934).

43. K.S. Pitzer and D.W. Scott, J. Amer. Chem. Soc., 65, 815, (1943).

44. A.R. Katritzky and J.M. Lagowski, J. Chem. Soc., 4155, (1958).

A.R. Katritzky, J. Chem. Soc., 4162, (1958).

A.R. Katritzky and P. Simmons, J. Chem. Soc., 2051, (1959).

A.R. Katritzky and P. Simmons, J. Chem. Soc., 2058, (1959).

45. A.R. Katritzky, Quart. Rev., 13, 353.

46. D.H. Whiffen and R.R. Randle, Molecular Spectroscopy Conference, held by the Institute of Petroleum, London, (1954).

D.H. Whiffen, J. Chem. Soc., 1350, (1956).

47. L.J. Bellamy, The Infrared Spectra of Complex Molecules, Methuen (1964).

48. W.R. McWhinnie and R.C. Poller, Spectrochim. Acta, 22A, 501, (1966).

49. S. Chattopadhyay, J. Ind. Phys. 42(6), 335, (1968).

50. S.S. Yoshida, Chem. and Pharm. Bull., 8, 389, (1960).

51. C. Garrigou-Lagrange, Thèse Faculté des Sciences, Bordeaux (1962).

52. J-M Lebas, J. Chim, Phys, 59, 1072, (1962).

53. V. Lorenzelli and K. Moller, Compt. rend. 249, 520 and 669, (1959).

54. G. Dellepiane and J. Overend, Spectrochim. Acta. 22A, 593,(1966).

55. A. Datin and J-M Lebas, Spectrochim. Acta. 25A, 169, (1969).

56. R.N. Jones and C. Sandorfy, Chemical Applications of Spectroscopy. Techniques in Organic Chemistry Vol. VIII. Ed. Weissberger, Interscience (1956).

57. N.L. Owen and N. Sheppard, Proc. Chem. Soc., 264, (1962).

58. F.E. Prichard, Spectrochim, Acta. 20, 925, (1964).

59. C. Garrigou-Lagrange, J-M Lebas and M-L Josien, Spectrochim. Acta., 12, 305, (1958).

60. D.H. Whiffen and R.R. Randle, Trans. Faraday Soc., 52, 9, (1956).

61. A.R. Katritzky and J. Lagowski, J. Chem. Soc., 2421, (1960).

62. J.H.S. Green, Spectrochim. Acta, 26A, 1503, (1970).

63. C. Garrigou-Lagrange and N. Calvé, Compt. rend. 262B, 947, (1966).

64. B. Nolin and R.N. Jones, Canad. J. Chem. 34, 1382 and 1392, (1956).

65. J-M.Lebas, C. Garrigou-Lagrange, N. Claverie and M-L Josien, J. Chim. Phys. 58, 559, (1961).

66. J.H.S.Green, J. Chem. Soc., 2236, (1961).

67. M. Davies and R. Lumley-Jones, J. Chem. Soc., 120, (1954).

68. R. Mecke and G. Rossmy, Z. Electrochem, 59, 866, (1955).

69. N.L. Owen and R.E. Hester, Spectrochim. Acta. 25A, 347, (1969).

70. H. Lee and J.K. Wilmshurst, Austral. J. Chem., 22, 691, (1969).

71. W. Moss and G. Zundel, Spectrochim. Acta, 26A, 1097, (1970).

72. C. Tanaka, K. Kurtani and S. Mizushima, Spectrochim. Acta, 9, 265, (1957).

73. J-M. Lebas, Thèse Faculté des Sciences, Bordeaux (1958).

74. H. Weiser, W. Laidlaw, H. Fuhrer and P.J. Kreuger, Spectrochim. Acta, 24A, 1055, (1968).

75. M. Charton, J. Amer. Chem. Soc., 91, 624, (1969).

76. L.J. Bellamy and R.L. Williams, J. Chem. Soc., 4294, (1957).

77. C.J.W. Brookes, G. Eglinton and J.F. Morman, J. Chem. Soc., 106, (1961)

78. J.H.S. Green, Spectrochim. Acta., 26A, 1523, (1970).

79. J.H.S. Green, Spectrochim. Acta., 26A, 1913, (1970).

80. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Interscience, 2nd Edition, (1970).

81. F. Ritschl, Spectrochim. Acta., 23A, 655, (1967).

82. J. Fabian and M. Legrand, Bull. Soc. Chim. France, 1461, (1956).

83. J. Fabian, M. Legrand and P. Poirier, Bull. Soc. Chim. France, 1499, (1956).

84. E. Melendez and V. Sanchez del Olmo, Ann. Quim. 66, 217, (1970).

85. B. Baccar, R. Mathis, A. Secches, J. Barrans and F. Mathis, J. Mol. Struct., 7, 369, (1971).

86. R. van der Linde, J.W. Dornseiffen and J.V., Veenland, Spectrochim. Acta. 25A, 375, (1969).

87. A.R. Philpotts and W. Thain, Nature, 166, 1028, (1950).

88. G. Varsányi, Vibrational Analysis of Benzene Derivatives, Academic Press, (1969).

89. M. Verderame, J. Pharm, Sci., 50, 312, (1961).

90. T. Veda, and S. Kato, JAPAN, 13, 917, (1960).

91. K.G. Lewis, J. Chem. Soc., 531, (1957).

92. N.E. Good, Plant Physiol. 36, 788, (1961).

93. R.I. Hewitt, and L.H. Taylor Jr., U.S. 2,877, 154, (1959).

94. H.A. Staab, and G. Walther, Ber., 95, 2070, (1962).

95. I. A. Berti, L.M. Ziti, Arch. Pharm., 285, 372, (1952).

96. J.F. Olin, U.S. 3,403, 994.

97. R, Stroh, J. Ebersberger, H. Haberland and W. Hahn, Angew, Chem., 69, 124, (1957).

98. Dictionary of Organic Compounds, Eyre and Spottiswoode, 4th Edition, London, (1965).

99. H.H. Bosshard, and H. Zollinger, Helv. Chim. Acta, 42, 1659, (1959).

100. D. Hadži, and D. Prevoršek, Spectrochim. Acta., 10, 38, (1957).

101. W. Seeliger, E. Aufderhaar, W. Diepers, R. Feinaver, R. Nehring, W. Thier, and H. Hellmann, Angew. Chem., 5, 875, (1966).

102. L.E. Clougherty, J.A, Sousa and G.M. Wyman, J. Org. Chem. 22, 462, (1957).

103. H. Kessler and A. Rieker, Annalen, 708, 57, (1967).

104. H. Kessler, Tetrahedron, 24, 1857, (1968).

105. H. Kessler, Angew. Chem., 9, 219, (1970).

106. J.W. Smith, J. Chem. Soc., 81, (1961).

107. J.W. Smith, J. Chem. Soc., 4700, (1961).

108. C.G. Le Fèvre and R.J.W. Le Fèvre, J. Chem. Soc., 1130, (1936).

109. M.M. Jamison and E.E. Turner, J. Chem. Soc., 145, (1955).

110. R.E. Richards and H.W. Thompson, J. Chem. Soc., 1248, (1947).

111. R.A. Nyquist, Spectrochim. Acta., 19, 509, (1963).

112. R.A. Nyquist, Spectrochim. Acta, 19, 1595, (1963).

113. R.A. Nyquist and R.D. McLachlan, Spectrochim. Acta., 20, 1397, (1964).

114. H. Suzuki, Bull. Chem. Soc., Japan, 33, 381, (1960).

115. H.H. Jaffé and M. Orchin, Theory and Applications of Ultra Violet Spectroscopy, John Wiley and Sons, (1962).

116. J.H.S. Green and D. J. Harrison, Spectrochim. Acta., 26A, 1925, (1970).

117. H. Baba and S. Suzuki, J. Chem. Phys., 32, 1706, (1960).

118. A.M. Bogomolov, Opt. Spectry (U.S.S.R.), 9, 162, (1960).

119. E.W. Schmid, J. Brandmuller and G. Nonnenmacher, Z. Electrochem, 64, 726, (1960).

120. S. Higushi, K. Nakamori, S. Tanaka and H. Kamada, Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Soc.), 89, 565, (1968).

APPENDIX

ASSIGNMENT TABLES

With broad absorptions (br) the centre of the absorption is given.

The position of absorptions are given under the heading cm^{-1} , the values quoted in wavenumbers.

Intensities are given under the heading I. The values quoted are relative to a value of 10 given to the most intense absorption in the spectrum and assigned proportionally.

For the infrared solution spectra tetrachloroethylene was used for the range 4000-1000 cm^{-1} and cyclohexane 1000-600 cm^{-1}.

Raman solution spectra were all measured in tetrachloroethylene.

The Raman intensities are given less rigorously in terms of:

s	strong
m	medium
w	weak

Other abbreviations used:

sh	shoulder
br	broad
mtpt	multiplet
β	in-plane deformation
γ	out-of-plane deformation
ν	bond stretching
α	in-plane ring deformation
ϕ	out-of-plane ring deformation
w	wag
r	rock
δ	deformation
X-sens	substituent sensitive mode.

Table 25

Ethyl benzoate (liquid film)

Infrared		Raman		Assignment
cm^{-1}	I(relative intensity)	cm^{-1}	I	
3065	1	3074	s	ν(C-H) aromatic
3040	0.5			ν(C-H) aromatic
2980	3	2980	m	ν(C-H) aliphatic
2940	1	2938	m-s	ν(C-H) aliphatic
2910	1	2902	w	ν(C-H) aliphatic
2880	0.5	2878	w	ν(C-H) aliphatic
1720	10	1738	s	ν(C=O)
1605	3	1604	s	ν(C-C) ring
1587	2.5	1587	w-m	ν(C-C) ring
1495	1	1494	w	ν(C-C) ring
1480	sh.1			Ethyl group bending mode
1465	sh 1			b_{as} (CH_3)
1452	6	1454	m	ν(C-C) ring
1392	2	1394	w	bs (CH_3)
1370	5	1370	w	w (CH_2)
1315	5	1316	w	ν(C-C) ring
1275	10	1278	s	ν(Ph-C) skeletal "A"
1175	5	1178	w-m	β(C-H) (a)
1108	7.5	1110	m	ν_{as}(C-O-C) skeletal "B"
1070	5			β(C-H) (d)
1028	6	1029	s	β(C-H)(b)
1000	1.5	1004	s	ring mode (p)
922 (sh)	< 0.5			γ(C-H)

Table 25 (continued)

Infrared		Raman		Assignment
cm^{-1}	I(relative intensity)	cm^{-1}	I	
970(sh)	<0.5			γ(C-H)
939	1			γ(C-H)
875	1.5			skeletal ν_s (C-O-C)
852	2	854	s	X sens.
835	<0.5			γ(C-H)
808(br)	1	808	w	CH$_3$ out of plane rock
782	1	784	w	CH$_2$ rock
712	10			γ(C-H) mode 11 of benzene
688	3.5			ϕ(C-C) mode 4 of benzene
677	3	676	m	β(C-C=O)
615	<0.5	620	m-s	α(C-C-C) mode 6b of benzene
500(sh)	<0.5			
		332	m-s	
		192	w-m	

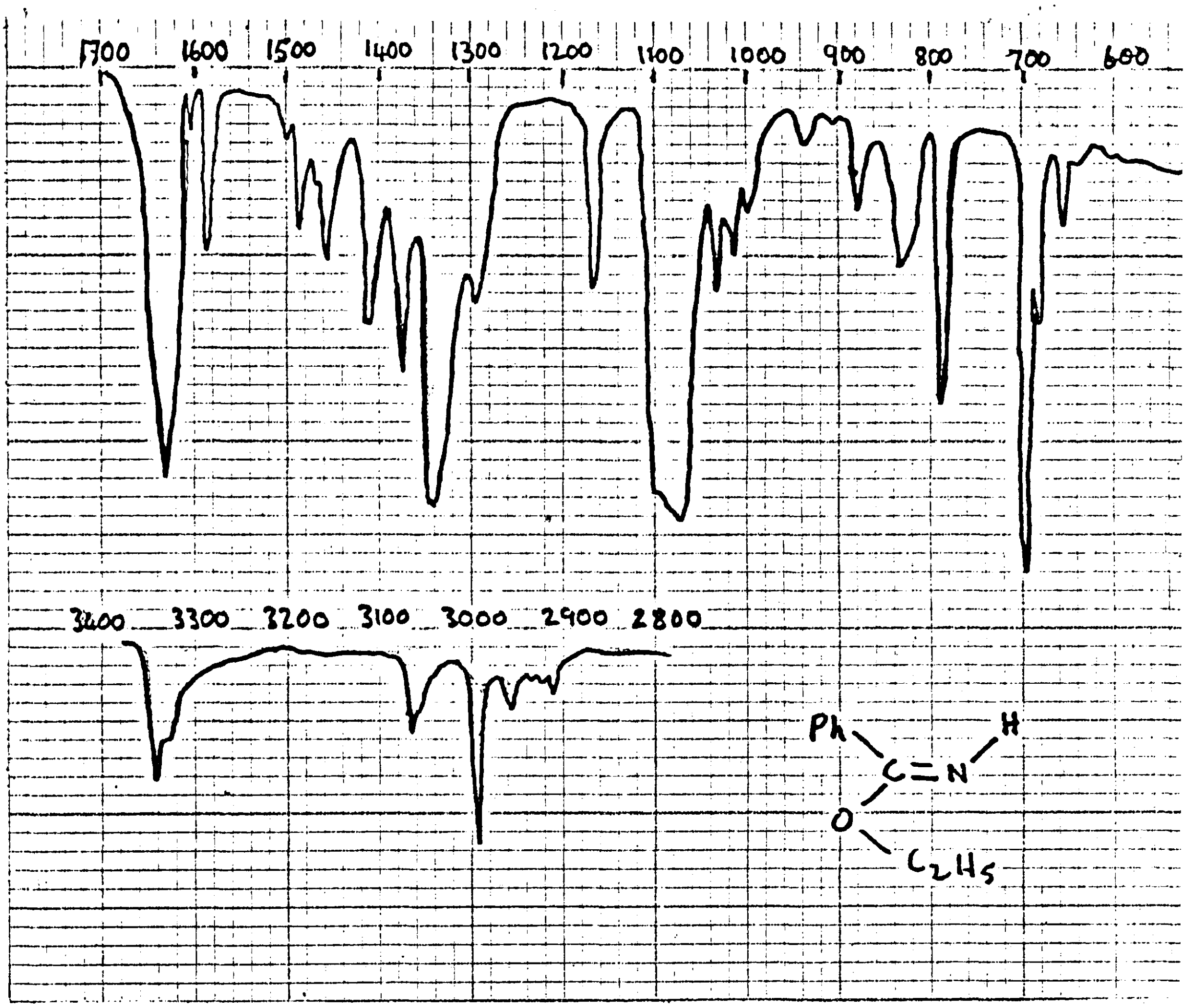
Table 26

Ethyl benzimidate (liquid film)

Infrared		Raman		Assignment
cm^{-1}	I	cm^{-1}	I	
3337	2	3336	w	ν(N-H)
3300 (br)(sh)	2			
3092(br)	<0.5			ν(C-H) aromatic
3060(br)	1	3072	s	ν(C-H) aromatic
3030(br)	0.5			ν(C-H) aromatic
2987	5	2980	m	
2941	2	2932	m-s	ν(C-H) aliphatic
2902	1.5	2898	m	ν(C-H) aliphatic
1640	10	1639	s	ν(C=N)
1604	2	1604	s	ν(C-C) ring
1580.5	6	1580	m-s	ν(C-C) ring
1496	1			ν(C-C) ring
1480.5	1.5			ethyl group bending mode
1460 (br)(sh)	2			b_{as} (CH_3)
1452.5	3	1450	m	ν(C-C) ring
1401.5	2.5	1400	w	bs (CH_3)
1377	3	1376	w	w (CH_2)
1335(br)	10	1332	w-m	skeletal mode A
1300	2			β(N-H)
1174.5	4	1164	s	β(C-H) (a)
		1116	w-m	
1075(br)	9			skeletal mode B
1031	4	1030	s	β(C-H)(b)

Table 26 (continued)

Infrared		Raman		Assignment
cm^{-1}	I	cm^{-1}	I	
1019.5	2			skeletal mode C
1003	1	1004	s	ring mode (p)
994(sh)	0.5			γ (C-H)
929.5	0.5			γ(C-H)
874	3	874	w-m	skeletal mode D
828(br)	3.5	830	m	γ(C-H) and γ(N-H)
784	5	784	w	CH$_2$ rock
698	10			γ(C-H)
682	3			ϕ(C-C) ring mode (4 of benzene)
655	3	656	m	bend (C-C=N)
		620	m-s	
612	0.5			α(C-C-C) ring mode (6b of benzene)
		404	w	
		340	m-s	
		194	w	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2900
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Ph
C=N
H
O
C2H5

Table 27

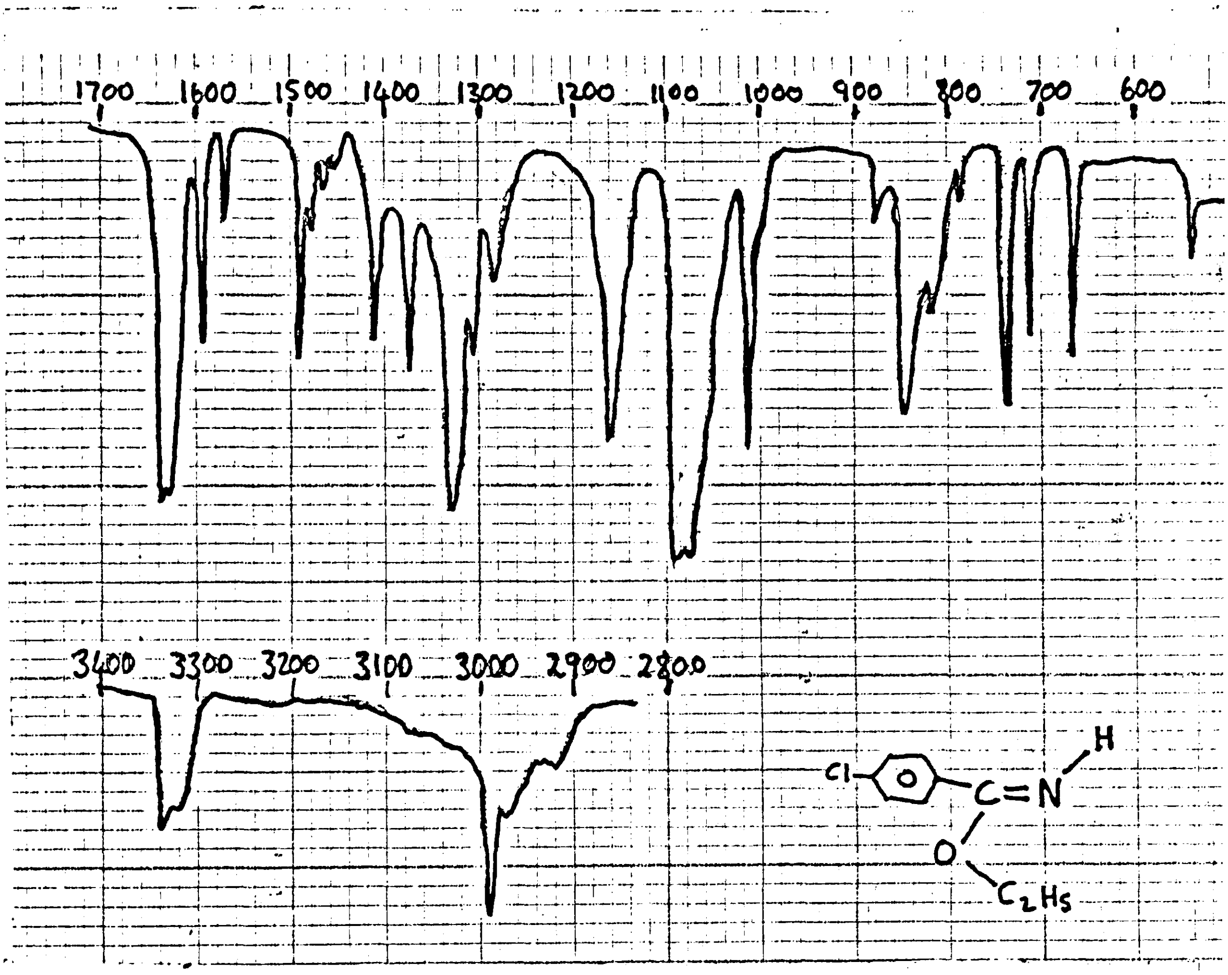
Ethyl-p-chlorobenzimidate (liquid film)

ν(cm^{-1})	Infrared Relative intensity	Assignment
3336 (br)	1.5	ν(N-H)
3311 (br)	1.5	
3050 (br)(sh)	0.5	ν(C-H) aromatic
2990.5	4	ν(C-H) aliphatic
2952 (br)	2	ν(C-H) aliphatic
2914	1.25	ν(C-H) aliphatic
1640	10	ν(C=N)
1599	7	ν(C-C) ring
1573	3	ν(C-C) ring
1494	6.5	ν(C-C) ring
1481	5.5	Ethyl group bending mode
1465	3.5	b_{as} (CH_3)
1451	3	ν(C-C) ring
1415	6.5	
1390 (sh)	5.5	bs CH_3
1376.5	7	w CH_2
1330 (br)	9.5	skeletal mode A
1304.5	5.5	β(C-H)
1280	3.5	β(N-H)
1169 (br)	7.5	β(C-H)
1095	10	β(C-H), X sens mode
1080 br	10	skeletal mode B
1017	9	β(C-H)
1000 (br)(sh)	3	skeletal mode C
877.5	3	skeletal mode D
843 (br)	7.5	γ(C-H) and γ(N-H)
810.5	6	CH_3 out-of-plane rock
737	6.5	γ(C-H) (mode 11 of benzene
712	4	X sens ?
668.5	5.5	ϕ(C-C)
628	0.5	α(C-C-C) ring mode (6b of benzene)
531	2.5	ϕ(C-C) ring mode (16b of benzene)

Table 28

Ethyl-p-toluimidate (liquid film)

Infrared cm^{-1}	I	Raman cm^{-1}	I	Assignment
3340.5	2	3338	w	ν(N-H)
3320(br)(sh)	1			
3050(br)(sh)	2.5	3072	s	ν(C-H)aromatic
		3018	m	ν(C-H)aromatic
2998	5	2976	m	ν(C-H)aliphatic
2950(sh)	4			ν(C-H) aliphatic
		2928	s	ν(C-H)aliphatic
1639.5	10	1636	s	ν(C=N)
		1614	s	ν(C-C) ring
1573	3	1574	m	ν(C-C) ring
1516	3.5	1518	w	ν(C-C) ring
1481.5	4			ν(C-C) ring
1465(br)(sh)	4.5			b_{as} (CH_3)
1450.5	4.5	1452	w-m	ν(C-C) ring
1410	7	1410	w	
1399	7	1396	w	b_s (CH_3)
1378	8	1380	m	w (CH_2)
1332.5(br)	9.5	1328	m	skeletal mode A
1312.5	7.5			ν(C-C) ring
1288	4			β(N-H) and β(C-H)
		1216	m	
1189.5	6	1188	m	
1170	7	1166	s	β(C-H)
		1116	m	
1080(br)	9.5			skeletal mode B and β(C-H)
1023	7	1022	w	skeletal mode C and β(C-H)
999	3.5	1004	w	
877.5	3.5	876	w	skeletal mode D
		842	s	
829(br)	8			γ(C-H) and γ(N-H)
		774	m	CH_2 rock
732.5	7.5	732	w	γ(C-H) (Mode 11 of benzene)
676	4.5			Ø(C-C) ring mode (4 of benzen
641	0.5	640	m-s	α(C-C-C)ring mode (6b of benzene)
601.5	0.5			Ø(C-C) ring mode (16b of benzene)
		320	m	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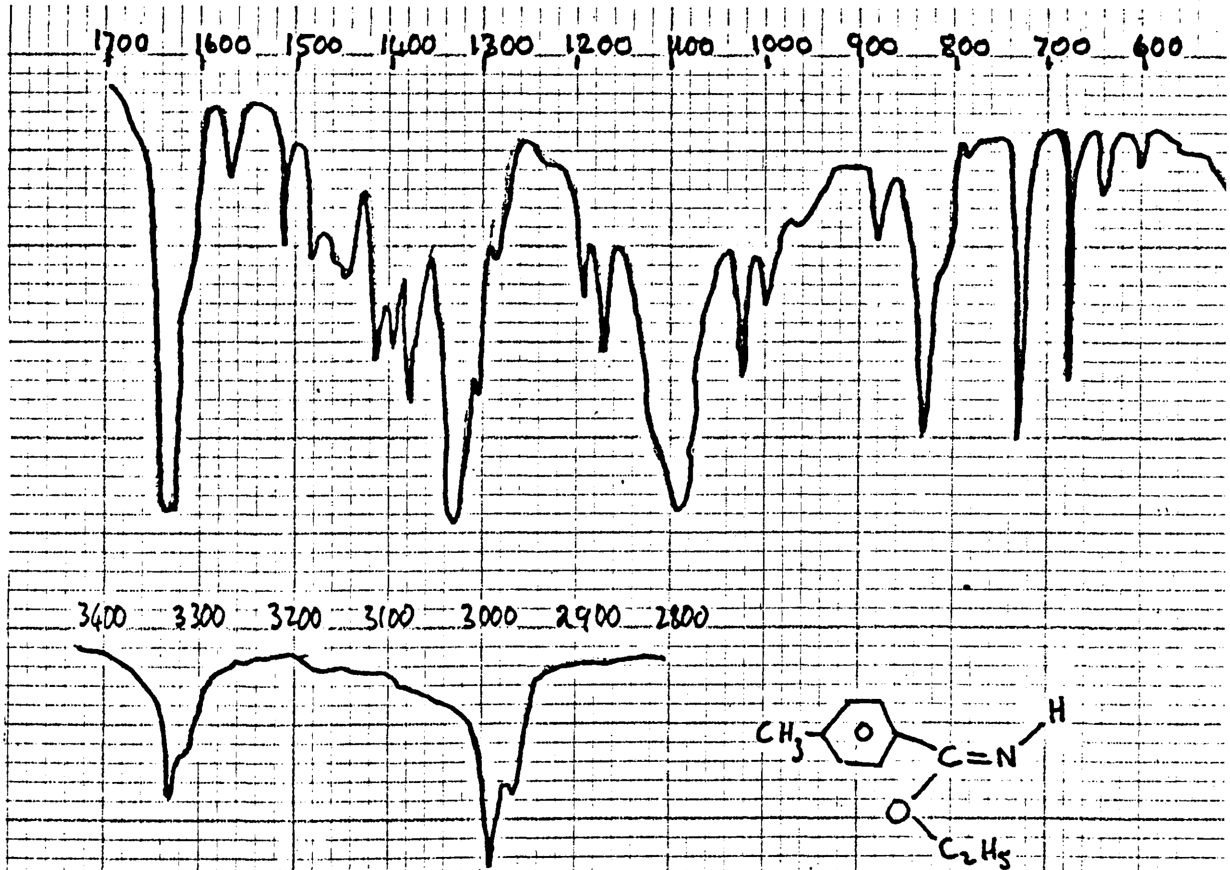
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CH3
O
C=N
H
O
C2H5

Table 29

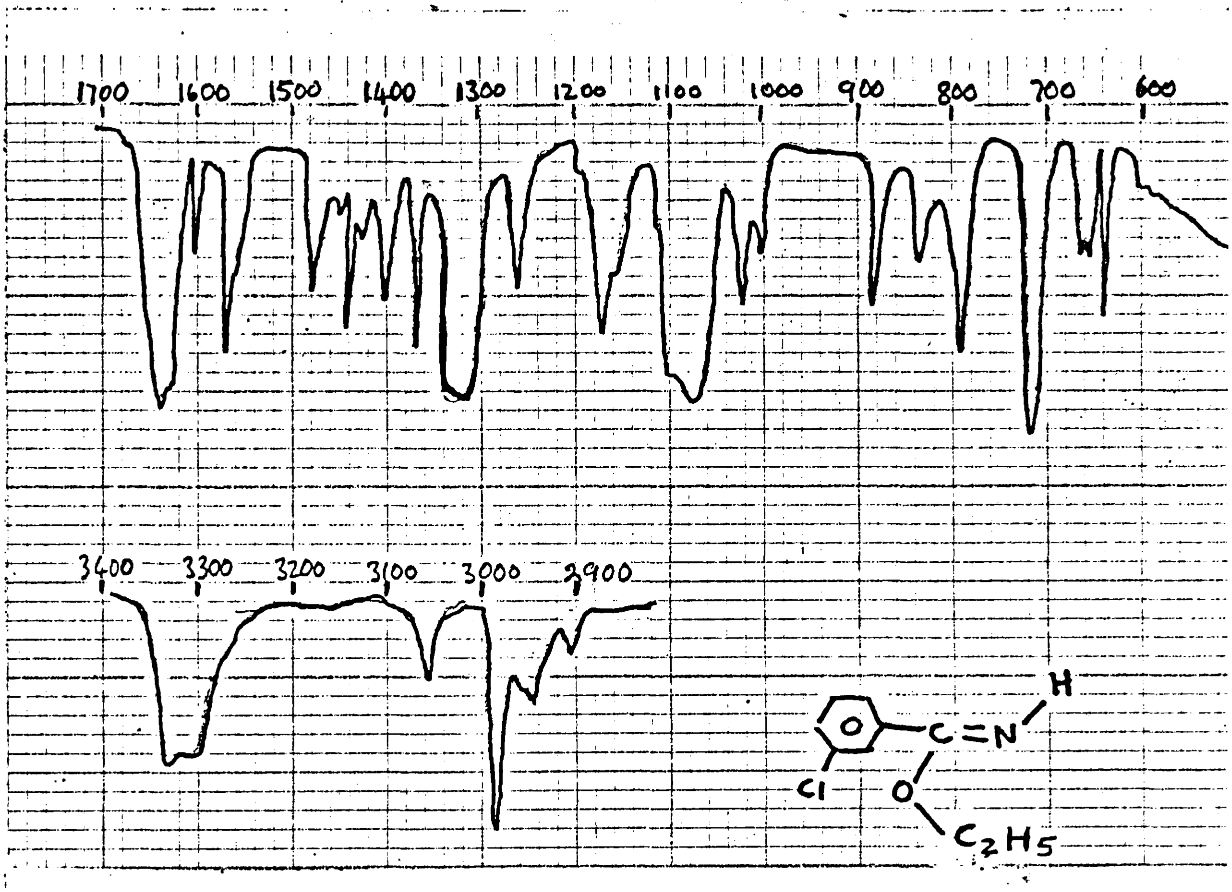
Ethyl-m-chlorobenzimidate (liquid film)

Infrared		
ν(cm^{-1})	Intensity	Assignment
333.5	2	ν(N-H)
3320 (br)(sh)	2	
~3050(br)(sh)	1	ν(C-H) aromatic
2962(br)	6	ν(C-H) aliphatic
2900 (br)	1.5	ν(C-H) aliphatic
1642	10	ν(C=N)
1599	4	ν(C-C) ring
1571	9	ν(C-C) ring
1479	6	ν(C-C) ring and $b_{as}(CH_3)$
1429.5	7	ν(C-C) ring
1402	6	b_s (CH_3)
1377	6	w (CH_2)
1325 (br)	10	skeletal mode A
1273	5	β(N-H) and β(C-H)
1178.5	6	β(C-H)
1095(sh)	9.5	β(C-H)
1080(br)	10	skeletal mode B
1072(sh)	9.5	β(C-H)
1021	6	skeletal mode C
1001	4.5	ring mode
881	6.5	skeletal mode D
834 (br)	5	γ(C-H) and γ(N-H)
795.5	7	γ(C-H)
717	8	γ(C-H) (mode 11 of benzene)
679.5	2	Ø(C-C) ring mode (mode 4 of benzene
668	2	bend (O-C=N)
650	3	X sens?
520 (br)	1	Ø(C-C) ring mode (16a of benzene)

Table 30

Ethyl-m-toluimidate (fluorescence in Raman)

Infrared		Raman		Assignment
cm^{-1}	I	cm^{-1}	I	
3336	3.5	~3340	w	ν(N-H)
3310	3			
3040(br)(sh)	3	~3064	m	ν(C-H) aromatic
2983	8			ν(C-H) aliphatic
2945(br)	6	2930	s	ν(C-H) aliphatic
2906	5.5			ν(C-H) aliphatic
1637	10	1638	s	ν(C=N)
1604	8	1615	m	ν(C-C) ring
1591	8.25	1592	m	ν(C-C) ring
1584	8.25			ν(C-C) ring
1480	7			ethyl group bend
1460 (sh)	7			b_{as} (CH_3)
1445	7.5	1450	w	ν(C-C) ring
1401(br)	8			b_s (CH_3)
1374.5	9.5	1382	w	w (CH_2)
1333.5	10	1328	w	skeletal mode A
1286	7			β(N-H) and β(C-H)
1229	7	1230	w-m	X sens?
1174	6			β(C-H)
1149 (br)	7.5			
1095 (br)(sh)	9.5			β(C-H)
1080 (br)	10			skeletal mode B
1072 (br)(sh)	9.5			β(C-H)
1024(br)	7.5			skeletal mode C
1004(sh)	5.5	1003	m-s	ring mode (p)
909(br)	3.5	910	w	skeletal mode D
867	4.5	868	w	γ(C-H)
830	6			γ(C-H) and γ(N-H)
798	8.5			γ(C-H)
777	1.5	776	w	CH_2 rock
763	1.5	760	w	
718	10			γ(C-H) (mode 11 of benzene)
680(sh)	1			ϕ(C-C) ring mode (4 of benzene
660	2	662	w	bend (O-C=N)
465	2			X sens?
		340	w	
		226	w	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700
600
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3300
3200
3100
3000
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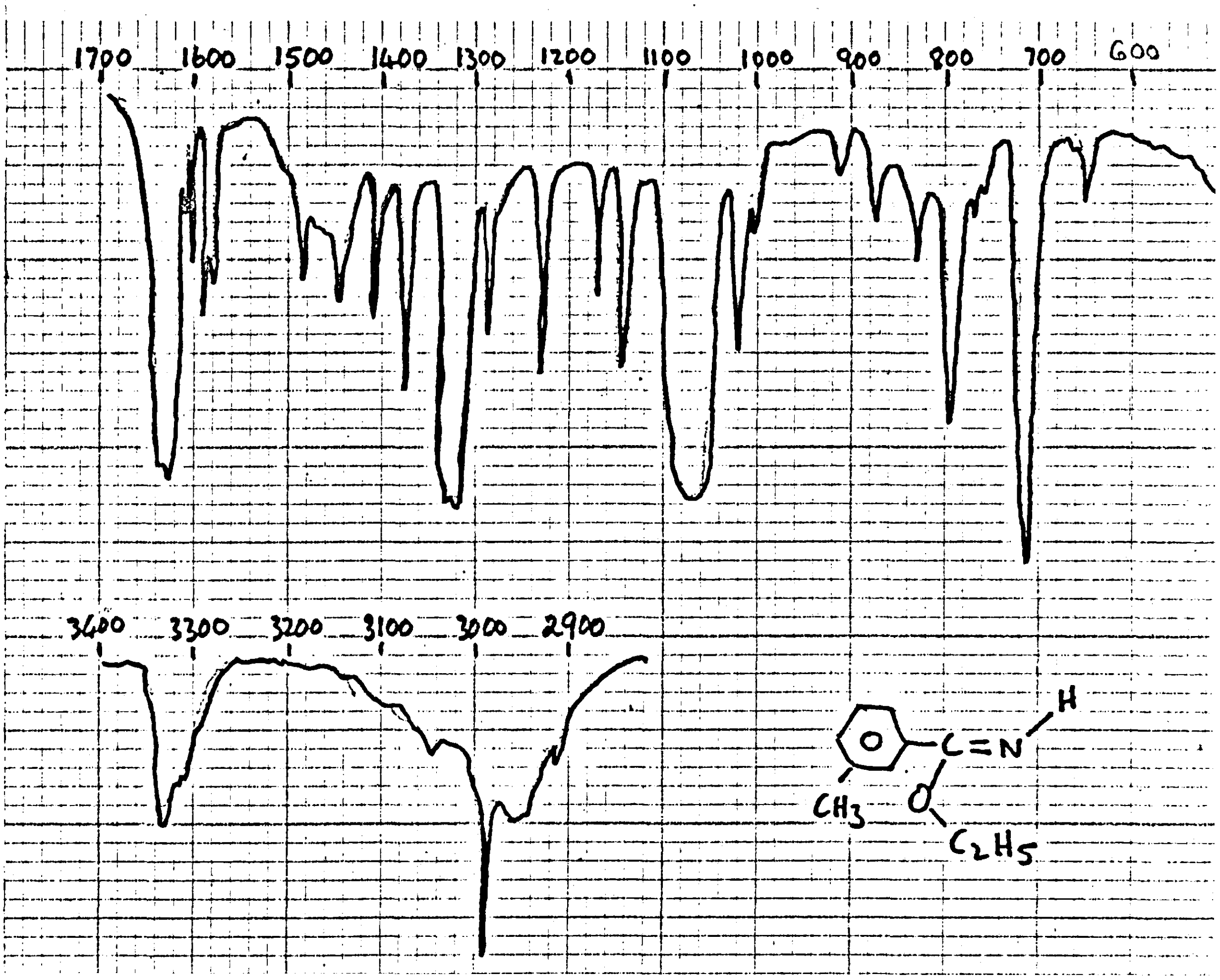
Cl
C=N
H
O
C2H5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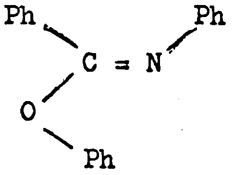
600
3400
3300
3200
3100
3000
2900
CH3
C=N
H
O
C2H5

Table 31

N-Phenyl ethyl benzimidate (liquid film)

Infrared		
cm^{-1}	Intensity	Assignment
3080	1	ν(C-H) aromatic
3060	1	
3030	1	
2980	3	ν(C-H) aliphatic
2940(br)	1	
2900	1	
2870	1	
1660(br)	10	ν(C=N)
1598	8	ν(C-C) ring
1580	2.5	ν(C-C) ring
1495	4	ν(C-C) ring
1490(sh)	3.5	
1480 (sh)	2.5	ethyl group bending mode
1460 (br)(sh)	1	b_{as} (CH$_3$)
1450	4	ν(C-C) ring
1390	1	b_s (CH$_3$)
1365	2.5	w (CH$_2$)
1318	2.5	
1285	8	ν(Ph-C)
1269	10	ν(Ph-N)
1250 (br)(sh)	4	β(C-H)
1180	1	
1160	2	β(C-H)
1112	10	ν_{as} (C-O-C)
1070	3	β(C-H)
1029	4	β(C-H)
1000	0.5	ring mode (p)
920	0.5	γ(C-H)
905	2	γ(C-H)
880	1	ν_s(C-O-C)?
778	4	γ(C-H)
768	4	
732	4	
725(sh)		
692	10	ϕ(C-C) ring mode (4)
668	1	
660	1	Bend (C-C=N)?

Table 32



N-Phenyl phenyl benzimidate

Infrared				Raman				
solid		solution		solid		solution		Assignment
cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	
3050(br)	1	3062	1					ν(C-H) aromatic
		3030	1					ν(C-H) aromatic
1655(br)	9	1670	8	1657	s	1650	s	ν(C=N)
		1655	7					ν(C=N)
1590	9	1592	8	1592	s	1592	s	ν(C-C) ring
1580(sh)	6							ν(C-C) ring
1485(br)	8	1490	9	1492	m			ν(C-C) ring
1450	5	1450	4	1450	w-m			ν(C-C) ring
		1325	1					
		1285	3					
1268	6	1268	7	1270	m-s			ν(Ph-C)
1235(br)	1	1230	5					ν(Ph-N)
1210(br)	10	1210 1205	10	1202	s	1212	m	ν(Ph-O)
1190(sh)	5							
1180	5			1181	s	1180	m	β(C-H)
1172	5							β(C-H)
1165	9	1168	4					β(C-H)
1150	4			1158	m			
		1088	3					X sens ?
1072	4	1072	4	1078	w-m			β(C-H)
1045	7	1050	6					ν(C-O)
1025	6	1027	5	1022	m	1030	w-m	β(C-H)
1018	6	1022	5					β(C-H)
1000	3	1000	1	1005	s	1010	s	ring mode (p) (Whiffen Randle)
928(br)	1							γ(C-H)
888(br)	1							
870	5							
825(br)	1			826	w			
810(br)	1							
770	9	770	7					

Table 32 (continued)

Infrared				Raman				
solid		solution		solid		solution		Assignment
cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	
		765	6					γ(C-H)
755	9	752	6					
738	9	725	2					
705	7			714	w			
690(br)	8	695	10					∅(C-C) ring mode (4)
665(br)	1							δ CCN ?
575	1							r CON ?
538	1							skeletal δ ?
525	5							∅(C-C)(Ph-O)(16b)
440	0.5							∅(C-C)(Ph-C)(16b)
395	0.5							X sens (6a)

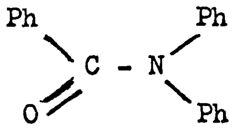


Table 33

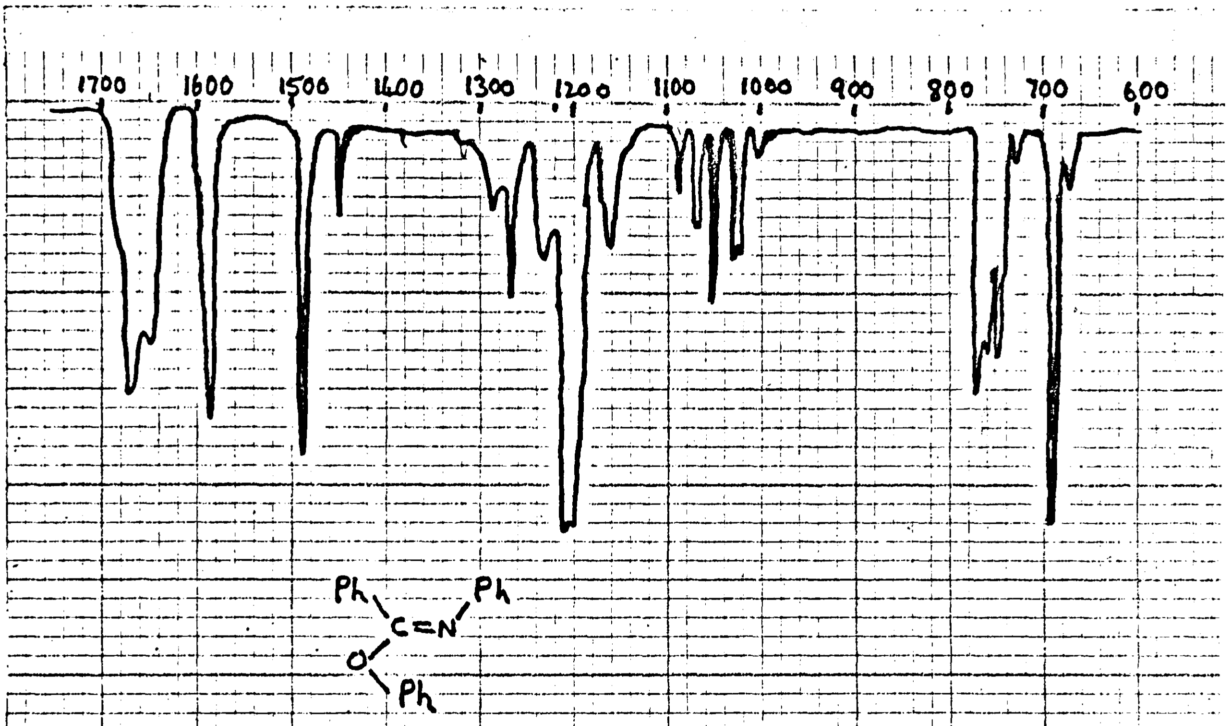
N-Benzoyl diphenylamine

		Infrared		
Disc.		Solution		Assignment
cm^{-1}	Intensity	cm^{-1}	Intensity	
3060	1	3064	1	ν(C-H) aromatic
		3040	1	ν(C-H) aromatic
3025(br)(sh)	1	3030	1	ν(C-H) aromatic
1655(sh)	10	1670	10	ν(C=N)
1650	10			ν(C=N)
1590(br)	5	1595	4	ν(C-C) ring
1490(br)	7	1492	7	ν(C-C) ring
1446	4	1453	2	ν(C-C) ring
		1448	3	ν(C-C) ring
1340	10	1337	8	skeletal modes involving (C-N$<^{Ph}_{Ph}$) and ν(Ph-C)
1322	6	1322	7	
1308	7	1304	8	
1290	4	1288	8	
1275(br)	3			
1215	1	1212	0.5	
1180	0.5	1180	1	β(C-H)
1170	1			β(C-H)
1110	1			X sens mode q ?
1075	1	1075	2	β(C-H)
1028	1	1030	2	β(C-H)
1000	0.5	1000(br)	0.5	ring mode p
960	1			γ(C-H)
900	1			
852	1			
788	5	788	3	
770	3	760(sh)	3	
755	5	755	5	
725	4	722	2	
702	7	705	5	
		700	7	

Table 33 (continued)

N-Benzoyl diphenylamine

Infrared				
Disc.		Solution		Assignment
cm^{-1}	Intensity	cm^{-1}	Intensity	
690	7	690	6	ϕ(C-C)ring mode (4)
660	3	660	2	β(C-C-O)
625	4	622	2	α(C-C-C) ring mode (6b)
615	2	615	2	
515	2			ϕ(C-C)ring mode (16b) (Ph-N)
448(br)	1			ϕ(C-C)ring mode (16b) (Ph-C)
415(br)				X sens (6a)
365	1			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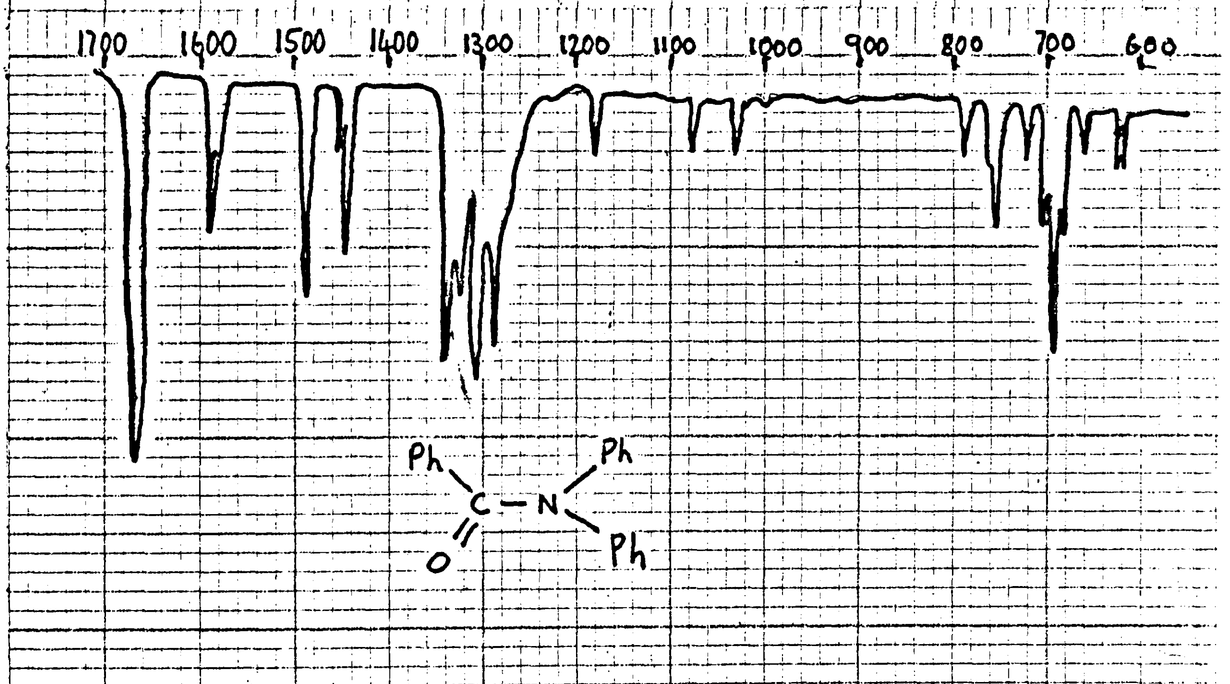
1300
1200
1100
1000
900
800
700
600
Ph
Ph
C=N
O
Ph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700
600
Ph
Ph
C
N
O
Ph

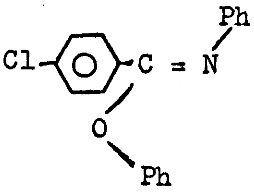


Table 34

N-Phenyl phenyl-p-chlorobenzimidate

Infrared				Raman				
solid		solution		solid		solution		Assignment
cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	
3050(br)	0.5	3060	1					ν(C-H) aromatic
		3030	1					ν(C-H) aromatic
1655(br)	8	1675) 1660) * 1655)	7	1656	s	1662	s	) ν(C=N)
1590(br)	8	1595	8	1592	s	1598	s	ν(C-C) ring
1488(br)	8	1490	10	1490	w	1490	w	ν(C-C) ring
1470(sh)	2							
1460(sh)	2	1455(sh)	1					ν(C-C) ring
1400	5	1400	3					
1285	2	1285	3					β(C-H)
1265	4	1265	5	1270	w	1276	w	ν(Ph-C)
		1230	4					ν(Ph-N)
1202	10	1208	10	1206	m	1210	m	ν(Ph-O)
1185	7			1196	w-m			
1160	8	1168	4	1179	w-m	1176	m	β(C-H)
1090	7	1090	5	1095	w-m	1096	w-m	X sens
		1080	3					β(C-H)
1072	2	1070	3					β(C-H)
1040	7	1048	5					ν(C-O)
1022	1	1025	2	1025	w	1030	w	β(C-H)
1010	7	1015	7					β(C-H)
1000	2	1000	2	1003	m	1010	m	ring mode p
905	0.5							)
880	3							)
840	5	845	3	846	w			) γ(C-H)
		825	2					)
795	5	800(br)	3	802	w			)

Table 34 (continued)

Infrared				Raman				
solid		solution		solid		solution		
cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	Assignment
760	5	762	5					γ(C-H)
	8	755	5					
742	8	745	2					
730	1			733	w			
705	2							
690	5			692	w			∅(C-C) ring mode(4)
588	1							δ(skeletal end ring)
538	1.5							
505	0.5							
480	2							
440	1.5							

* centre of band.

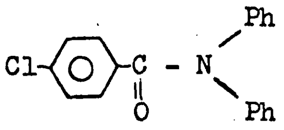


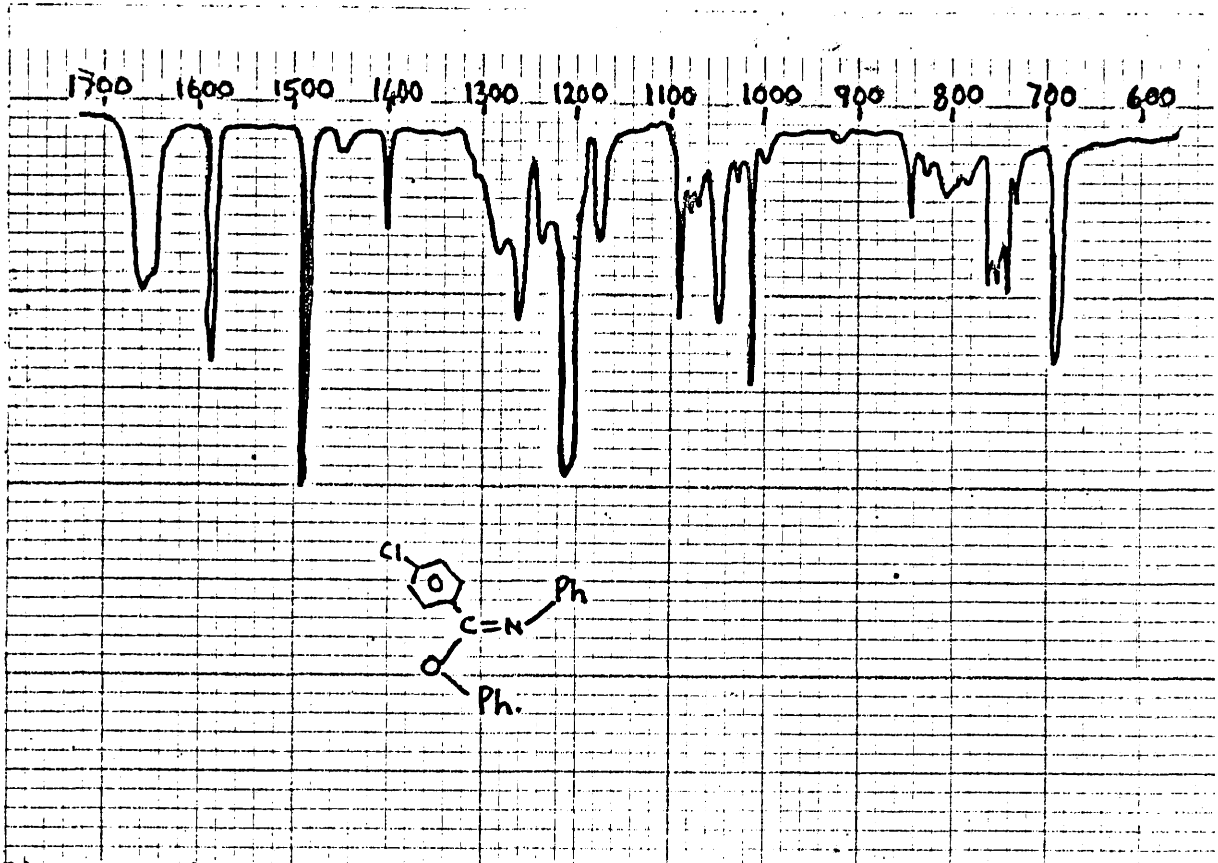
Table 35

N-p-chlorobenzoyldiphenylamine

Disc. cm^{-1}	Intensity	Infrared solution cm^{-1}	Intensity	Assignment
3060	1	3065	1	ν(C-H) aromatic
3040	1	3040	1	ν(C-H) aromatic
1650(br)	10	1675	10	ν(C=O)
1590	7	1595	6	ν(C-C) ring
1490	9	1490	9	ν(C-C) ring
1450	2	1453	2	ν(C-C) ring
1400		1400	3	
1342	10	1338	9	skeletal involving (C - N(Ph)Ph) and ν(Ph-C) β(C-H)
1328	7	1325	8	
1308	7	1305	9	
1290	5	1290	7	
1270(br)	4			
1235(vbr)	1	1230(vbr)	1	
1212	1	1212	1	
1180	1	1178	2	β(C-H) p
1170	1			
1110	3	1105	3	β(C-H)
1090	4	1090	3	X sens
1075	2	1075	2	β(C-H) p
1030	2	1030	2	β(C-H)
1018	4	1018	4	β(C-H) p
1000(br)	1	1000 (br)	1	ring mode p
960	2			γ(C-H)
955	2			
858	4			
835	5	835	5	
		825	2	
760	6	758	8	
750	5	750	5	
738	2	740	2	
700	5	700	8	

Table 35 (continued)

Disc		Infrared solution		Assignment
cm^{-1}	Intensity	cm^{-1}	Intensity	
690	6	692	7	Ø(C-C) ring mode (4)
680	2			δ(skeletal and ring modes)
630	2	632	2	
620	3	620	3	
560	3	555	2	
525	2			
478	3			
438	2			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1300
1200
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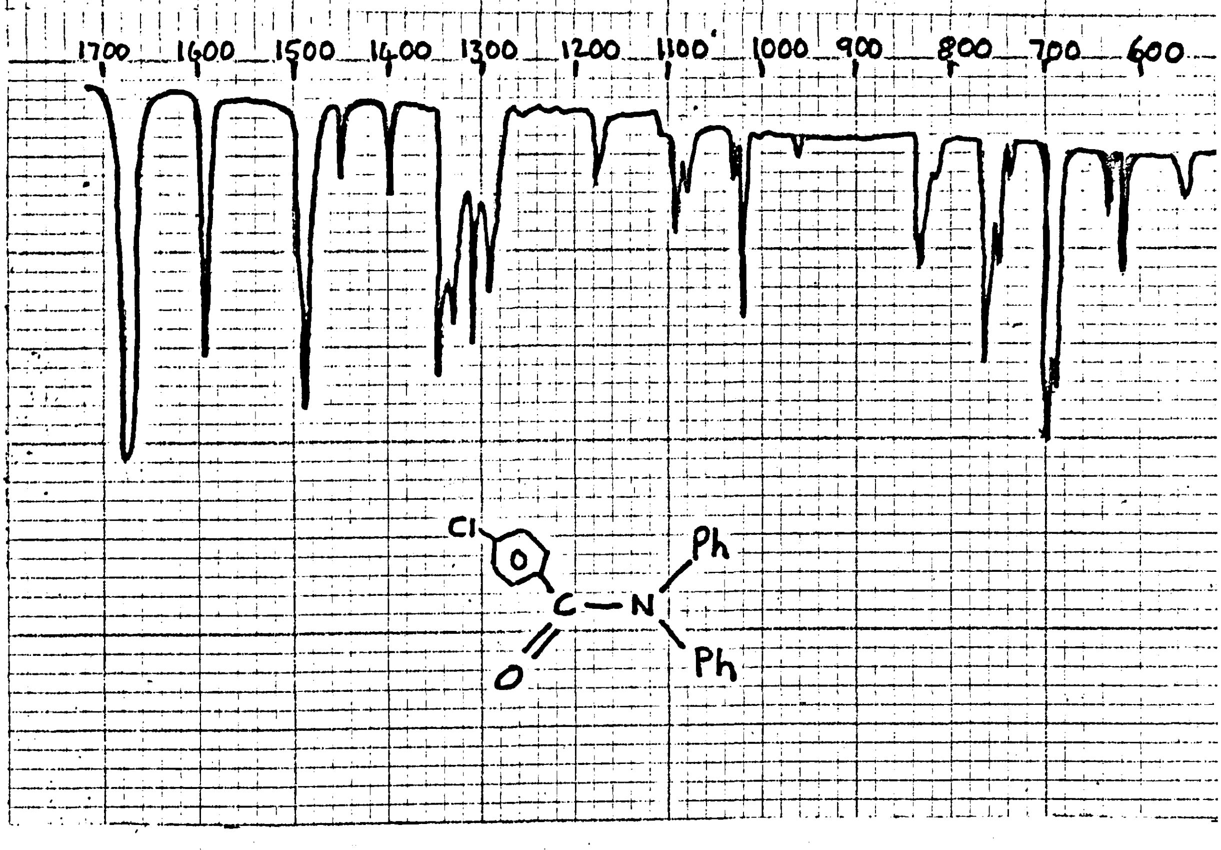
1000
900
800
700
600
Cl
O
C=N
Ph
O
Ph.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Cl
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C
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Ph
Ph
O

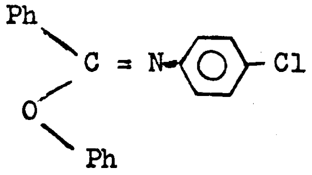


Table 36

N-p-chlorophenyl phenyl benzimidate

Infrared solid cm^{-1}	I	Infrared solution cm^{-1}	I	Raman solid cm^{-1}	I	Raman solution cm^{-1}	I	Assignment
3060	1	3060	1					ν(C-H)
3030	1	3035	1					ν(C-H)
		1672	7					)ν(C=N)
1640(br)	9	1655	7	1650	s	1656	s	)
1585(br)	8	1592	6	1589	s			ν(C-C) ring
1485(br)	9	1490	10					ν(C-C) ring
1450	5	1450	3					ν(C-C) ring
1400(br)	1	1400(br)	1					
1335(br)	1							
1315(br)	1	1315(br)	1					
1290(br)		1295(br)	2					β(C-H)
1272	7	1275	6	1278	w			ν(Ph-C)
1235(sh)	1	1235(sh)	4					ν(Ph-N)
		1210	10	1210	m	1212	w	) ν(Ph-O)
1205(br)	10	1202	10					)
		1180	2	1178	w			
1170	9	1170	3			1174	w	β(C-H)
1100(br)	2							
1082	5	1090	5	1088	w			X sens
1075	5	1075	2					β(C-H)
1046	8	1050	5					ν(C-O)
1020	7	1025	4	1026	w	1028	w	β(C-H)
1010	6	1012	3					β(C-H)
1000	4	1000(br)	2	1007	m	1010	m-	ring mode p
935	1	920	2					)
895	2							)
878	3	885	2					)
830	7	830(br)	4					) γ(C-H)
810	4							)
803	6							)

Table 36 (continued)

Infrared				Raman				
solid		solution		solid		solution		
cm^{-1}	I	cm^{-1}	I	xm^{-1}	I	cm^{-1}	I	Assignment
		770	3					γ(C-H)
		760	3					
752	9	748	5					
708	7	702	4					
680(br)	6	690	6					Ø(C-C) ring mode (4)
530(br)	6							δ (skeletal and ring)
505(br)	1							
462	2							
410(br)	2							
355	2							

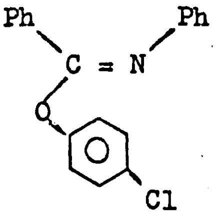


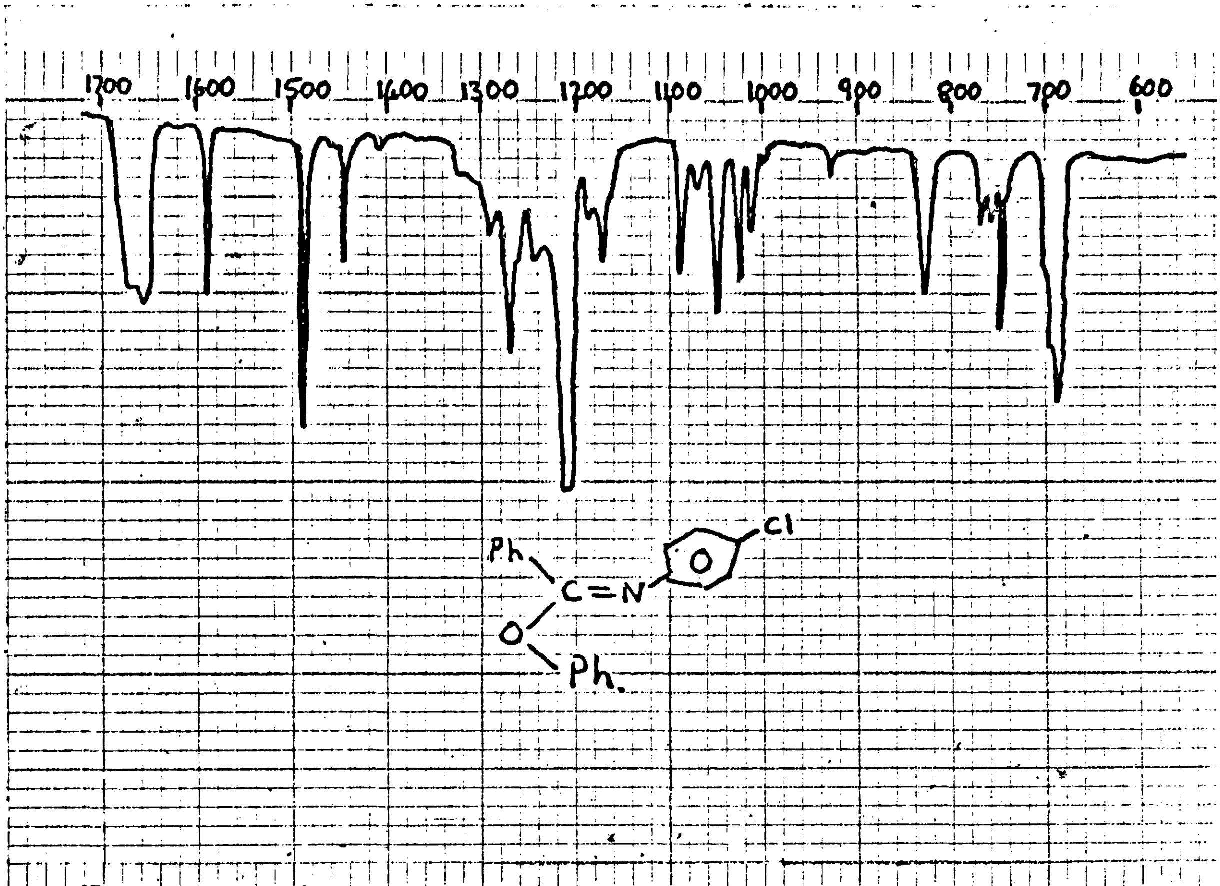
Table 37

N-Phenyl-p-chlorophenyl benzimidate

Infrared solid cm^{-1}	I	Infrared solution cm^{-1}	I	Raman solid cm^{-1}	I	Raman solution cm^{-1}	I	Assignment
3070(br)	1	3060(br)	1					ν(C-H) aromatic
3020(br)	1	3030(br)	1					ν(C-H) aromatic
1665(br)	10	1670(br)	6	1668	s	1650	s	ν(C=N)
		1600	4	1602	m-s	1600	s	ν(C-C) ring
1595	7	1595	4					ν(C-C) ring
1590	7							ν(C-C) ring
1485(br)	9	1488	10					ν(C-C) ring
1448	7	1450	3					ν(C-C) ring
1400	2	1400(br)	0.5					
1318	3	1315(br)	1					
1300	4							
1290	4							
1285	6	1285	3	1272	w			β(C-H)
1265	9	1268(br)	5					ν(Ph-C)
1225	9	1225(sh)	3	1230	w			ν(Ph-N)
1220	9							ν(Ph-N)
1205	10	1208	8			1210	w	ν(Ph-O)
1175(sh)	4	1165(br)	3	1182	w	1176	w	β(C-H)
1158	6							
1090	6	1085	4					X sens
1078(sh)	9							β(C-H)
1065(br)	9	1070	4					β(C-H)
		1048	4					ν(C-O)
1028	6	1030(sh)	3	1030	w	1030	w	β(C-H)
		1022	4					β(C-H)
1010	8	1015	4					β(C-H)
1000	4	1000(br)	1	1004	s	1008	s	ring mode p
908 (br)	7							γ(C-H)
890(br)	2							
832	6							
825	6							
820	6	822	5					

Table 37 (continued)

Infrared				Raman				Assignment
solid		solution		solid		solution		
cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	
778	6	775	5					γ(C-H)
762	7	768	4					
		745	4					
733	7	735	3	730	w			
712	2	718	4	720	w			
690	9	695	7					Ø(C-C) ring mode (4)
555	2							δ(skeletal and ring)
538	4							
508	5							
480	1.5							
442	4							
425	2							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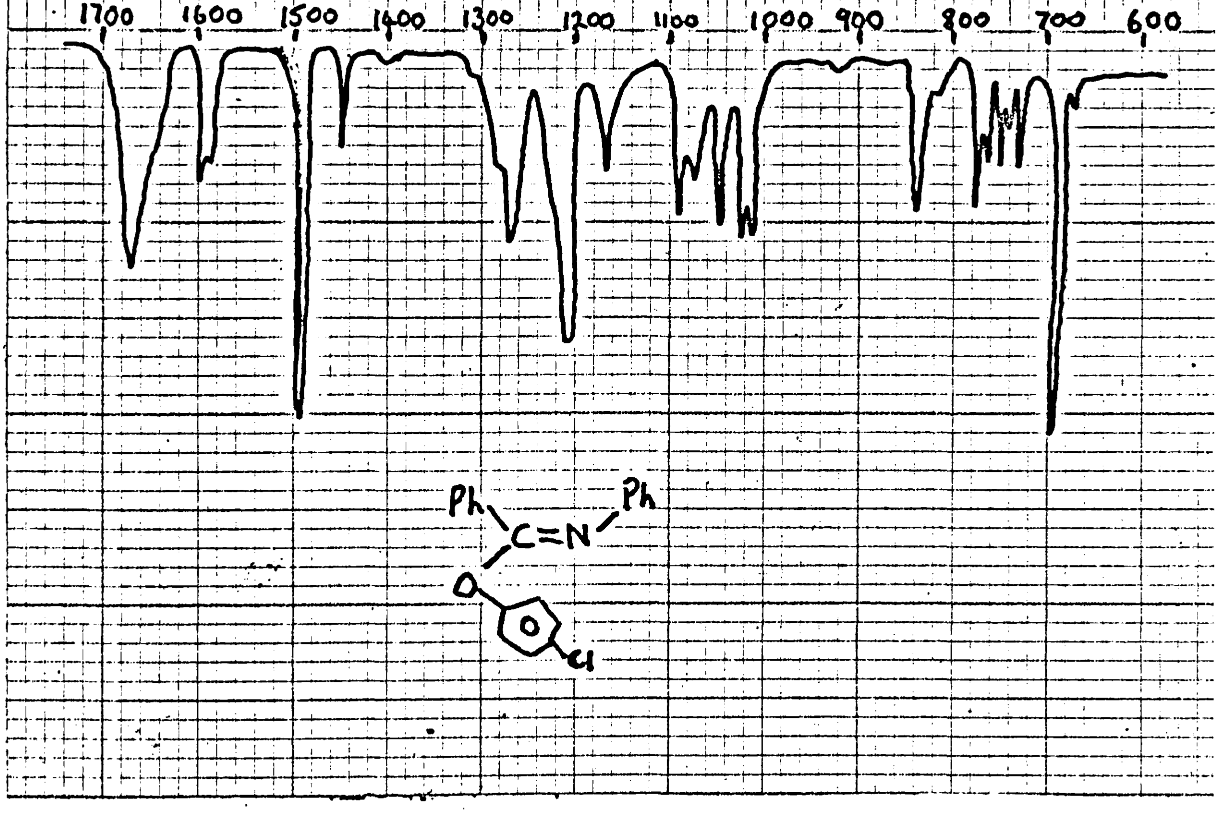
1400
1300
1200
1100
1000
900
800
700
600
Ph
C=N
O
Cl
O
Ph.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1000
900
800
700
600
Ph
C=N
Ph
O
O
Cl

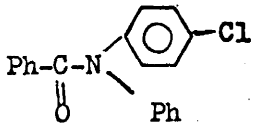


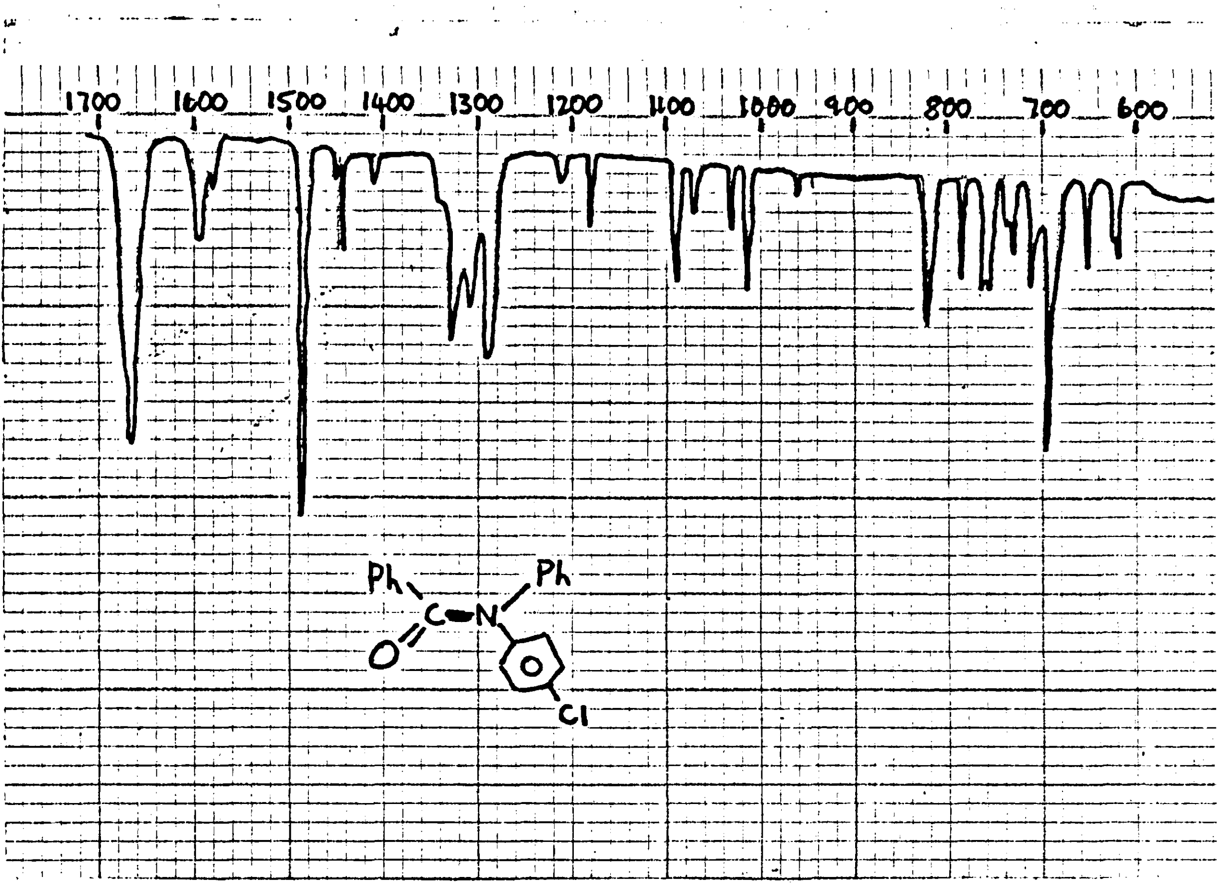
Table 38

N-Benzoyl-p-chlorodiphenylamine

Infrared				
Disc		Solution		Assignment
cm^{-1}	Intensity	cm^{-1}	Intensity	
3085	1			ν(C-H)
3060	1	3065	1	ν(C-H)
3040(br)	1	3040	1	ν(C-H)
1655	10	1673	9	ν(C=N)
1595	5	1595 (br)	3	ν(C-C) ring
1580(br)(sh)	4	1585	2	ν(C-C) ring
1488	9	1492	10	ν(C-C) ring
1455	3	1455	2	ν(C-C) ring
1448	4	1449	3	
1400	3	1410	1	
1340	9	1335	7	skeletal involving $\nu(C-N\genfrac{}{}{0pt}{}{Ph}{Ph})$ ν(C-C) and β(C-H)
1325(br)	6	1322	8	
1305	7	1305	7.5	
1285	9	1285	8	
1215	1	1215	1	
1180	4	1180	2	β(C-H)
1165	2			
1160	1			
1105(sh)	2			
1100	3			
1087	6	1090	4	X Sens.
1075(sh)	3	1075	2	β(C-H)
1025	1	1030	2	β(C-H)
1012	3	1018	3.5	β(C-H)
1002	3	1005(br)	0.5	ring mode (p)
965(br)	1	960(br)	0.5	γ(C-H)
925(br)	1	925?(br)	0.5	
900(br)	0.5	900?(br)	0.5	
863	3			
843	0.5			

Table 38 (continued)

Infrared				
Disc		Solution		Assignment
cm^{-1}	Intensity	cm^{-1}	Intensity	
758	6	758	3	γ(C-H)
		748	2	
		740	2	
720	0.5			
708	6	710	4	
695	6	698	9	ϕ(C-C) ring mode (4)
652	5	650	3	δ(skeletal and ring)
		620	2	
550	2			
522	3			
508	2			
472	2			
435(br)	2			
375(br)				


1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
Ph
Ph
C
N
O
Cl

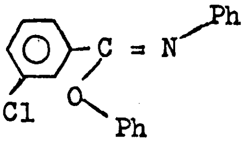


Table 39

N-Phenyl phenyl-m-chlorobenzimidate

Infrared				Raman				
solid		solution		solid		solution		Assignment
cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	
3060(br)	1	3070	1					ν(C-H)
3030(br)	1	3030	1					ν(C-H)
1660(br)	9	1672	5	1673	s			ν(C=N)
		1655	5	1664	s	1658	s	ν(C=N)
1590	9	1595	7.5	1595	s	1598	s	ν(C-C) ring
1570(sh)	6	1572	3					ν(C-C) ring
1485(br)	9	1490	8.5					ν(C-C) ring
1475(sh)	6	1475(sh)	2.5					
1475(sh)	6	1475(sh)	2.5					
1450(mtpt)	2	1450(mtpt)	1					ν(C-C) ring
1412(br)	3	1422	2					
1325(br)	0.5	1325	0.5					
1285	5	1285	3					
1260	4.5	1260	4	1256	w	1260	w	ν(Ph-C)
1250	6	1250	4					ν(Ph-N)
1228	4.5	1230	4					ν(Ph-N)
1200(br)	10	1202	10	1215	w-m	1212	w-m	ν(Ph-O)
1168	6	1165	3	1171	w	1176	w	β(C-H)
1152	4.5	1155(br)	1	1156	w			
1105(br)	2	1100(br)	1					X sens
1065(br)	6	1072	3					β(C-H)
1058(br)	2	1060(sh)	3					β(C-H)
		1050	4					ν(C-O)
1020(br)	2	1025	2	1027	w	1030	w	β(C-H)
998(br)	2	1000	1	1003	w-s	1006	w	ring mode p
935(br)	2	935(br)	1					
900	3							
882	6	880(br)	3	888	w			γ(C-H)
		855(br)	3					

Table 39 (continued)

Infrared				Raman				
solid		solution		solid		solution		Assignment
cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	
830(br)	4	835(br)	3					γ(C-H)
795	2	795(sh)	2					
780	7	785	5					
770	5			770	w			
765	7	765	5					
742	7	750	5					
725	4.5	732(br)	3	731	w			
705	2							
692	5	692	5					φ(C-C)
682	5	685	5					φ(C-C) ring mode 4
672	4	678	2					δ(skeletal and ring
550	0.5							
522	4.5							
505	1							
475	1							

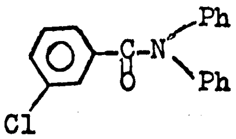


Table 40

N-m-chloro benzoyldiphenylamine

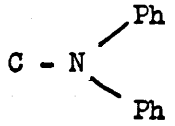
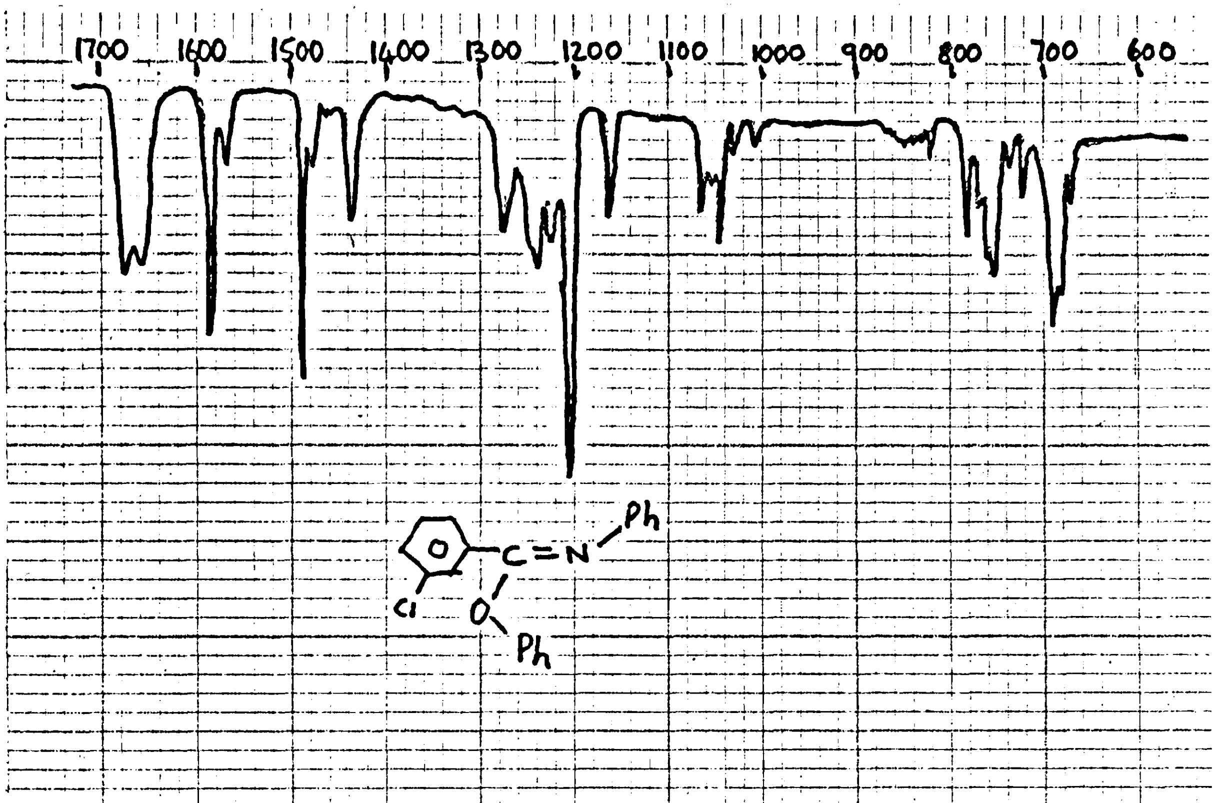
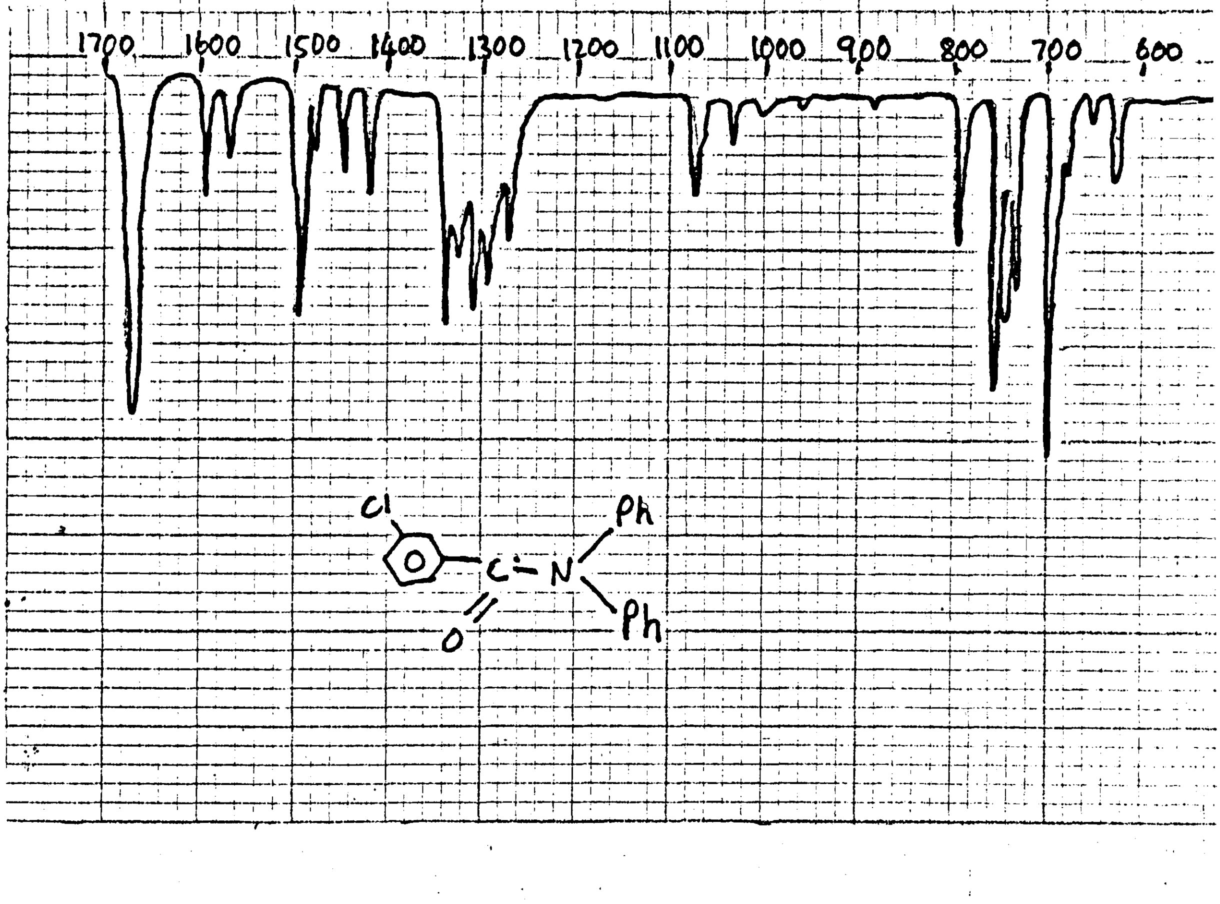
Infrared				
Disc.		Solution		Assignment
cm^{-1}	Intensity	cm^{-1}	Intensity	
3060	1	3065	2	ν(C-H)
3040(br)	1	3040	2	ν(C-H)
1650	10	1675	10	ν(C=N)
1590	5	1595	5	ν(C-C) ring
1570	4	1572	3.5	ν(C C) ring
1495(sh)		1500(sh)		
1490	7	1492	8	ν(C-C)ring
1480(sh)		1475	2	
1450	3	1453	2.5	ν(C-C)ring
1415(br)	2	1418	3	
1345	10	1338	8	skeletal involving 
1322	4	1324	7	
1308	6	1308	8	
1292	5	1292	7	
1270	5	1270	6	ν(Ph-C)
1215(br)	2	1212	1	
1175(br)	2			
1125	3	1120	2	β(C-H)
1092(br)	2			
1075	3	1078	3	β(C-H)
1030	2	1032	2	β(C-H)
1002	2	1000(br)	1	ring mode (p)
962	2	962	2	γ(C-H)
910	3			
905	2	892(br)	1	
868	2			
803	5	797	4	
762	7	758	8	
758	4			
738	7	742	6	
		735	6	
702	7			

Table 40 (continued)

Disc		Infrared Solution		Assignment
cm^{-1}	Intensity	cm^{-1}	Intensity	
695	6	699	9	Ø(C-C) ring mode (4)
685	4	680	2.5	Ø(C-C) ring mode (4)
655	3	655	1	δ(skeletal and ring)
630	3	628	2.5	
555	2			
525	1			
512	2			
460	1			
425	2			
365	2			


1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
Ph
C=N
Cl
O
Ph


1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
Cl
Ph
C–N
O
Ph

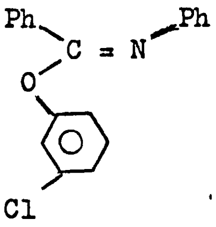


Table 41

N-Phenyl-m-chlorophenyl benzimidate

Infrared				Raman				
solid		solution		solid		solution		Assignment
cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	
3060(br)	1	3060	1					ν(C-H) aromatica
3020(br)	1	3025	1					ν(C-H) aromatic
1670	10	1675	7	1678	s			ν(C=N)
1655(sh)	9	1660(sh)				1662	s	ν(C=N)
1585(br)	9	1590	10	1604	m-s	1600	s	ν(C-C) ring
		1495	3			**1500**	**w**	**ν(C-C) ring**
		1488	4					
1470(br)	7	1475	8					
1448	6	1450	3.5					ν(C-C) ring
1428	5	1430	2.5					
1318	3	1315	1					
1300(sh)	3	1300	2					
1280	8	1285(sh)	3					β(C-H)
1270	9	1265(br)	6	1272	w	1276	w	ν(Ph-C)
1258	10			1262	w			ν(Ph-N)
1230	9			1233	w-m			ν(Ph-N)
1205	10	1208	10			1210	m	ν(Ph-O)
1185	4	1178	2.5			1176	m	β(C-H)
1160	4	1170	2.5					β(C-H)
1150	3							β(C-H)
1090(br)	8	1090	4					β(C-Hε
1065(br)	9	1072	5					β(C-H)
		1045	6					ν(C-O)
1025(br)	5	1025	6			1032	w	β(C-H)
1000	5	1000	1	1004	s	1006	s	ring mode (p)
968	3							γ(C-H)
920	8	920	2					
900	3							
880	8	880	2					
862	2	865(br)	2					
785	8							
778	9	778	6					

Table 41 (continued)

Infrared				**Raman**				
solid		solution		solid		solution		Assignment
cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	
762	8	768	5					γ(C-H)
		750	3					
730	4	725	1	730	w			
690	9	690	9					Ø(C-C) ring mode(4)
670	6	678	4					δ(skeletal and ring)
660	6							
570	3							
528	5							
475	1							
450	1							
420	1							

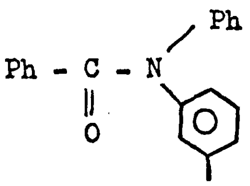


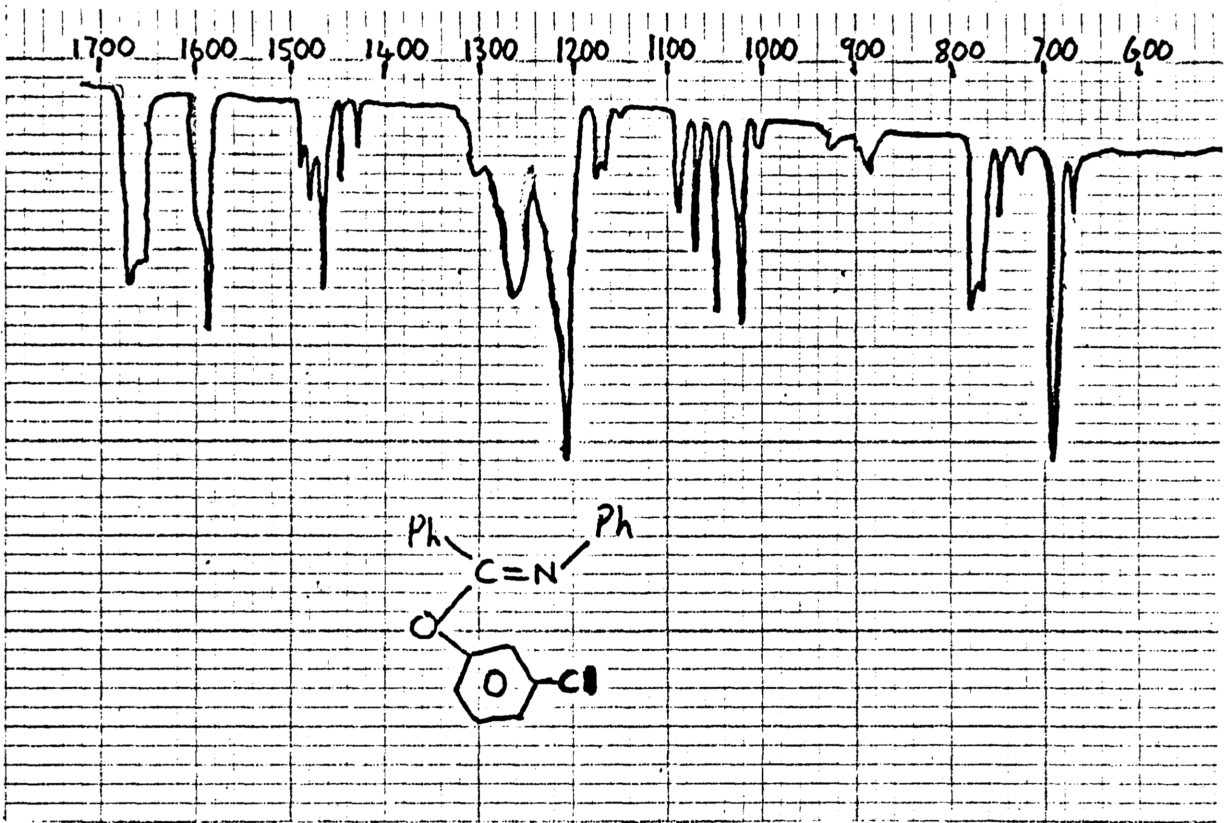
Table 42

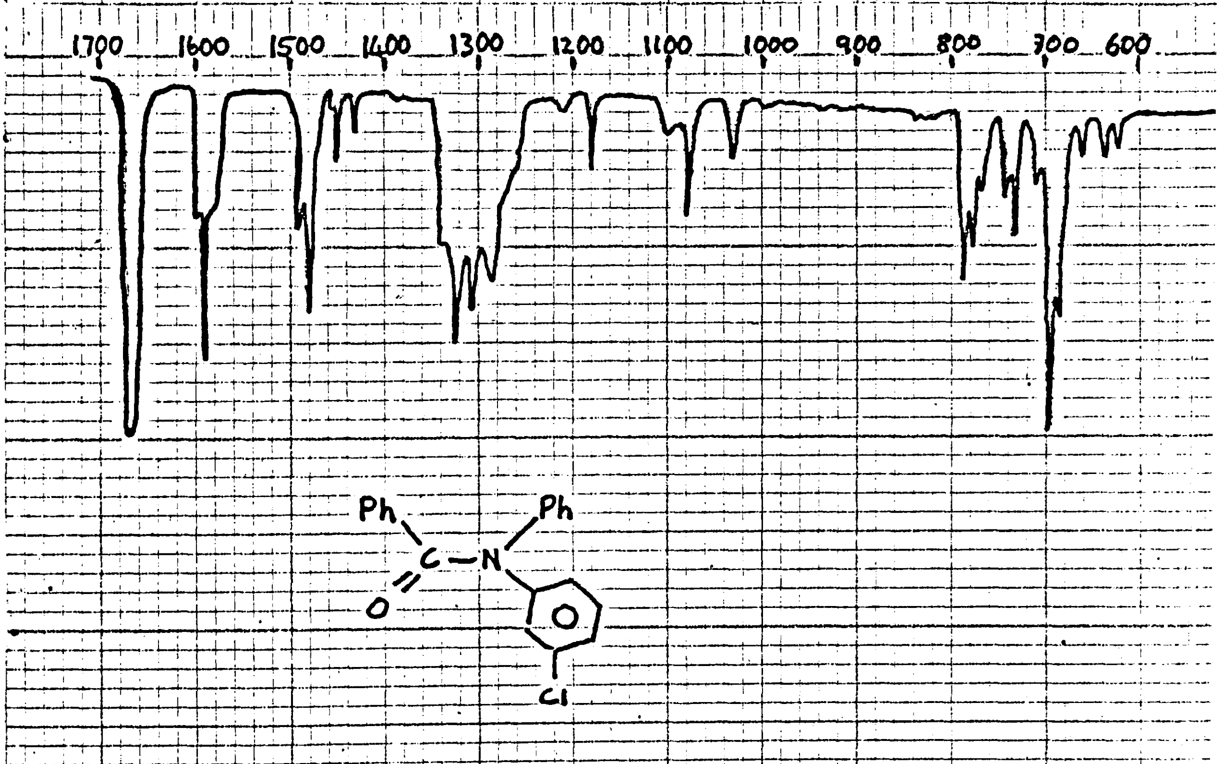
N-Benzoyl-m-chlorodiphenylamine

Infrared Disc cm^{-1}	Disc Intensity	Solution cm^{-1}	Solution Intensity	Assignment
3040(br)	1	3060	1	ν(C-H) aromatic
(3080-3020)		3030	1	ν(C-H) aromatic
1660	10	1675	10	ν(C=O)
1598	3	1599	4	ν(C-C) ring
1588	7	1592	7.5	
1580	5	1580	4	
1492	4.5	1492	4	ν(C-C) ring
1475	5.5	1478	6	ν(C-C) ring
1455	2	1455	1	ν(C-C) ring
1445	3.5	1450	2.5	ν(C-C) ring
1430	2.5	1430	2	
1325	8	1322	7.5	skeletal involving $(C-N{<}^{Ph}_{Ph})$
1315	8			
1309	7	1307	7	
1285(br)	7	1285(br)	6.5	skeletal ν(Ph-C)?
1265	4	1260	2	
1210(br)	2	1215	1	
1175	0.5	1180	2	β(C-H)
1165	0.5			
1110	2			
1090	1	1100(br)	1.5	β(C-H)
1080	2	1078	2.5	β(C-H)
1070	2			
1028	2	1030	2	β(C-H)
1000(br)	0.5	1000(br)	0.5	ring mode p
970	2			γ(C-H)
930	0.5			
920	0.5			
895	2			
882	3			
862	2			
792	7	790	5	

Table 42 (continued)

Infrared				
Disc		Solution		Assignment
cm^{-1}	Intensity	cm^{-1}	Intensity	
777	6	778	4	γ(C-H)
		770	2.5	
750	0.5			
		745	3	
738	4	738	4	
712	5	710	3	
705	7.5	700	10	
688	6	680	6	ϕ(C-C) ring mode (4)
680	3	680	3	ϕ(C-C) ring mode (4)
662	2	660	2	δ(skeletal and ring)
638	2	638	2	
620	2	618	2	


1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
Ph
Ph
C=N
O
O
Cl


1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
Ph
Ph
C
N
O
O
Cl

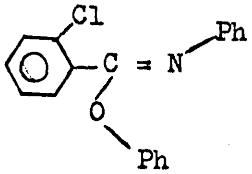


Table 43

N-Phenyl phenyl-o-chlorobenzimidate

Infrared				Raman				
solid		solution		solid		solution		Assignment
cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	
3060(br)	1	3060	1					ν(C-H) aromatic
3020(br)	1	3030	1					ν(C-H) aromatic
1668(br)	9	1680	7.5	1671	s	1680	m-s	ν(C=N)
1588(br)	8	1600	5	1597	s	1600	m	ν(C-C) ring
1580(sh)	5	1592	7					ν(C-C) ring
1570(sh)	3							
1560(sh)	2							
1487(br)	8	1490	8					ν(C-C) ring
1470(sh)	4							
1447(br)	4	1440	2.5					ν(C-C) ring
1305(sh)	4							
1290	9	1295	8	1294	w			ν(Ph-C)
1275	5	1280(sh)	4					β(C-H)
1240	7.5	1248	8	1250	w	1250	w	ν(Ph-N)
1230	7.5	1230(sh)	4	1238	w			
1190	10	1199	10					ν(Ph-O)
1160	7	1162	4	1176	w			β(C-H)
1155(sh)	5							
1105	7.5	1105(br)	3	1112	w			X sens
1070	4	1072	1.5					β(C-H)
1042	4	1048	4					ν(C-O)
1030	3	1030(sh)	1.5			1030	m	β(C-H)
1020	3	1025	2					β(C-H)
1000	2	1000	1	1002	s	1006	s	ring mode (p)
950	1	945	0.5					γ(C-H)
922	5	922	2					
900	2	900(br)						
830(br)	1	830	2					
777	8	778	2.5					

Table 43 (continued)

Infrared				**Raman**				
solid		solution		solid		solution		Assignment
cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	
		765	8.5	768	w			γ(C-H)
758	8	755	5					
740	6	740	6					
725	3	730	2					
705	3	705(sh)	2	710	w			
688	7	695	6					∅(C-C) ring mode(4)
675	2.5	688	4	680	w			∅(C-C) ring mode(4)
655	1	660	1					δ(skeletal and ring)
550	0.5							
532	1							
510	2							
490	1							
440	1							
430	1.5							

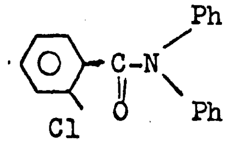


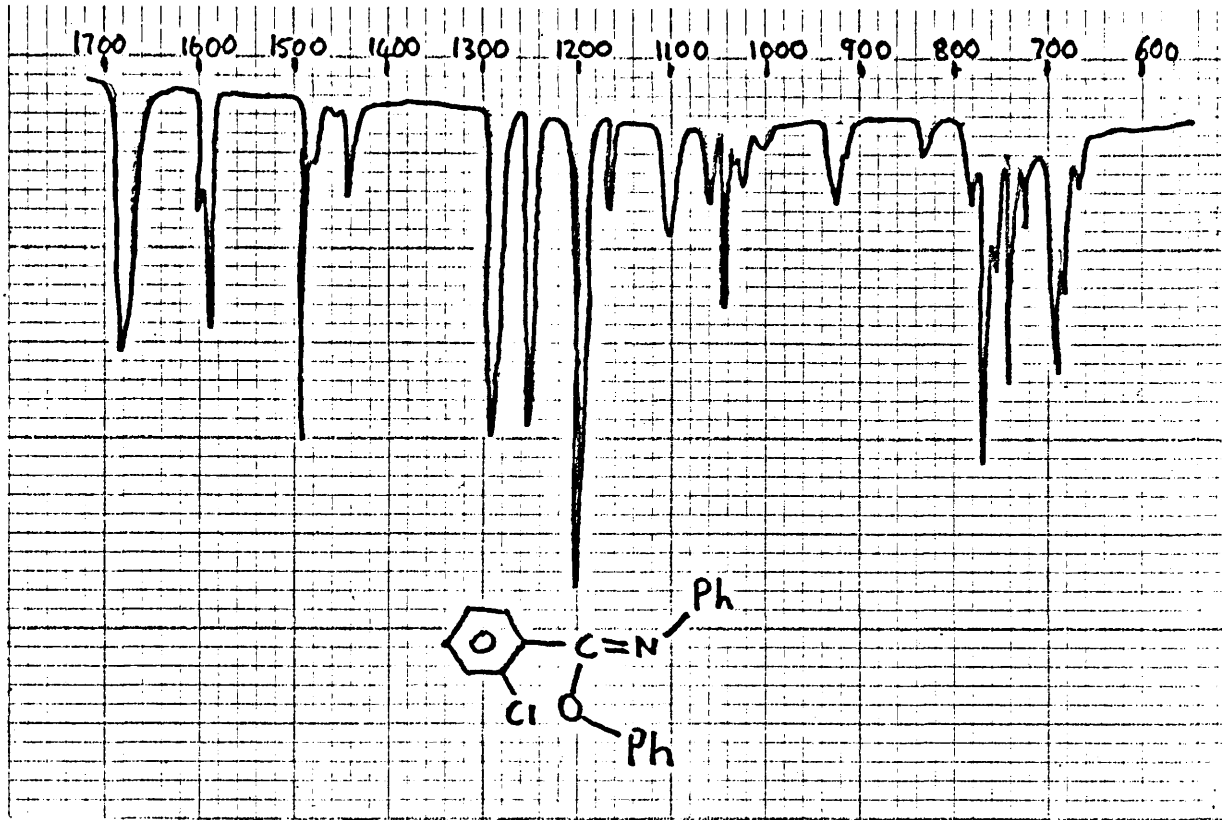
Table 44

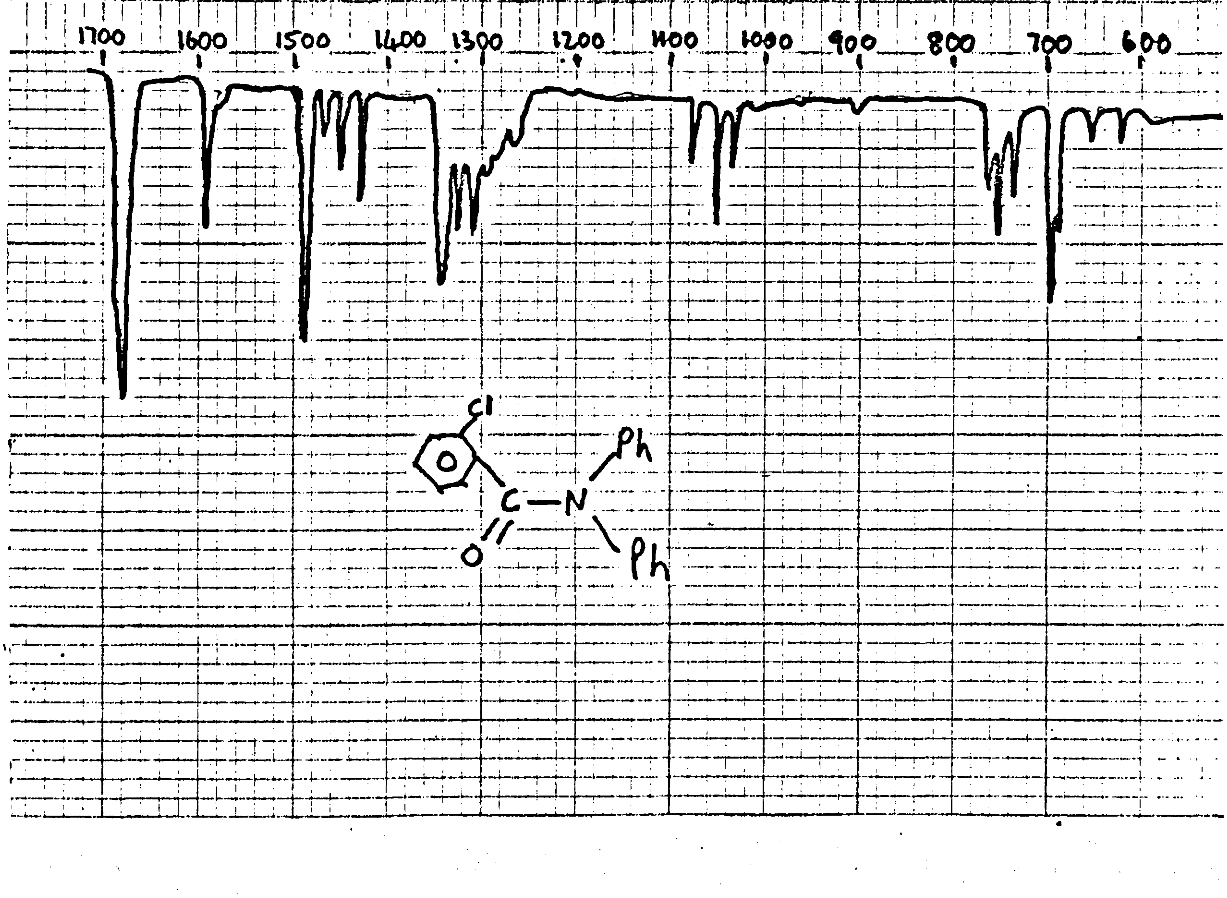
N-o-chlorobenzoyldiphenaline

		Infrared		
Disc.		Solution		Assignment
cm^{-1}	Intensity	cm^{-1}	Intensity	
3070	1	3070	1	ν(C-H)
3040	0.5	3040	1	ν(C-H)
3030	0.5	3030(sh)	0.5	ν(C-H)
1658	10	1678	10	ν(C=N)
1590	6	1595	5	ν(C-C) ring
1580(sh)	3			ν(C-C) ring
1570(sh)	2	1570(sh)	1	ν(C-C) ring
1560(sh)	1			ν(C-C) ring
1500(sh)	2.5	1500(sh)	2.5	ν(C-C) ring
1492	8	1492	9	ν(C-C) ring
1475	3	1475	2	ν(C-C) ring
1452	3	1452	2.5	ν(C-C) ring
1435	3	1435	3.5	
1345(br)	9.5	1343	8.5	skeletal involving (C - N$^{\diagup Ph}_{\diagdown Ph}$) β(C-H) and ν(Ph-C)
1325	6.5	1327	6.5	
1311	5.5	1310	6.5	
		1295	4	
1275(br)	4	1275(sh)	3	
		1260	3	
1210(br)	0.5	1210(br)	0.5	
1170(br)	0.5	1175(br)	0.5	β(C-H)
1157(br)	0.5	1160(br)	0.5	β(C-H)
1122	2.5	1115(br)	0.5	X sens
1075	2	1078	1.5	β(C-H)
1050	2.5	1055	2.5	β(C-H)(C-Cl involved in X sens mode).
1035(sh)	2	1038(sh)	2.0	β(C-H)
1030	2	1030	2.0	β(C-H)
1005	1	1000(br)	0.5	ring mode (p)
960	2	960(br)	0.5	γ(C-H)
955(sh)	2			
850(br)	0.5	850(br)	0.5	
830(br)	0.5			

Table 44 (continued)

Infrared				Assignment
Disc		Solution		
cm^{-1}	Intensity	cm^{-1}	Intensity	
770	6.5	768	5	γ(C-H)
760	6	757(br)	6	
750	6.5	740	5.5	
720	3	720(br)	0.5	
700	6.5	700	8.5	
692	6.5	695	8.5	Ø(C-C) ring mode (4)
650	2	650	2.4	δ(skeletal and ring)
622	5	620	4	
550	0.5			
520	1			
470	1			
460(sh)	1			


1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
Ph
C=N
Cl
O
Ph


1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
Cl
Ph
C—N
O
Ph

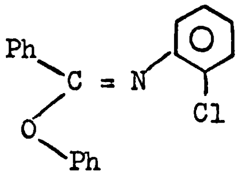


Table 45

N-o-Chlorophenyl phenyl benzimidate

Infrared				Raman				
solid		solution		solid		solution		
cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	Assignment
3060(br)	0.5	3060	1.5					ν(C-H) aromatic
		3040	1					ν(C-H) aromatic
3030(br)	0.5	3030	1					ν(C-H) aromatic
		1678	9	1675	s			ν(C=N)
1670(br)	10	1665(sh)	7	1672	s	1664	s	ν(C=N)
		1655(sh)	6					ν(C=N)
				1604	m	1606	m	ν(C-C) ring
1590(br)	5	1590	6	1593	s	1590	s	ν(C-C) ring
1490	6	1490	6			1500	w	ν(C-C) ring
1470	3	1470	4.5					
1455	1	1455	1					
1448	2.5	1448	3					ν(C-C) ring
1440	2.5	1440	2					
						1404	w-m	
1318	1	1318	1.5					ν(C-C) ring
1278	9	1285	5.5	) 1288	m	1280	m	β(C-H)
		1275	5.5	)				
1258	6	1260	6			1258	w-m	ν(Ph-C)
1240	4	1235	4.5					ν(Ph-N)
1215	1	1218	7			1222	w-m	
1198	10	1200	10					ν(Ph-O)
		1178	3			1180	w	β(C-H)
1162	3	1162	3	1160	w	1162	w	β(C-H)
1090	6	1088	3	1090	w	1090	w	β(C-H)
		1075	3					β(C-H)
1068(br)	2.5	1065	3.5					β(C-H)
1055	3	1048	4.5					β(C-O)
1030(br)	2	1030(sh)	2.5	1037	m	1036	m	β(C-H)
1022(br)	2	1025	4					β(C-H)
1000(br)	1	1000(br)	1	1000	s	1006	s	ring mode (p)

Table 45 (continued)

Infrared				Raman				
solid		solution		solid		solution		Assignment
cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	
922	2.5	925	1					γ(C-H)
890	1							
820(br)	0.5							
770	6.5	770	6					
		765(sh)	5					
		750	7					
		740	4.5					
735	1	735	4					
722	2	725	3					
		720	2.5					
698	6.5			696	w			Ø(C-C) ring mode(4)
690	7.5	690	7					Ø(C-C) ring mode(4)
550	1							δ(skeletal and ring)
542	1							
465	1							
455	1							
410(br)	1							

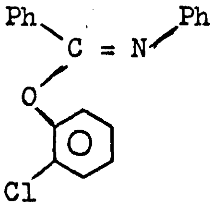


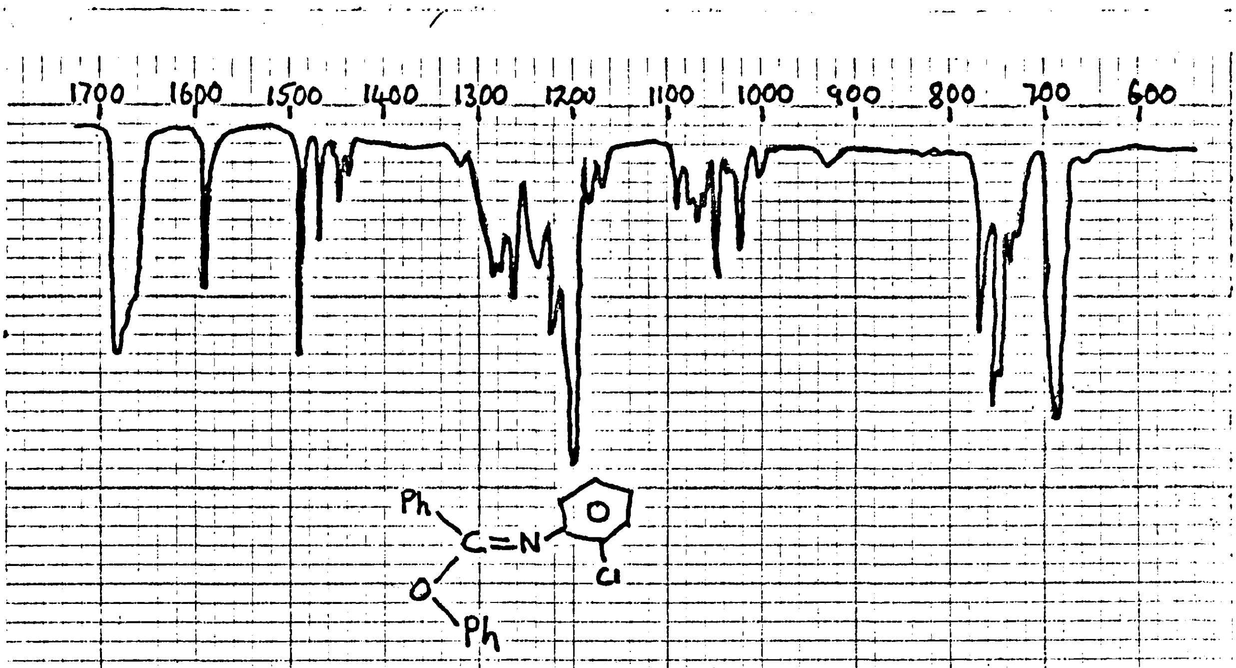
Table 46

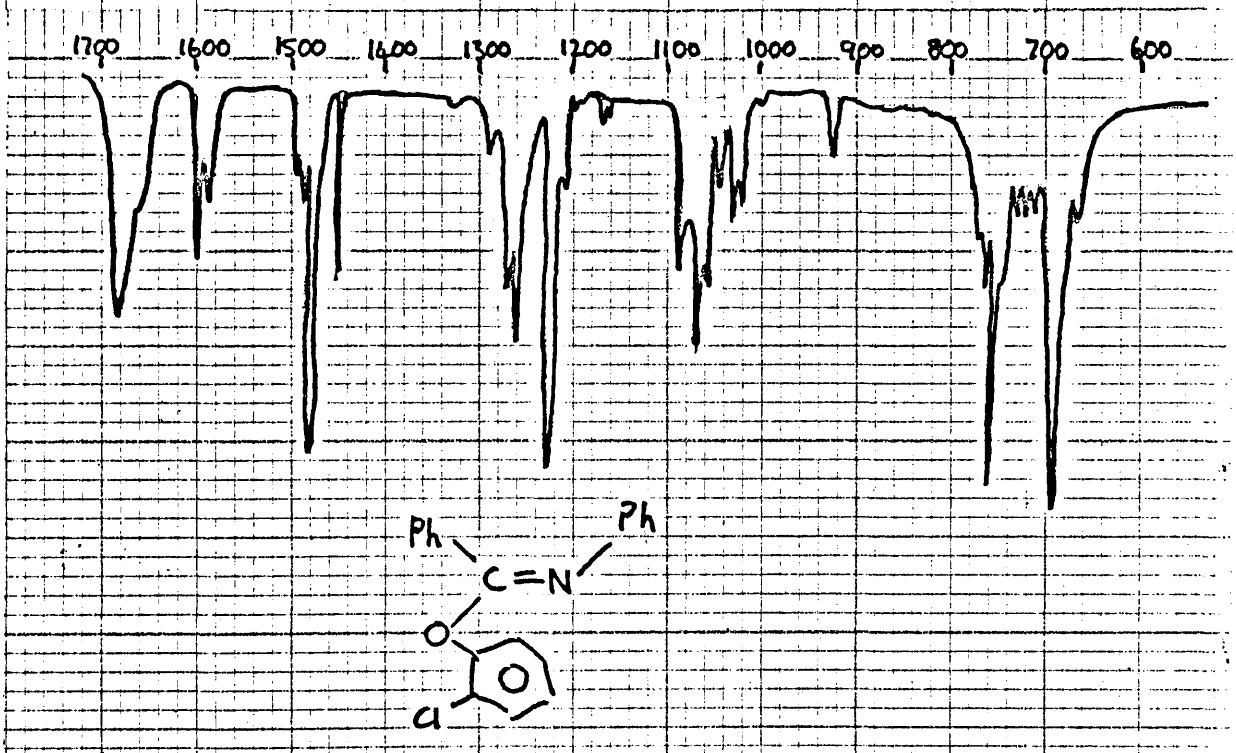
N-Phenyl-o-chlorophenyl benzimidate

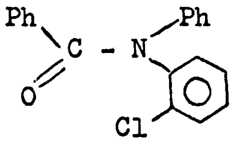
Infrared				Raman				
solid		solution		solid		solution		Assignment
cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	
3060	1	3070	2					ν(C-H) aromatic
3020	1	3030	1					ν(C-H) aromatic
1665	10	1678	7.5	1669	s	1666	s	ν(C=N)
1598	7	1600	5	1598	m	1602	s	ν(C-C) ring
1585(br)	6	1587	4					ν(C-C) ring
		1498	3.5					ν(C-C) ring
1488	6	1488	4					ν(C-C) ring
1448	7	1450	5.5					ν(C-C) ring
1315	3	1318(br)	1					
1300(br)	3	1300(br)	1.5					
1285	7	1285	4	1292	w			β(C-H)
1270	7.5	1270	6	1274	w	1276	w	ν(Ph-C)
1250(sh)	6							
1225	10	1228	10	1230	w-m	1232	w	ν(Ph-N)
1211	10	1205	4			1212	w	ν(Ph-O)
1172	4	1175(br)	1.5	1175	w	1176	w	β(C-H)
1160	2.5			1156	w	1160	w	β(C-H)
1122	1							X sens
1080	8	1085	5	1090	w			β(C-H)
1065	8	1070	6					β(C-H)
1058	7	1060	5.5					X sens
		1047	3					ν(C-O)
		1030	3.5	1028	w	1032	w-m	β(C-H)
1022	5	1020	3					β(C-H)
1000	1	1000	0.5	1006	m-s	1006	s	ring mode (p)
945	3	938	1.5					)
905	4.5							)
895	3							)
								)
860	2							)γ(C-H)
840	1							)
								)
778	5	775	4					)

Table 46 (continued)

Infrared				Raman				
solid		solution		solid		solution		
cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	cm^{-1}	I	Assignment
768	9	768	5	765	w			γ(C-H)
762	9	760	9.5					
		750	4.5	744	w			
732	6	735	2.5					
710	5	715	2.5					
690	9	690	10	681	w			Ø(C-C) ring mode(4)
675	6	670	2.5	665	w			δ(skeletal and ring)
660	3							
535	3							
520	0.5							
495	2							
480	0.5							
450	0.5							
415	2							


1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
Ph
C=N
O
Ph
Cl


1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
Ph
C=N
Ph
O
Cl



(probably a diasteriomeric mixture)

Table 47

N-Benzoyl-o-chlorodiphenylamine

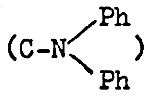
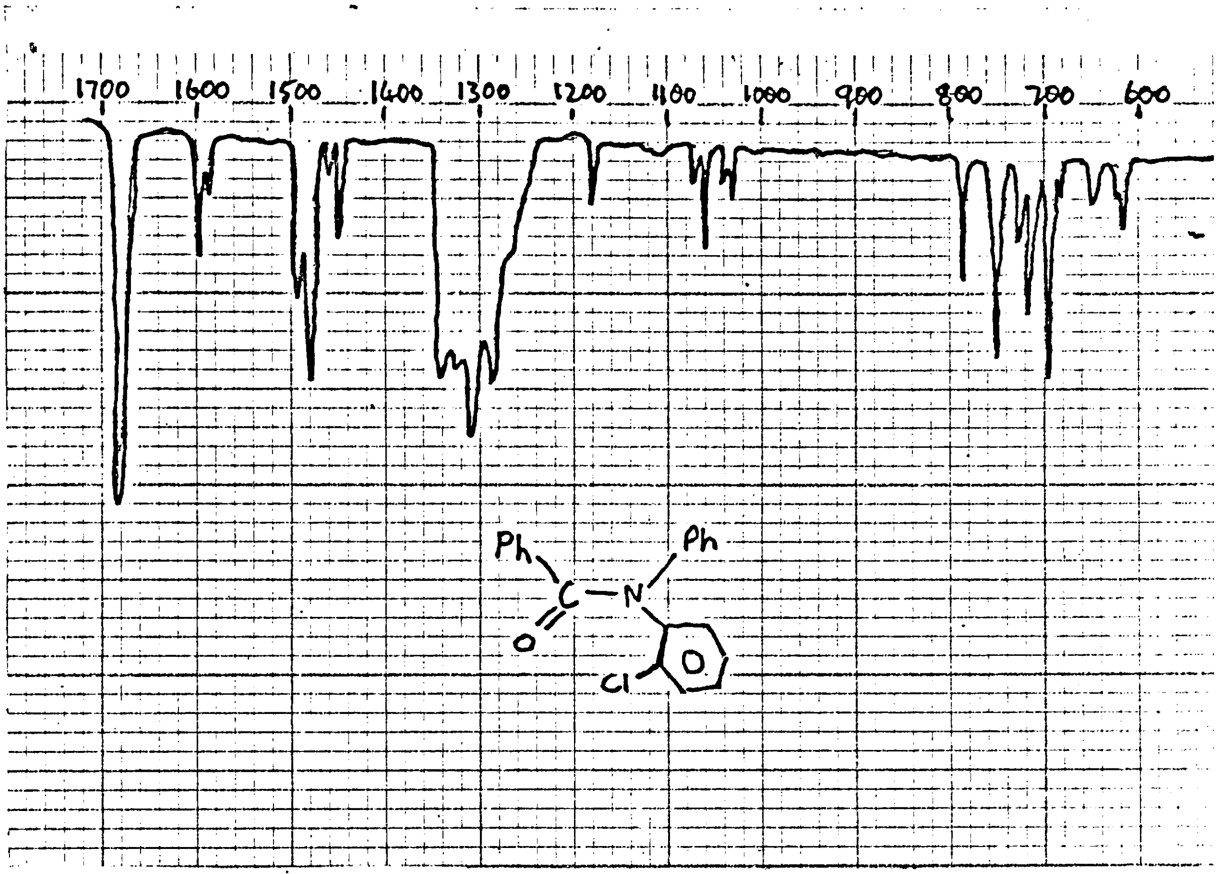
Infrared				
solid		solution		Assignment
cm^{-1}	I	cm^{-1}	I	
3060	1	3060	1.5	ν(C-H) aromatic
3040	0.5	3040	1.0	ν(C-H) aromatic
1670	10	1678	10	ν(C=N)
1657	9.5			ν(C=N)
1592	5	1599	3	ν(C-C) ring
1490	5	1495	5	ν(C-C) ring
1477	5.5	1480	6.5	ν(C-C) ring
1455	2.5	1455	1	ν(C-C) ring
1440(br)(sh)	2	1449	3.5	ν(C-C)
1338	9.5	1338	6	skeletal involving  $(\mathrm{C{-}N}\langle^{\mathrm{Ph}}_{\mathrm{Ph}})$ β(C-H) and ν(Ph-C)
		1320(sh)		
1308	7	1308	7	
1290	7	1290	6	
1265(sh)	1	1268(sh)	1	
1215(br)	0.5	1220(br)	0.5	
1178	1	1180	1.5	β(C-H)
1160	0.5			
1110(br)	0.5	1105	1	
1075	1	1075	1.5	β(C-H)
1060	1.5	1062	2.5	β(C-H)
		1035(sh)	1.0	β(C-H)
1025(br)	1	1030	1.5	β(C-H)
1000(br)	0.5	1000(br)	0.5	ring mode (p)
960(br)	0.5	960(br)	0.5	γ(C-H)
865(br)	0.5	865(br)	0.5	
850(br)	0.5	850(br)	0.5	
790	2.5			
782	2.5			

Table 47 (continued)

Infrared				
solid		solution		
cm^{-1}	I	cm^{-1}	I	Assignment
762	7			γ(C-H)
760	7			
735(sh)	2.5	732	3	
730	2.5	728	3	
710	5	710	5	
695	5	698	7	∅(C-C) ring mode(4)
655	2.5	658	2	δ(skeletal and ring)
620	2.5	625	2.5	
		619	2.5	
500	1			
460	1			


1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
Ph
C
O
N
Ph
Cl

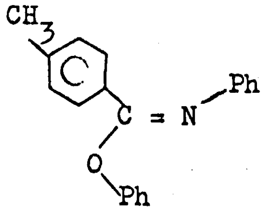


Table 48

N-Phenyl phenyl-p-toluimidate

Infrared

solid		solution		Assignment
cm^{-1}	Intensity	cm^{-1}	Intensity	
3070	1	3070	1	ν(C-H) aromatic
3035	1	3035	1	ν(C-H) aromatic
2975(v.br)	1	2975(v.br)	1	ν(C-H) aliphatic
1655	10	1670)	7	ν(C=N)
		1655)	6.5	
1610	5	1612	2	ν(C-C) ring
1595) 1589)	7.5	1592	7	ν(C-C) ring
1580(sh)	5	1580(sh)	2	ν(C-C) ring
1510	2.5	1510	2	ν(C-C) ring
1485	8	1490	7.5	ν(C-C) ring
1450	3.5	1450	1	ν(C-C) ring
1400	2	1410	0.5	
1311	3.5	1310(sh)	1	ν(C-C) ring
1295	3.5			
1285	6	1285(sh)	3	β(C-H)
1268	9.5	1268	4.5	ν(Ph-C)
1245(sh)	6			
1230	9.5	1230	4.5	ν(Ph-N)
1211	8.0			
1195	10	1205	10	ν(Ph-O)
1185	9.5	1185	3	β(C-H)
		1178	5.5	β(C-H)
1160	7	1168	3	β(C-H)
1120	1			
1082	9.5	1081	4	β(C-H)
1070	6	1072	3	β(C-H)
1055	3	1048	5	ν(C-O)
1038	1.5	1035(sh)	2	β(C-H)
1020	4	1018	3	β(C-H)
1001	3	1000(br)	0.5	ring mode (p)

Table 48 (continued)

Infrared				
solid		solution		
cm^{-1}	Intensity	cm^{-1}	Intensity	Assignment
928	5	920(br)	1	γ(C-H)
900	1			
842	3	840	1.0	
828	2	830	1.0	
810	4			
800	3	800	2	
765	10	765	6	
720	5	725	1.5	
700	7	695	6	ϕ(C-C)
690	7	690	6	ϕ(C-C) ring mode (4)
670	3			δ(skeletal and ring)
640	2			
540	3			
520	4			
440	3			

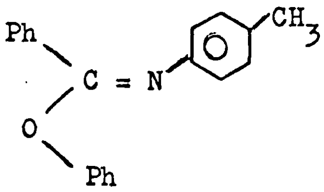


Table 49

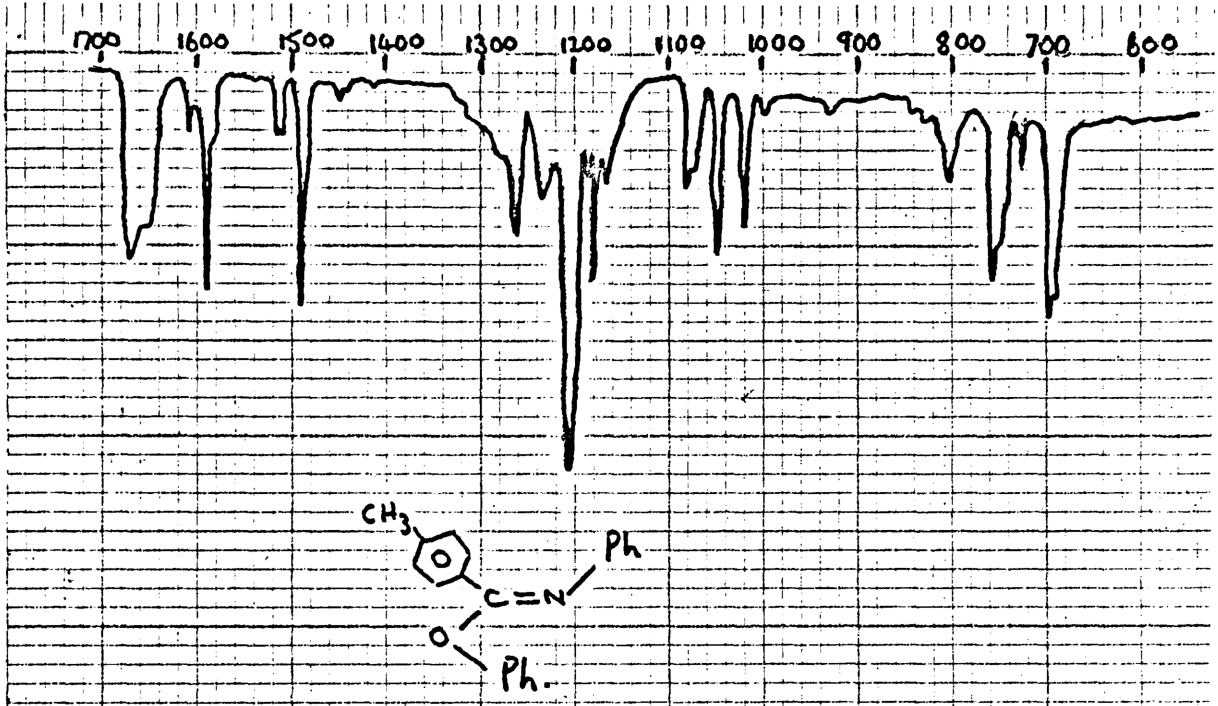
N-p-tolyl phenyl benzimidate

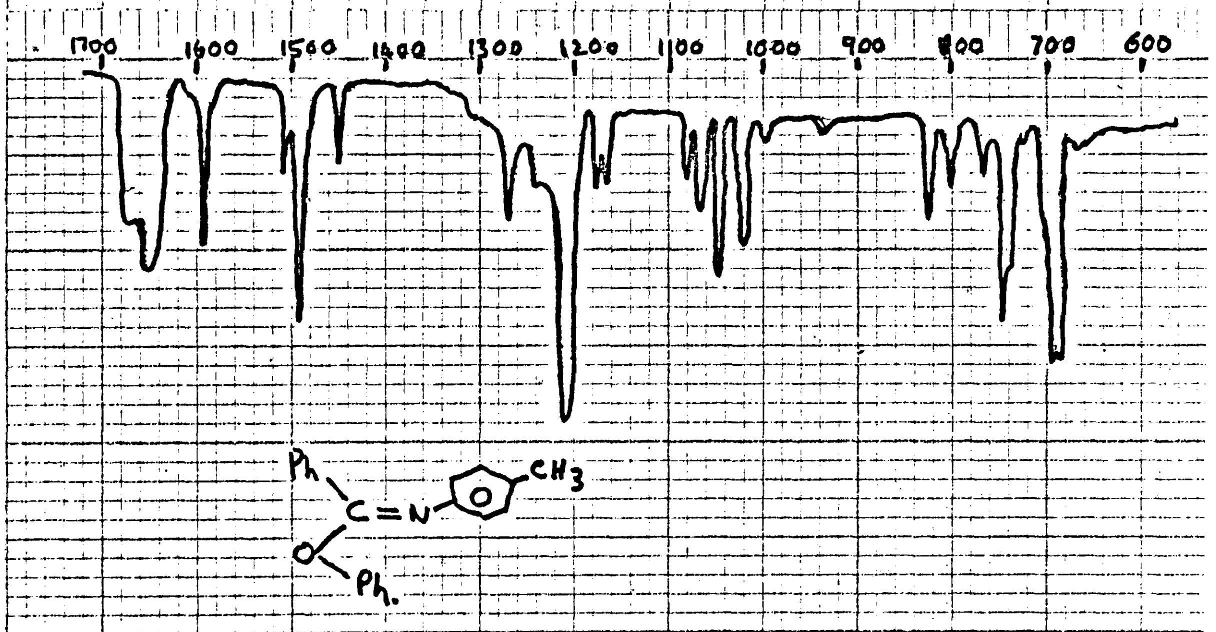
Infrared

Disc		Solution		Assignment
cm^{-1}	Intensity	cm^{-1}	Intensity	
3080	1	3060	1.5	ν(C-H) aromatic
3020	1	3025	1.5	ν(C-H) aromatic
2920	1	2920	1.5	ν(C-H) aliphatic
2875(br)	0.5	2880		ν(C-H) aliphatic
1645(br)	8.5	1670(br)	6	ν(C=N)
		1655(br)	7	ν(C=N)
1590	7.5	1592	6.5	ν(C-C) ring
1580	6.5	1580(br)(sh)	1.5	ν(C-C) ring
1500	5.5	1505	4.5	ν(C-C) ring
1488(br)	7	1490	7.5	ν(C-C) ring
1450	4.5	1450	3.5	ν(C-C) ring
1315	1.0	1315	1.5	ν(C-C) ring
1269	6	1268	5	ν(Ph-C)
1238	2	1229	4.5	ν(Ph-N)
1205	10	1205	10	ν(Ph-O)
1172	9	1175	4	β(C-H)
1165	9	1168	4	β(C-H)
		1085	2	β(C-H)
1075	2.5	1072	3	β(C-H)
1040	7.5	1048	5	ν(C-O)
1020	6.5	1025	4	β(C-H)
1015	6.0	1020(sh)	3	β(C-H)
1000	2	1000	1	ring mode (p)
932	0.5	930	1	γ(C-H)
890	1	885	0.5	
875	3	870	0.5	
840	0.5	835(br)	2.5	
830	1.5			
820	4.5	817	3.5	
800	6	805	3	
		768	2.5	

Table 49 (continued)

Infrared				
Disc.		Solution		
cm^{-1}	Intensity	cm^{-1}	Intensity	Assignment
755	8	755	6	γ(C-H)
748	9	748	5	
710	5.5	705(sh)	3.5	
685	5.5	695	6	∅(C-C) ring mode (4)
		690	6	
650	1			δ(skeletal and ring)
532	3			
512	2			
495	2			
440	1			
420	1			
400	1			
360	2			


1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
CH3
C=N
Ph
O
Ph.


1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
Ph
C=N
CH3
O
Ph.

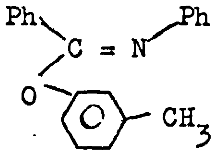


Table 50

N-Phenyl-p-tolyl benzimidate

Infrared				
Disc		Solution		Assignment
cm^{-1}	Intensity	cm^{-1}	Intensity	
3080	1			ν(C-H) aromatic
3050	2	3060	1.5	ν(C-H) aromatic
3035	2	3035	1.5	ν(C-H) aromatic
2975	1	2980	1	ν(C-H) aliphatic
2920	1	2920	1	ν(C-H) aliphatic
1660(br)	10	1670	7	ν(C=N)
		1655	6	ν(C=N)
1610	3	1610	2	ν(C-C) ring
1595	8	1598	5	ν(C-C) ring
1580	3.5	1580(sh)	2	ν(C-C) ring
1505	7.5	1508	7	ν(C-C) ring
1495	7.5	1495	4	ν(C-C) ring
1487	7.5	1485	3	$\delta_{as}(CH_3)$
1450	7	1450	3.5	ν(C-C) ring
1380	1	1380	0.5	$\delta_s(CH_3)$
1320	2.5	1300(sh)	2	ν(C-C) ring
1285	7.5	1287	3.5	β(C-H)
1262	10	1270	5.5	ν(Ph-C)
1238	9.5	1232	4.5	ν(Ph-N)
		1215(sh)	8	
1200	10	1205	10	ν(Ph-O)
1185	6			β(C-H)
1175	4	1170	4.5	β(C-H)
1162	7	1167	4	β(C-H)
1100	2			
1090	8	1089	3	β(C-H)
1075(mtpt)	7.5	1070	3	β(C-H)
		1050	5	ν(C-O)
1025	5	1028(sh)	3.5	β(C-H)
1020	4	1022	4.5	β(C-H)
1000	1	1000	0.5	ring mode (p)

Table 50 (continued)

Infrared					
Disc		Solution			
cm^{-1}	Intensity	cm^{-1}	Intensity		Assignment
940	1	935	0.5	)	γ(C-H)
908	3			)	
815	10	815	3	)	
		805	2	)	
785	8	782	2	)	
765	8	765	3	)	
750	2	755	4	)	
730	8	735	3		
698	10	700 **(sh)**	3		Ø(C-C) ring mode (4)
692	10	692	10		Ø(C-C) ring mode (4)
672	2			)	δ(skeletal and ring)
660	2			)	
578	2			)	
535	3			)	
515	2			)	
470	3			)	
428	2			)	

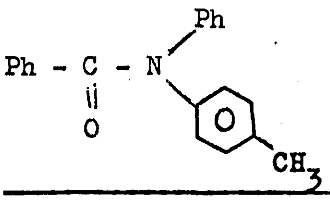


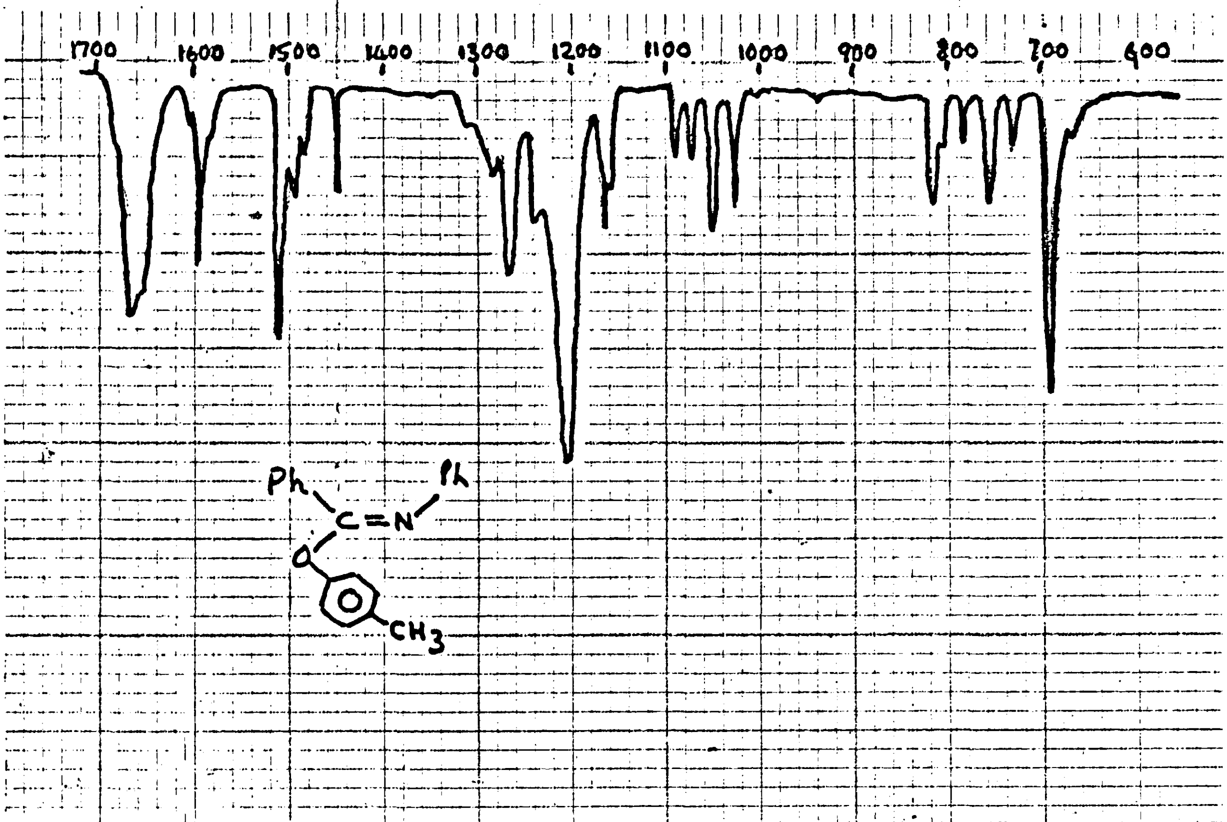
Table 51

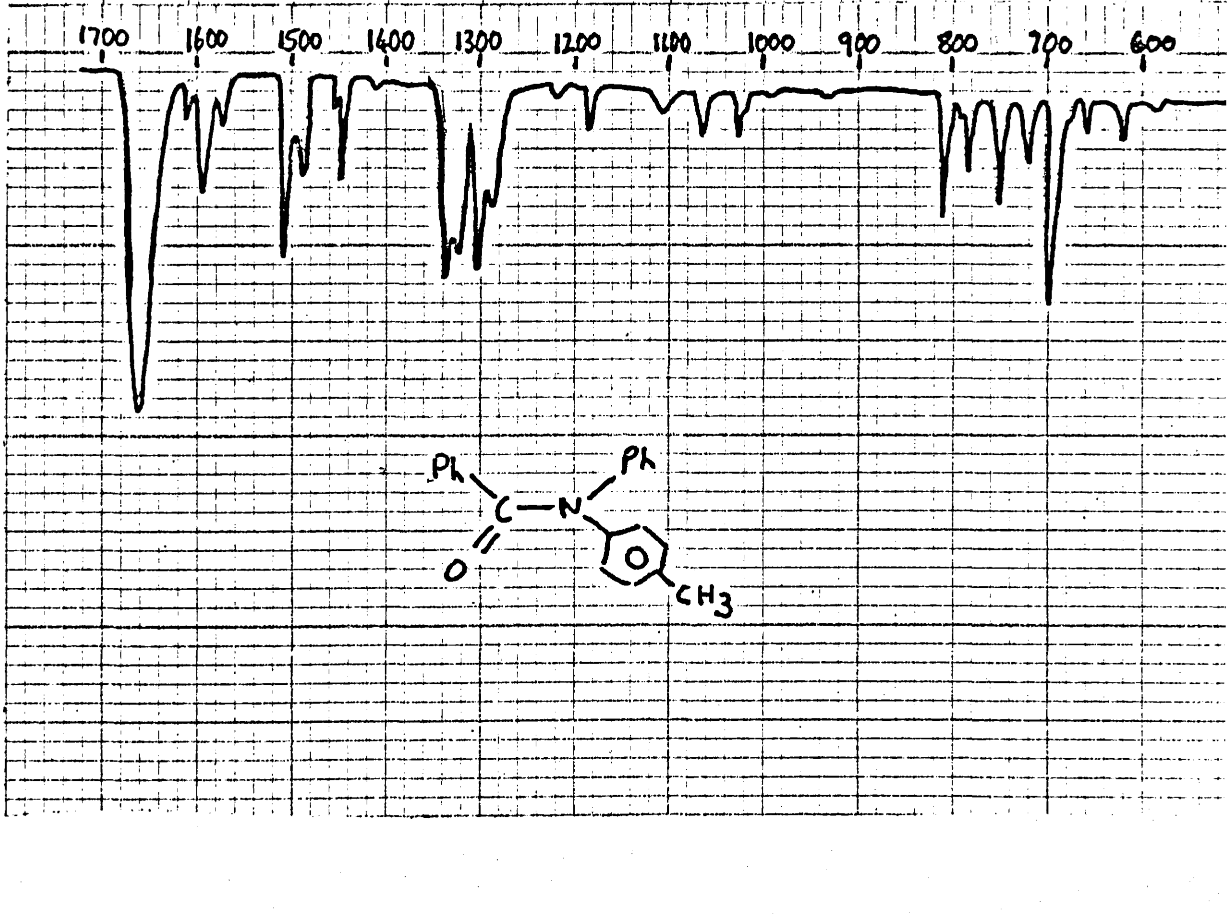
N-Benzoyl phenyl-p-tolylamine

Infrared				
solid		solution		
cm^{-1}	Intensity	cm^{-1}	Intensity	Assignment
3050(br)	1.5	3060	1	ν(C-H) aromatic
3030(br)	1.5	3030	1	ν(C-H) aromatic
2920	< 0.5	2920	0.5	ν(C-H) aliphatic
1655(br)	10	1668	10	ν(C=O)
1592	5	1598	2.5	ν(C-C) ring
1580	4	1580	1.5	ν(C-C) ring
1510	6	1510	7.5	ν(C-C) ring
1490	6	1495	3.5	ν(C-C) ring
1450	5	1450	2.5	ν(C-C) ring
1340(br)	9	1335	8	skeletal (involving $(\mathrm{C{-}N}\langle^{\mathrm{Ph}}_{\mathrm{Ph}})$ β(C-H) and ν(Ph-C)
1322	8	1322	7.5	
1301	9	1301	7.5	
1290(br)(sh)	8	1289	6.5	
1182	2.5	1180	2	β(C-H)
1175	2.5			β(C-H)
1110	2.5			
1075	2.5	1075	1	β(C-H)
1028	2.5	1028	1	β(C-H)
1005	0.5	1005(br)	r	ring mode (p)
960	1	970(br)	0.5	γ(C-H)
928	0.5			
860	0.5			
830	1.0			
812	5.5	812	4	
789	6	782	2	
758	7	752	4.5	
725	7			
718	5	718	4	
705	7.5			

Table 51 (continued)

Infrared				
solid		solution		Assignment
cm^{-1}	Intensity	cm^{-1}	Intensity	
695	8	698	8	φ(C-C) ring mode (4)
658	3	658	1	δ(skeletal and ring)
625	5.5	620	2	
585	2			
525	2			
512	3			
455	< 0.5			
425	< 0.5			
380				


1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
Ph
Ph
C=N
O
CH3


1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
Ph
Ph
C—N
O
CH3

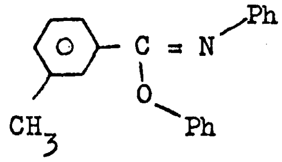


Table 52

N-Phenyl phenyl-m-toluimidate

Infrared				
Disc.		Solution		
cm^{-1}	Intensity	cm^{-1}	Intensity	Assignment
3090-3000(br)	0.5	3070	1	ν(C-H) aromatic
		3030	1	ν(C-H) aromatic
2920	0.5	2920	0.5	ν(C-H) aliphatic
2960	0.5	2960	0.5	ν(C-H) aliphatic
1657	10	1670	6	ν(C=N)
		1655	5.5	
1605(sh)	4	1595(sh)	6.5	ν(C-C) ring
1590	9	1592	7	ν(C-C) ring
1580(sh)	5	1580(sh)	2	ν(C-C) ring
1490	9	1490	8	ν(C-C) ring
1455	3	1455	1	ν(C-C) ring
1450	2.5	1450	1.5	ν(C-C) ring
1315(br)(sh)	1	1315(sh)	1	ν(C-C) ring
		1295	3	β(C-H)
1285	6	1285	3.5	β(C-H)
		1274	4	ν(Ph-C)
1235	2	1235	2.5	ν(Ph-N)
1210	9.5	1205	10	ν(Ph-O)
1188	8.5	1188	5	β(C-H)
1172	6	1180	4.5	
		1168	4	
1155	0.5	1155	0.5	
1088	1			
1075	2.5	1070	3	β(C-H)
1052	7	1050	3	ν(C-O)
1025	1	1025	1	β(C-H)
1000	1	1000	0.5	ring mode (p)
920	1	930	0.5	γ(C-H)
899	2	890	1	
855	3	850(br)	0.5	
790	4	790	3	
780	3			

Table 52 (continued)

Infrared				
Disc.		Solution		Assignment
cm^{-1}	Intensity	cm^{-1}	Intensity	
750	9	760) 755)	5	)
710	3.5	715	2.5	) γ(C-H)
695	3	695	5	φ(C-C)
690	3.5	690	5	φ(C-C) ring mode (4)
685	3			)
668	1			)
572	0.5			)
538	0.5			) δ(skeletal and ring)
510	0.5			)
468	0.5			)
420	1			)

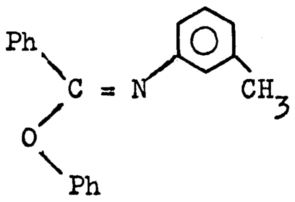


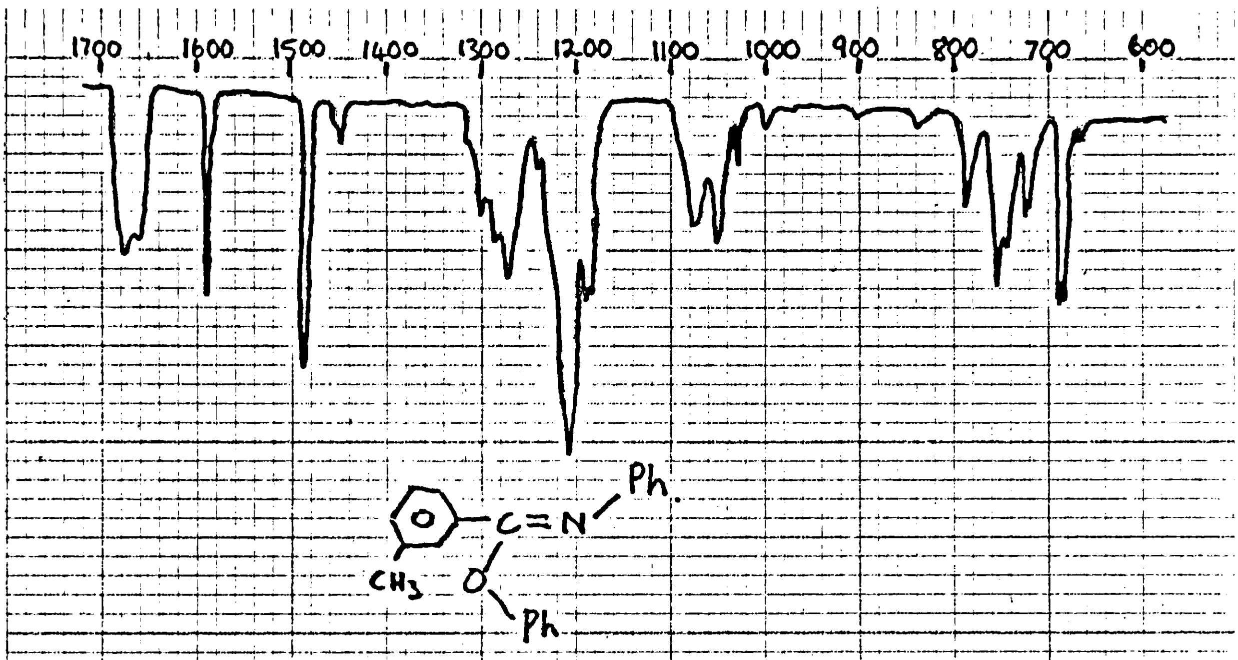
Table 53

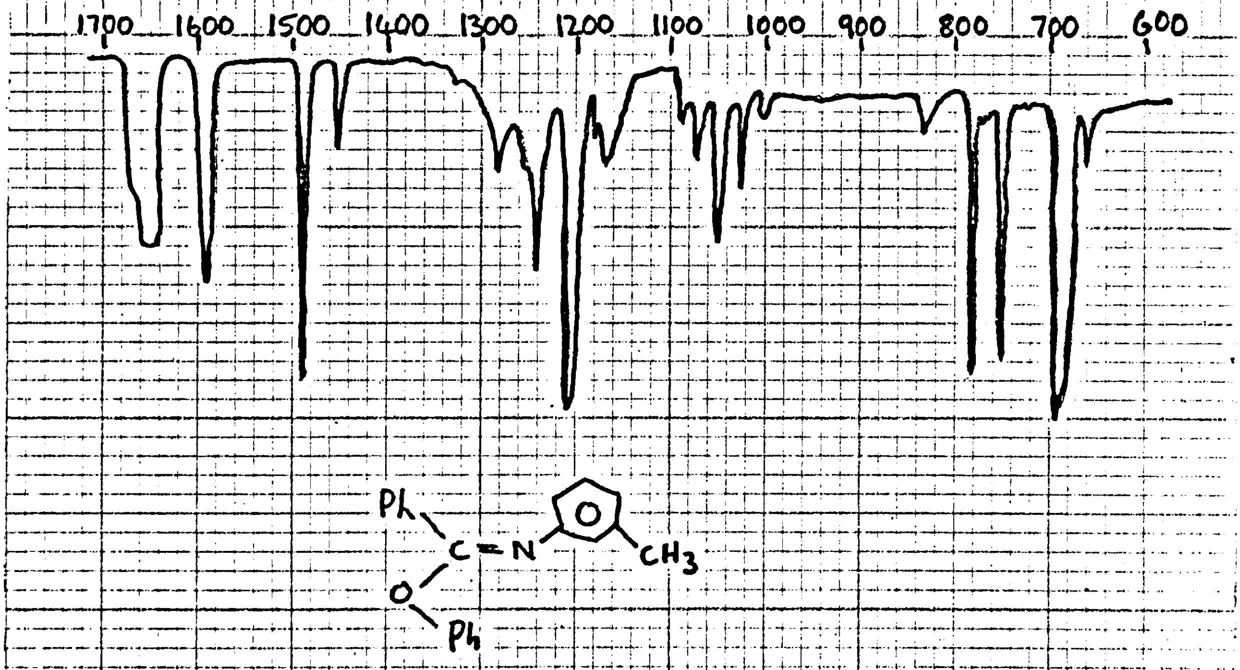
N-m-tolyl phenyl benzimidate

Infrared				
Disc		Solution		
cm^{-1}	I	cm^{-1}	I	Assignment
3060	0.5	3060	1	ν(C-H) aromatic
3020	0.5	3030	1	ν(C-H) aromatic
2920	0.5	2920	0.5	ν(C-H) aliphatic
1660(br)	9	1670(br)	6	ν(C=N)
1590	7	1592	6	ν(C-C) ring
1580	6.5	1585	4	ν(C-C) ring
1488(br)	6.5	1490	7.5	ν(C-C) ring
1448	4.5	1450	2.5	ν(C-C) ring
1315	1	1315	0.5	ν(C-C) ring
1274	7.5	1280	3.5	ν(Ph-C)
1240(br)	9	1240(br)	6	ν(Ph-N)
1205	10	1208	10	ν(Ph-O)
1182	4.5	1185	2	β(C-H)
1165	3	1165	3	β(C-H)
1155	2.5	1155	2.5	
1082(sh)	5	1085	1.5	β(C-H)
1070(br)	7	1072	3	β(C-H)
		1050	4.5	ν(C-O)
1020	2.5	1025	3.5	β(C-H)
1000	2	1000	1	ring mode (p)
950	1	950	0.5	γ(C-H)
925	1	925	0.5	
885	1	885	0.5	
865	1			
835	1	825	1.5	
832	3			
825(sh)	2			
788	6.5	780	6.5	
770	5	765	2.5	
755	5	750	6	
715	1	715	0.5	

Table 53 (continued)

Infrared					
Disc		Solution			
cm^{-1}	I	cm^{-1}	I		Assignment
690	8	692	8		Ø(C-C) ring mode(4)
670	1.5	670	2.5	)	
660	1.5			)	
540	1			)	
520	0.5			)	
505	0.5			)	
450	1			)	δ(skeletal and ring)
425	0.5			)	


1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
Ph
C=N
CH₃
O
Ph


1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
Ph
C=N
CH₃
O
Ph

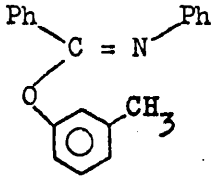


Table 54

N-Phenyl-m-tolyl benzimidate

Infrared				
Disc		Solution		
cm^{-1}	I	cm^{-1}	I	Assignment
3060	1	3060	1	ν(C-H) aromatic
3030	1	3030	1	ν(C-H) aromati
2920	1	2920	1	ν(C-H) aliphatic
1670(br)	9	1665(br)	7	ν(C=N)
1605	3	1610	3	ν(C-C) ring
1595	5	1598	5	ν(C-C) ring
1585	5.5	1585	6	ν(C-C) ring
1490(sh)	4.5	1490(sh)	4	ν(C-C) ring
1485	6.5	1485	6	ν(C-C) ring
1445	5	1448	6	ν(C-C) ring
1318	2	1313	1	ν(C-C) ring
1302	2.5	1300	1	
1280	6.5	1282	3	β(C-H)
1268	8.5	1265	5	ν(Ph-C)
1242	10	1241	10	ν(Ph-O)
		1210	6	ν(Ph-O)
1182	1.0	1175	1.5	β(C-H)
1147	8.5	1142(br)	6	
		1120(br)(sh)	3	
1087	5.5	1087	2.5	β(C-H)
1070	5.5	1070	2	β(C-H)
		1050	5	ν(C-O)
1028	3	1025	4	β(C-H)
1000	2	1000	0.5	ring mode (p)
930	1	940 (br)	1	γ(C-H)
920	5	920(br)	1	
895	1			
790	3	790(sh)	2	
782	7	778	5	
768	5.5	768	5	
728	2	730	2.5	
692	8.5	692	10	Ø(C-C) ring mode (4)

Table 54 (continued)

Infrared				
Disc		Solution		Assignment
cm^{-1}	I	cm^{-1}	I	
678	3	672	2.5	δ(skeletal and ring)
661	2			
610	0.5			
568	1			
532	1			
522	0.5			
480	0.5			
450	0.5			
425	0.5			

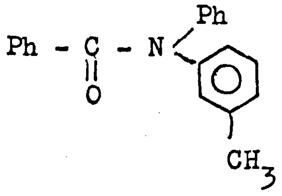


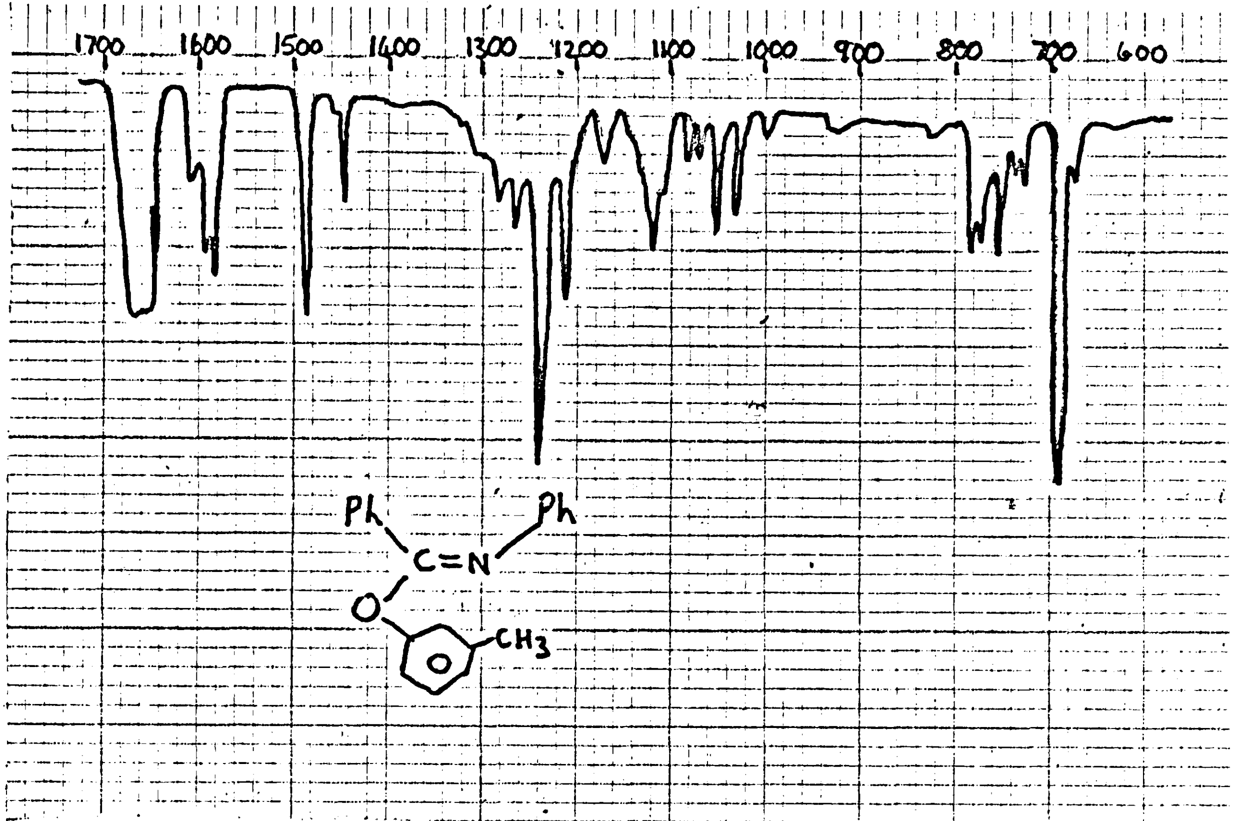
Table 55

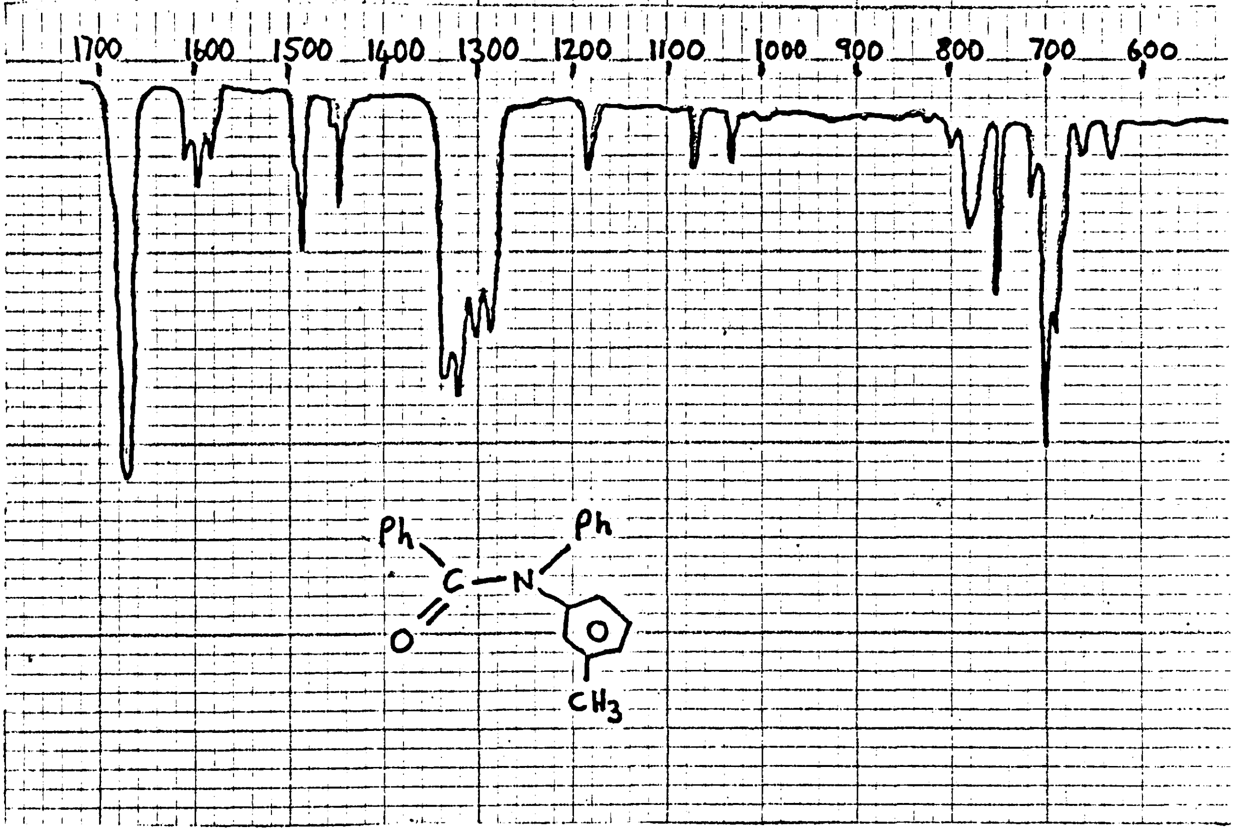
N-Benzoyl phenyl-m-tolylamine

Infrared				
solid		solution		
cm^{-1}	Intensity	cm^{-1}	Intensity	Assignment
3060	1.5	3060	1	ν(C-H) aromatic
3030	1.0	3030	1	ν(C-H) aromatic
1655	10	1670	10	ν(C=O)
1608	4.5	1608	3.	ν(C-C) ring
1590	5.5	1598	3.5	ν(C-C) ring
1580(sh)	4.5	1590	3	ν(C-C) ring
1489	8	1480	5	ν(C-C) ring
1448	5	1449	2.5	ν(C-C) ring
1338(br)	9.5	1335	7.5	skeletal involving (C-N<Ph Ph) β(C-H) and ν(Ph-C)
		1325	8	
1305(br)	6.5	1302	6.5	
1285	6	1288	6	
1175	1	1180	1.5	β(C-H)
1110	1			
1090	0.5			β(C-H)
1075	1.5	1075	1	β(C-H)
1028	1.5	1030	1.5	β(C-H)
1002	1	1000(br)	0.5	ring mode (p)
965	0.5			γ(C-H)
920	1			
875	1			
808	1.5	808	0.5	
782	5	780	4	
775	5			
757	5	751	5.5	
722	3	718	3	
702	9	700	8.5	
692	8	692	5.5	ø(C-C) ring mode (4)

Table 55 (continued)

Infrared				
solid		solution		
cm^{-1}	Intensity	cm^{-1}	Intensity	Assignment
660	2	660	2	δ(skeletal and ring)
630	3.5	628	2.5	
618	1	618	1	
560	0.5			
520	1			
445	1			
420	1			


1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
Ph
Ph
C=N
O
CH3


1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
Ph
Ph
C—N
O
CH3

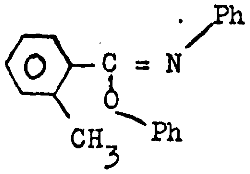


Table 56

N-Phenyl phenyl-o-toluimidate

Infrared				
Disc.		Solution		Assignment
cm^{-1}	I	cm^{-1}	I	
3060(br)	0.5	3060(br)	1	ν(C-H) aromatic)
3020(br)	0.5	3020(br)	1	ν(C-H) aromatic
1665	10	1672	10	ν(C=N)
1590	7.5	1595	7.5	ν(C-C) ring
1580	2	1580	2	ν(C-C) ring
1488	7.5	1490	9	ν(C-C) ring
1450(mtpt)	2.5	1450(mtpt)	1	ν(C-C) and $\delta_{as}(CH_3)$
		1320	1	
1305	2			
1292	8.5	1295	7	ν(Ph-C) and β(C-H)
1258	8.5	1262	8.5	ν(Ph-N)
1225	6	1230	4.5	β(C-H)
1205	8	1205	9	ν(Ph-O)
1192	10	1198	10	ν(Ph-O)
1162	6.5	1162	4	β(C-H)
1158	3.5			
1122	3.5	1125	2.5	
1080	6.5	1080	6.0	ν(C-O)
1070	4.5	1070	4.5	β(C-H)
1040	1.5	1045	1.5	β(C-H)
		1035	1	β(C-H)
1020	1	1025	1.5	β(C-H)
1000	1	1000	0.5	ring mode (p)
925	3.5	922	2	γ(C-H)
900	1	900(br)	1.5	
840	1	830	1.5	
770	8.5	765(sh)	7.5	
760	8	762	10	
740	5	730	6	
720	2			

Table 56 (continued)

Infrared				
Disc		Solution		Assignment
cm^{-1}	I	cm^{-1}	I	
690	8.5	695	7.5	ØC-C) ring mode (4)
		690	6	Ø(C-C) ring mode (4)
668	0.5			δ(skeletal and ring)
570	0.5			
538	0.5			
508	0.5			
420	0.5			

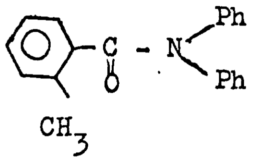


Table 57

N-o-toluoyl diphenylamine

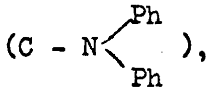
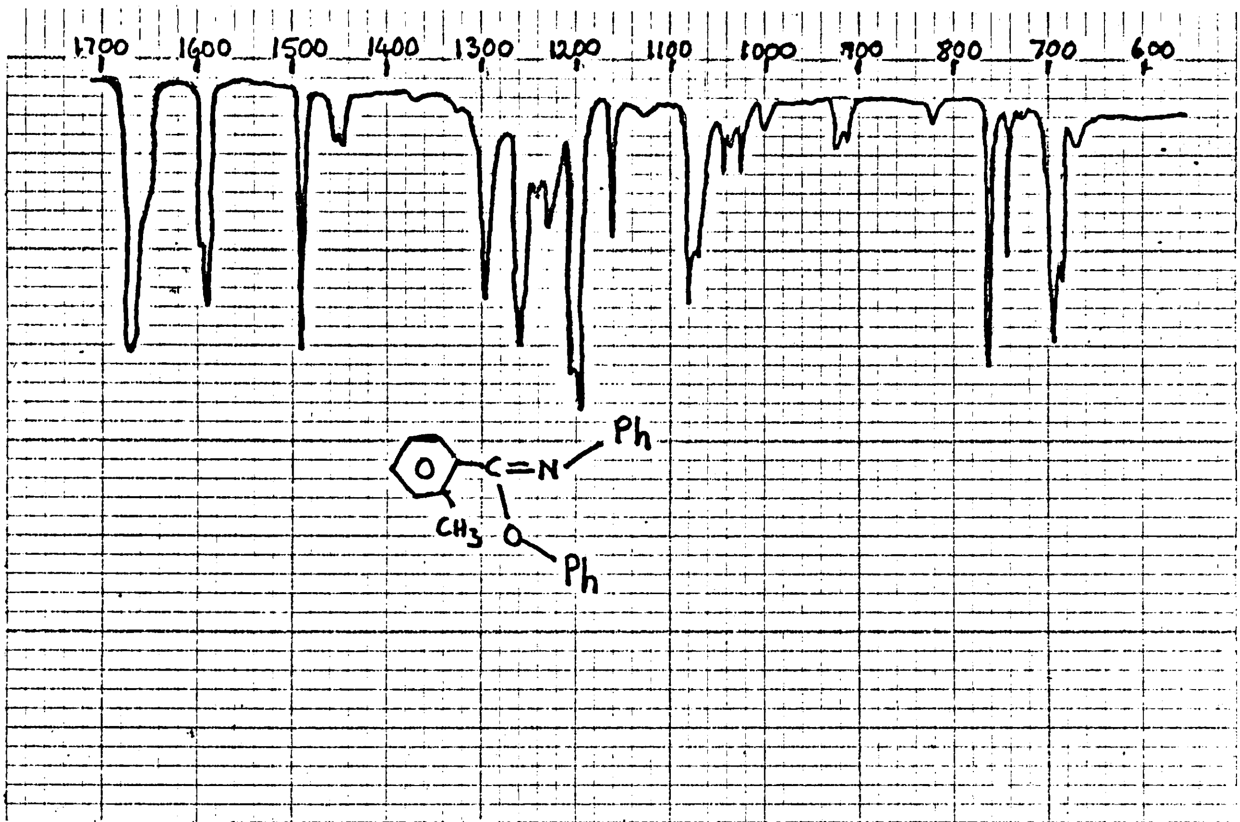
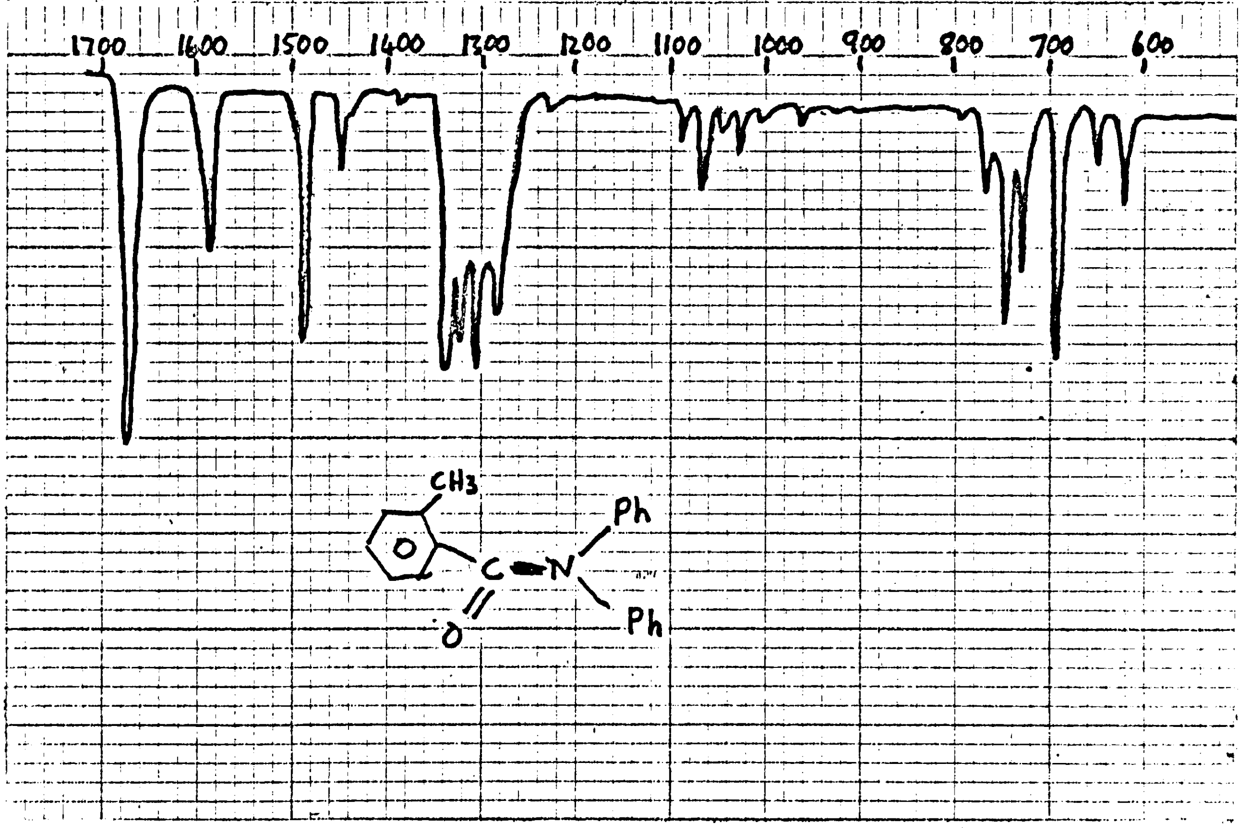
Infrared				
solid		solution		
cm^{-1}	Intensity	cm^{-1}	Intensity	Assignment
3060	2	3070	1.5	ν(C-H) aromatic
3030(br)	2	3035(br)	1.5	ν(C-H) aromatic
1650(br)	10	1672	10	ν(C=O)
1590(br)	9	1592	4	ν(C-C) ring
1488(br)	9	1492	7	ν(C-C) ring
1450	8	1452	2	ν(C-C) ring
1380	5.5	1380	0.5	$\delta_s (CH_3)$
1335(br)	10	1335	7	skeletal involving  $(C - N(Ph)_2)$, β(C-H) and ν(Ph-C)
1320(br)	9.5	1322	6	
1305	9.5	1305	6.5	
1280(br)	9	1280	5.5	
1218	1.5	1218	0.5	β(C-H)?
1170	1			
1135	1			
1092	6	1088	1	β(C-H)
1075	5.5	1075	1.5	β(C-H)
1045	1	1045	< 0.5	β(C-H)
1030	5	1032	0.5	β(C-H)
1002	3	1000(br)	< 0.5	ring mode (p)
960	5	960	0.5	γ(C-H)
920	1			
900	1			
878	1			
858	1.5			
800	4	798	0.5	
777	9			
768	8	770	3	
758	9	755	6	
740	9	738	5.5	

Table 57 (continued)

		Infrared		
	solid		solution	
cm^{-1}	Intensity	cm^{-1}	Intensity	Assignment
702	9	699	6.5	ø(C-C) ring mode (4)
691	9	692(sh)	45	ø(C-C) ring mode (4)
655	7	655	2	δ(skeletal and ring)
622	8	622	3	
535	3			
525	3			
512	3			
462	3			
445	2			
410	1			
355	2			


1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
C=N
Ph
O
Ph
CH3


1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
CH3
C
N
Ph
Ph
O

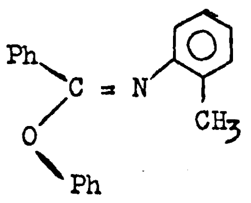


Table 58

N-o-tolyl phenyl benzimidate

Infrared				
Disc		Solution		
cm^{-1}	I	cm^{-1}	I	Assignment
3060(br)	0.5	3065	1	ν(C-H) aromatic
		3040	0.5	ν(C-H) aromatic
3030(br)	0.5	3030	0.5	ν(C-H) aromatic
		2970	0.5	ν(C-H) aliphatic
		2950	0.5	ν(C-H) aliphatic
1660(br)	8.5	1675	6.5	ν(C=N)
		1655	6	ν(C=N)
1590	7.5	1592	6	ν(C-C) ring
1580(br)	5.5	1580	2	ν(C-C) ring
1485(br)	8	1490	8	ν(C-C) ring
1460	3	1460	2	$\delta_{as}(CH_3)$
1450	5	1450	3	ν(C-C) ring
1378	1	1378	1	$\delta_{s}(CH_3)$
1315	1	1315	1	ν(C-C) ring
		1280	3.5	β(C-H)
1268	6.5	1265	5	ν(Ph-C)
1230	4	1235	5	ν(Ph-N)
1215(sh)	8	1215(sh)	6	ν(Ph-O)
1205	10	1205	10	ν(Ph-O)
1185	7	1175	2	β(C-H)
1165	8	1165	3	β(C-H)
1150	5			
1110	2			
		1085	3	β(C-H)
1072	2	1072	3.5	β(C-H)
1040	7	1050	4.5	ν(C-O)
1020	7	1025	3.5	β(C-H)
1000	3	1000	1	ring mode (p)

Table 58 (continued)

		Infrared		
Disc		Solution		
cm^{-1}	I	cm^{-1}	I	Assignment
925	1	922	1	γ(C-H)
885	1	886	0.5	
877	2			
862	1.5	860	0.5	
851	1			
		800	2	
770	9	775	4.5	
		765	5.5	
752	8	752	6.5	
742	9			
		728	3	
715	6.5	715	2	
702	6	695	6.5	φ(C-C) ring mode (4)
		690	6.5	φ(C-C) ring mode (4)
662	1			δ(skeletal and ring)
590	0.5			
550	0.5			
525	1			
460	0.5			
422	0.5			
360	0.5			

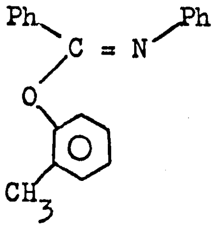


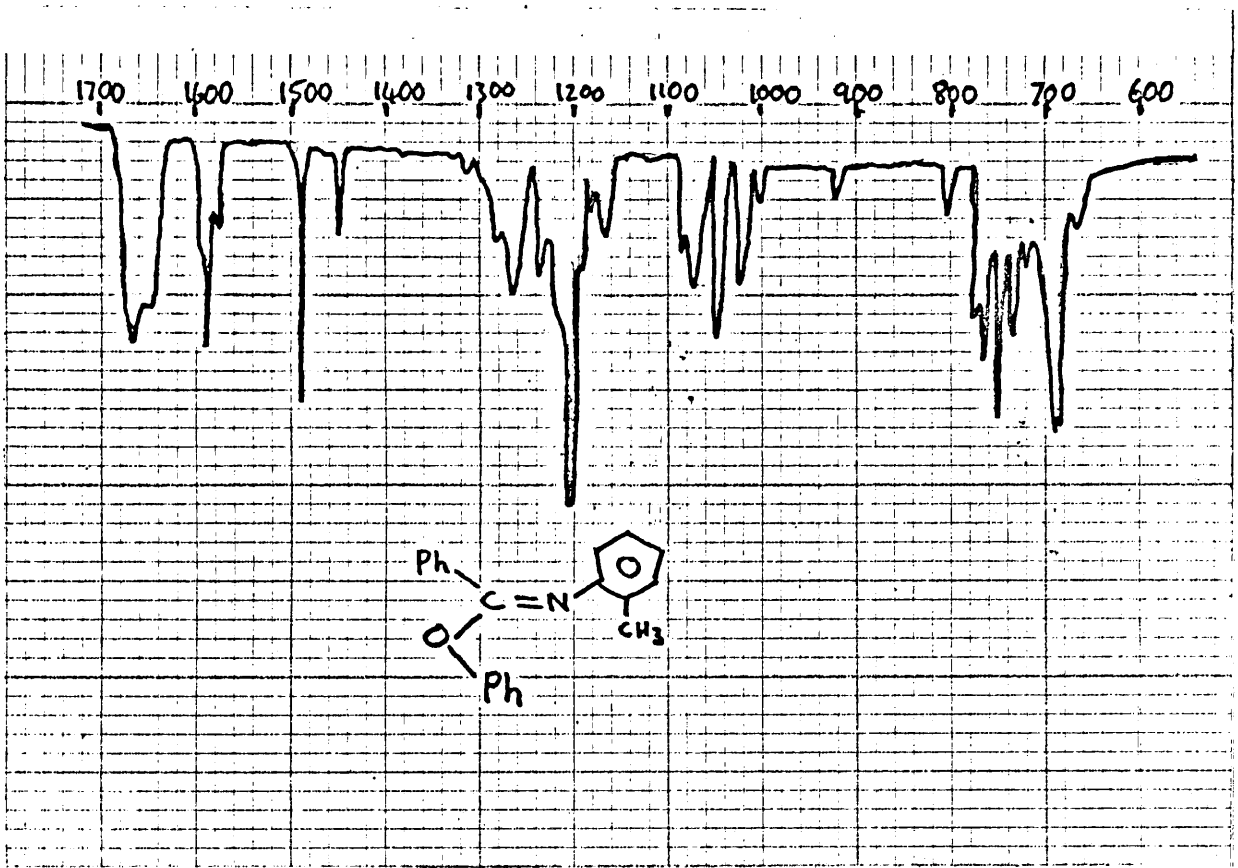
Table 59

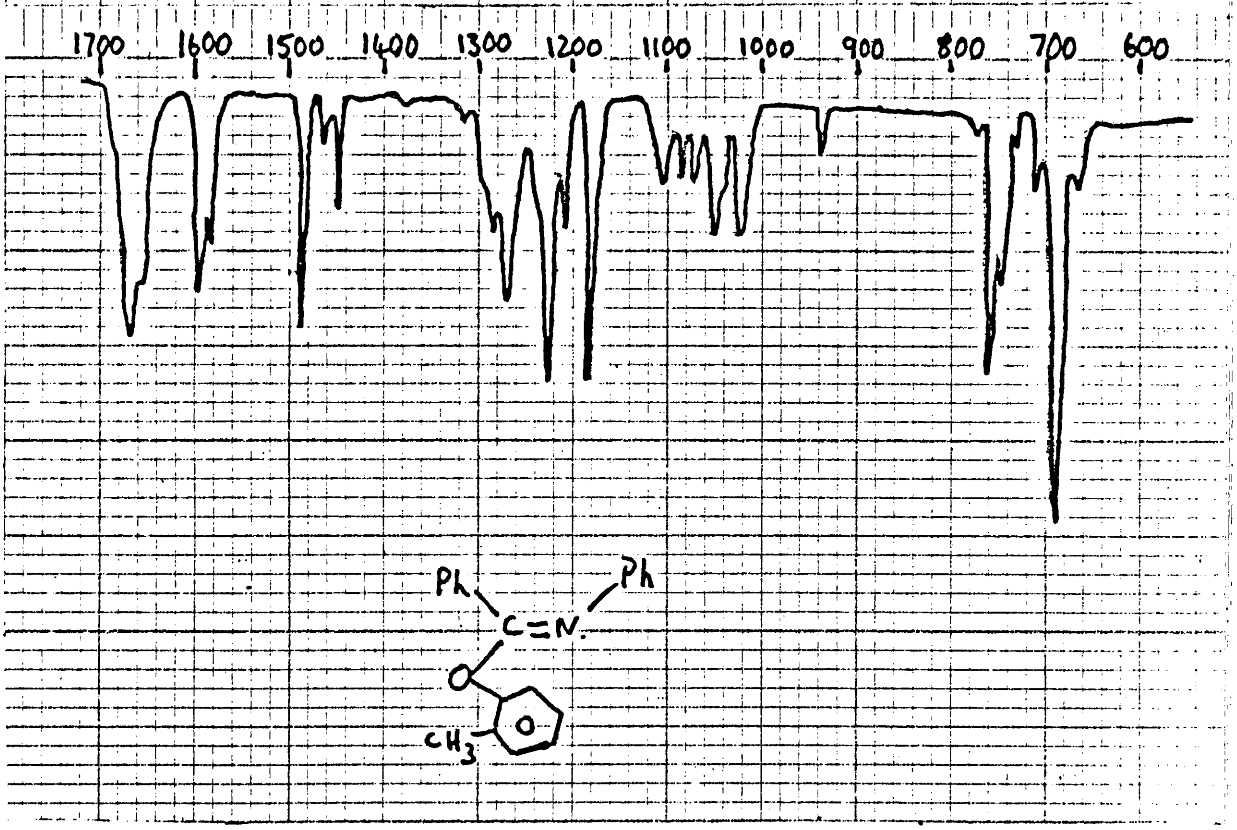
N-Phenyl-o-tolyl benzimidate

Infrared				
Disc.		Solution		
cm^{-1}	I	cm^{-1}	I	Assignment
3060	0.5	3060	1	ν(C-H) aromatic
3020	1	3030	1	ν(C-H) aromatic
2920	0.5	2920	0.5	ν(C-H) aliphatic
1660	10	1670	8	ν(C=N)
		1655(sh)	5.5	ν(C=N)
1595	6	1600	5.5	ν(C-C) ring
1582 (br)	4	1587	3.5	ν(C-C) ring
1490(br)	7	1490	7.5	ν(C-C) ring
1462	2	1462	1	$\delta_{as}(CH_3)$
1450	5	1450	3.5	ν(C-C) ring
1380	0.5	1380	0.5	$\delta_s(CH_3)$
1315	1.0	1315	1	ν(C-C) ring
1285	6	1285	3.5	β(C-H)
1268	9.5	1269	7	ν(Ph-C)
1234	8.5	1238	8.5	ν(Ph-N)
1225(sh)	7.5			ν(Ph-O)
		1210	4.5	ν(Ph-O)
1178	7.5	1180	8.5	β(C-H)
1172(sh)	7			β(C-H)
1155	1			
1110	7.5	1110	2	ν(C-O)
1087	6.5	1087	2	β(C-H)
1080	5			β(C-H)
1070	5	1070	2	β(C-H)
		1050	3.5	ν(C-O)
1022	3.5	1025	3	β(C-H)
1000	0.5	1000	0.5	ring mode (p)

Table 59 (continued)

Infrared					
Disc.		Solution			
cm^{-1}	I	cm^{-1}	I		Assignment
940	0.5	940	0.5	)	
908	4			)	
840	0.5			)	
785	3	785	2	)	
767	9	765	10	)	γ(C-H)
		750	5	)	
725	2	730	2	)	
710	4.5			)	
695	8	695	10		Ø(C-C) ring mode (4)
670	2	670	2	)	
615	1			)	
550	2			)	
538	2			)	δ(skeletal and ring)
532	2			)	
420	1			)	


1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
Ph
C=N
O
Ph
CH3


1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
Ph
Ph
C=N
O
CH3

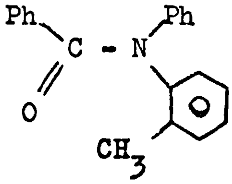


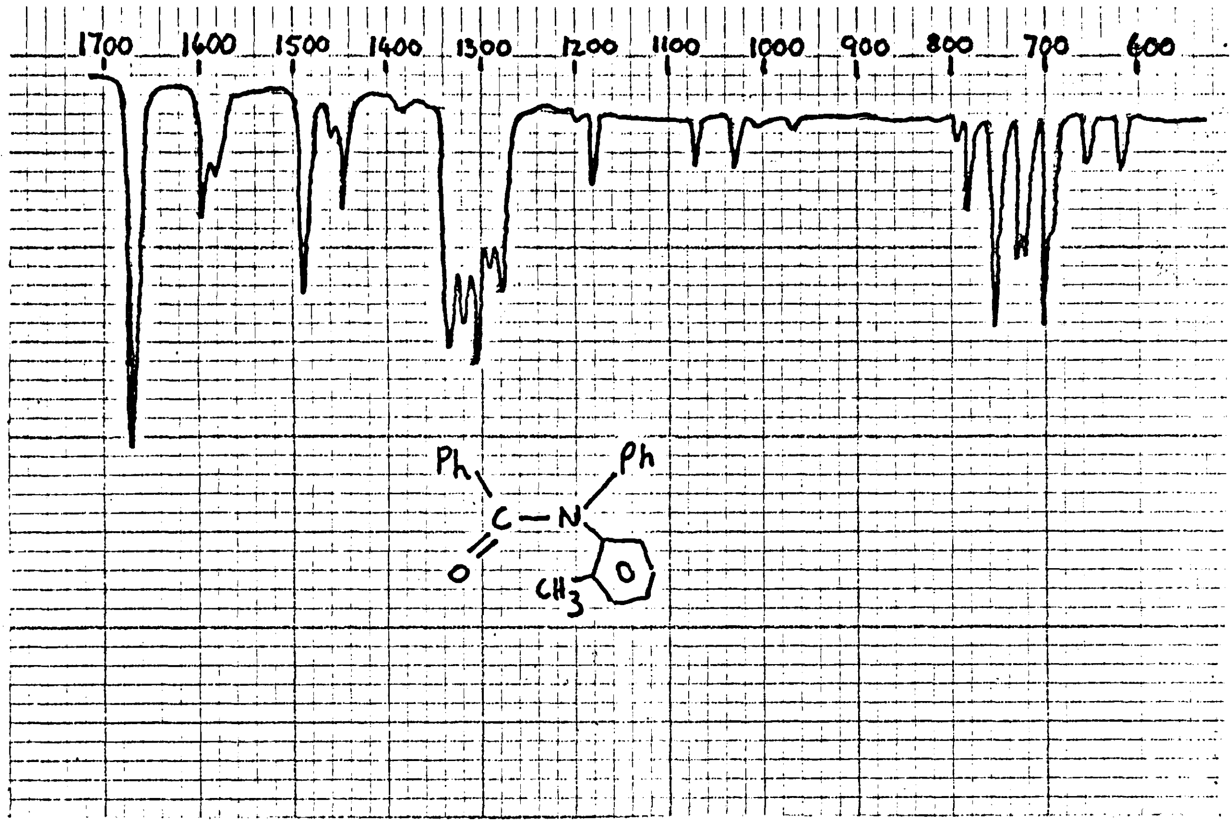
Table 60

N-Benzoyl phenyl-o-tolylamine

		Infrared		
	solid		solution	
cm^{-1}	I	cm^{-1}	I	Assignment
3060	1.5	3060	1.5	ν(C-H) aromatic
3030	0.5	3030	1.5	ν(C-H) aromatic
1650	10	1670	10	ν(C=O)
1595	4	1599	3	ν(C-C) ring
1580	3	1580	2	ν(C-C) ring
1490	7.5	1492	5.5	ν(C-C) ring
1465	1	1465	0.5	$\delta_{as}(CH_3)$
1455	1	1455	1	ν(C-C) ring
1448	4	1449	3	ν(C-C) ring
1380	1	1380	0.5	$\delta_s(CH_3)$
1340(br)	9.5	1337	7	skeletal involving $(C - N{<}^{Ph}_{Ph})$ β(C-H) and ν(Ph-C)
1330(sh)	6.5	1320	6.5	
1308	5.5	1309	7.5	
1292	5	1292	5	
1285	4	1282	5	
1270	2.5	1275	3.5	
1180	1	1180	1.5	β(C-H)
1120	1			
1078	1	1075	1	β(C-H)
1025	0.5	1025	2	β(C-H)
1002	0.5			ring mode (p)
960	0.5	960	0.5	γ(C-H)
808	2			
799	1.5	795	0.5	
785	3	785	3	
765	8	765(sh)	4	
755	4	755	7.5	
722	6	725	4.5	
		718	4.5	

Table 60 (continued)

	Infrared			
	solid		solution	
cm^{-1}	I	cm^{-1}	I	Assignment
701	6	700	7.5	Ø(C-C) ring mode (4)
695	6			Ø(C-C) ring mode (4)
660	2.5	658	1	δ (skeletal and ring)
628	2.5	620	1	
515	1			
460				
422	1			
360	1			


1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
Ph
Ph
C
N
O
CH3
O