SOME CYCLIC COMPOUNDS DERIVED FROM 6,6'-DICHLORODIPHENIC ACID

A Thesis submitted to the University of London
for the degree of Doctor of Philosophy
by
Patricia Ann Browne

January 1968

Bedford College
University of London

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

Acknowledgments

I should like to express my gratitude to Dr. D. M. Hall for her help and encouragement.

I wish also to thank Bedford College for a Bursary during 1962-1964 and Dorset County Council for a Grant during 1965-1966.

ABSTRACT

6,6'-Dichlorodiphenic acid was prepared by an easier route than that of Christie, James and Kenner. The acid was optically resolved, and the diol and bisbromomethyl compound prepared from the dextrorotatory enantiomer. The diol was converted into the oxepin and the bisbromomethyl used to prepare the azepinium bromide; the circular dichroism spectra of these products were measured. Measurements of racemisation rates were made, and the oxepin and azepinium bromide were found to have activation energies of 34.8 and 38.3 Kcal/mole respectively. Racemic azepinium bromide was subjected to Hofmann degradation conditions and the products investigated. The neutral fraction gave a small yield of 4,5-dichlorophenanthrene, and the basic part gave four products; of these the main product was the expected dichloro-9-dimethylamino-dihydrophenanthrene; a second product proved to be an unbridged amine. Traces of other amines were found in different experiments and the nature and ratio of the products would appear to be very sensitive to the conditions.

4,5-Dichloro-9,10-dihydrophenanthrene was prepared in small yield from dichlorobisbromomethylbiphenyl.

The ultraviolet spectra of the bridged biphenyls and the infrared spectra of most compounds are recorded and discussed.

CONTENTS

INTRODUCTION PAGE

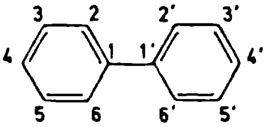
DISCUSSION

Infrared spectra

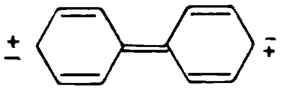
INTRODUCTION

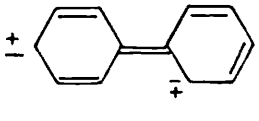
CONJUGATION AND ULTRAVIOLET SPECTRA OF BIPHENYLS

The biphenyl molecule is a collinear structure, which, in the crystal, is planar,[1,2,3,4] but in the free molecule has the benzene rings at an angle of about 45°, as shown by electron diffraction measurements on the vapour.[5,6].



The stabilisation from the conjugation of the two benzene rings with each other is comparable to the repulsion of the ortho hydrogen atoms, hence the deviation from planarity in the vapour and in solution.[7] The energy barrier to rotation has been calculated[8] to be 3.9 Kcal. mole^{-1}. However, there is sufficient conjugation to produce an intense band in the ultraviolet spectrum at 2490 Å with ε_{max} 17,300 (in ethanol) which is ascribed to a transition from a homopolar ground state to a dipolar excited state, of which there are 10 contributing ionic structures,[9,10,11]. e.g.





With small interplanar angles, there will still be considerable overlap of the π orbitals, and thus the conjugation band will still appear, although modified in position and intensity. As the interplanar angle θ increases, conjugation will continue to decrease, reaching zero, or a small value, at an angle of 90°. Mulliken[12] also considers that the lowest of these excited states will have lower energy, relative to the ground state, the greater the extension of the conjugated system, and that the absorption intensity will increase with the degree of polarity of the molecule in the excited state. Thus, substituents in the _para_ position would be expected to shift the conjugation band to longer wavelength and raise the intensity.

Table 1

Conjugation band in some 4,4'-disubstituted biphenyls

	solvent	λ Å	ε_{max}	ref.
Ph-Ph soln.	96% EtOH	2490	17,300	13
Ph-Ph solid		_ca._ 2520	not less than in solution	14
KCl disc		2530		15
4,4'-dinitro-	EtOH	3060	27,500	17
4,4'-dimethoxy-	_n_-hexane	2630	21,700	16
4,4'-dichloro-	96% EtOH	2590	25,200	18

Table 2

Conjugation bands in 2- and 2,2'- substituted biphenyls

	solvent	λ Å	ε_{max}	ref.
Ph-Ph	96% EtOH	2490	17,300	13
2-fluoro-	96% EtOH	2415	16,500	11
2,2'-difluoro-	" "	2335	13,800	11
2,2'-dichloro-	" "	(2300)	6,600	11
2,2'-dibromo-	" "	(ca.2280) v.faint	12,000	11
2,2'-diiodo-	" "	absent		
2-methyl-	light petroleum b.p.100-120°	2365	10,250	19
2,2'-dimethyl-	" "	(2280)	6,000	19
2-ethyl	not reported	2330	9,000	20
2,2'-diethyl-	96% EtOH	(ca.2270)	6,000	13
2,2'-dihydroxy-	EtOH	2420	10,000	16
2,2'-dinitro-	EtOH	2570	12,000	16

Values in parentheses are inflections

Substitution in the ortho position will, by repulsion and steric hindrance, cause the biphenyl skeleton to exist in a twisted form; the two rings may, or may not, be able to rotate round the 1,1' bond at room temperature. The conjugation band will indicate the angle between the planes of the two phenyl rings, since it will be modified by the amount of conjugation present, but it will also be affected by any substituents present. As the interplanar angle increases, the spectrum will resemble more and more that of the separate phenyl chromophores, and long-wave features will become resolved. Decrease in conjugation should lead to displacement of the conjugation band to shorter wavelength and a decrease in intensity. As can be seen from table 2, increasing the size of the ortho group increases the angle between the rings, decreasing the conjugation as shown by the expected wavelength shifts and decrease of intensity. Further, there is interaction between some substituents and the ring, which, by reducing the energy of the excited state, may move the conjugation band to longer wavelength, and may, in fact, cancel out, or swamp the opposing shift due to decrease of conjugation of the rings with each other. O'Shaughnessy and Rodebush[21] indicate that, theoretically and practically, substituents such as the halogens, methyl or NH_3^+ exhibit very little electronic interaction with the aromatic ring, while hydroxyl, methoxyl and amino groups show more, and unsaturated groups a great deal. Thus, amino, methoxyl and nitro groups will move the band to longer wavelength whatever position they occupy.

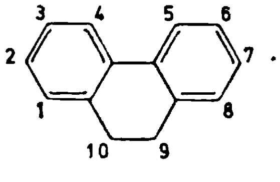
The effect of position of a group can be seen by comparing the position and intensity of absorption of the conjugation band for diethylbiphenyls:[13]

Table 3

Position	λ Å	ε max.
2,2'	(*ca.* 2270)	6,000
3,3'	2510	16,500
4,4'	2565	22,500
Solvent: 96% EtOH		
Value in parenthesis is inflection		

The ultraviolet spectra of the biphenyls are further modified by bridging in the *ortho* position, and this factor will dominate the geometry of the molecule if the bridge is small. The bridge will then tend to hold the molecule closer to planarity than in biphenyl and the conjugation band would be expected to show a bathochromic shift, together with increased intensity.

Models show 9,10-dihydrophenanthrene to have an interplanar angle of 15°-16° (depending on the length of the central diphenyl bond)[18]



Thus, to accommodate large groups in the *ortho* 4,5-position, there must be considerable distortion.

Table 4

Conjugation bands in some biphenyls with a 2-atom bridge

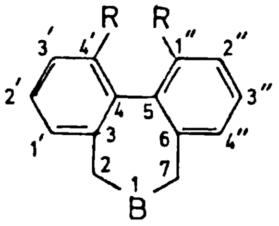
	λ Å	ε max.	ref.
9,10-dihydrophenanthrene[a]	2640	17,000	22
4,5-dimethoxy-9,10-dihydrophenanthrene[a]	2720 (2630)	13,500 12,500	22
4,5-dimethyl-9,10-dihydrophenanthrene[b]	2610	15,000	23
9-dimethylamino-9,10-dihydrophenanthrene[c]	2520 2600 2655	15,700 16,000 15,900	24

Solvent: a, ethanol; b, iso-octane; c, 96% ethanol

Values in parentheses are inflections

Conjugation band in some Bridged Biphenyls

Table 6



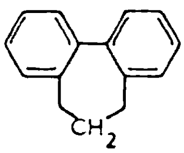
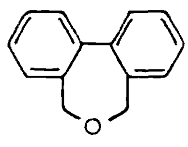
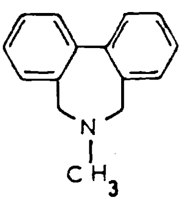
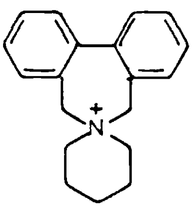
B = O	λ Å	ε_{max}	Solvent	Ref.
R = H	2505	16,500	EtOH	25
R = OMe	2530	8,700	Hexane	22
R = Me	2440	11,000	Dioxan	26
$B = \overset{+}{N}(CH_2)_5$				
R = H	2480	15,000	water	22
R = F	2435 241o	12,600 12,600	96% EtOH	27
R = Cl	2470	10,000	" EtOH	27
R = Br	(2460)	8,850	" EtOH	27
R = I	(2540)	13,000	" EtOH	27
R = OMe	2375	11,500	water	22
$B = N(CH_3)$				
R = H	241	12,800	96% EtOH	24
$B = \overset{+}{N}(CH_3)_2$				
R = H	2490	14,200	96% EtOH	24
R = Me	2420	9,100	EtOH	26,26a
$B = C(COOEt)_2$				
R = F	(2440 (2415	13,100 13,000	96% EtOH	27
R = Cl	2440	10,200	iso-octane	26
R = Me	2430	15,800	dioxan	26
$B = CH.CO_2Me$				
R = H	2485	15,500	96% EtOH	28
$B = CH_2$				
R = H	2470	15,700	EtOH	28a
R = Me	2400	11,500	iso octane	26

Values in parentheses are inflections

With a bridge of three atoms, making a seven-membered ring, the interplanar angle of the phenyl rings is between 40-50°. There is little strain, and the compounds are easily made.

Table 5

Ring angles of some bridged biphenyls calculated from molecular dimensions

					
					ref.
Ring angle	49°	43°		47°	18
	51.6°	44.1°	45.8°		23

The conjugation band is similar in position and intensity to that of biphenyl. Data for such compounds with homocyclic and heteocyclic bridges and substituted in the 4',1"- positions are given in table 6. The 4',1"-diiodo-2,7-dihydro-3,4:5,6-dibenzazepinium-1-spiro-1"'-piperidinium bromide has a broad band at a longer wavelength which is attributed to overlapping of the iodophenyl band by the residual conjugation band. Comparison of the 2400-2600 Å region with that of 2,2'-iodobiphenyl suggests that there is still appreciable conjugation^{27}. Mislow^{26} and his colleagues have demonstrated that 2,2'-bridged biphenyls with a homo- or heterocyclic seven-membered bridging ring absorb at λ_{max} 2490±20Å, and ε_{max} ca.15,000 and suffer a blue shift and lowering of intensity to λ_{max} 2420 ± 20Å and ε_{max} ca. 10,000 on substitution in the 6,6'-position by methyl or chlorine.

Because the bridge length determines the angle of torsion, the size of the bridge can be inferred from the ultraviolet spectrum[26].

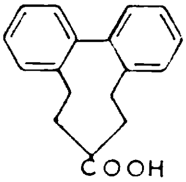
Table 7

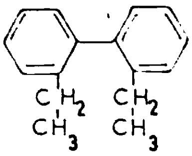
Conjugation band in biphenyls with different sized bridging rings

No. of bridging atoms	Wavelength range	
2	2600–2640	ab
3	2430–2560	ab
4	2350–2390	b
5	(2310) inflection	b

a = substituted in 6,6'-position; b = unsubstituted

The value for the compound with the five-membered bridge is for



The longwave features are resolved and the spectrum is similar to that of the unbridged compound  indicating greatly reduced conjugation.

This shows that the effect of the bridge decreases rapidly with size, and the degree of twist is governed more by the ortho $-CH_2-$ substituents.

As the size of the bridging ring increases, it becomes more flexible, and conformations with large dihedral angles are more easily accommodated.

ULTRAVIOLET SPECTRA OF PHENANTHRENES

In phenanthrene, there is greater conjugation, for this can occur through the unsaturated bridge which holds the molecule planar[7]. The spectrum of phenanthrene shows three main regions of absorption 3100-3400 Å, 2700-2900 Å and 2500 Å [29].

The three regions are also distinguished by intensity:

Group 1. are weak bands $\varepsilon = 10^2 - 10^3$, often possessing a complicated vibrational structure.

Group 2. are moderately intense bands ε ca. 10^4 and usually show a regular fine structure.

Group 3. are strong bands ε ca. 10^5 with rather less fine structure.

These are called α, p and β bands by Clar[30] and ^1L_b, ^1L_a and ^1B (^1B_a or ^1B_b) by Platt[31].

Apart from intensity, frequency and structural characteristics, Clar distinguished the α band by the fact that it moves to shorter wavelength on lowering the temperature, whereas the p and β bands move to longer wavelength.

The α and β transitions are longitudinally polarised and the p transitions transversely polarised.

When there are ortho substituents, the steric hindrance of these can be relieved in three ways:

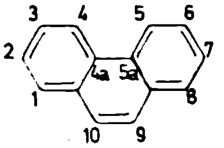
1) the groups lie in the same plane as the aromatic rings, but bent away from each other.

2) the aromatic rings are distorted.

3) the groups are bent out of the plane of the aromatic rings.

If the compound can be obtained optically active, 1) is invalid. Newman and Hussey[32] have assumed that since the spectrum of the resolvable 4,5-dimethylphenanthrene resembles that of phenanthrene, 2) does not operate, and the methyl groups are bent out of the plane of the aromatic rings.

However, Murrell[35] considers that the steric hindrance is relieved by both displacement of the substituent out of the plane and twisting about the central 4a,5a bond.



He suggests that the distortion gives a much larger red shift in the ^1L_a band than would be expected from a methyl group. Changes of frequency in this band due to distortion are much greater than changes in intensity.

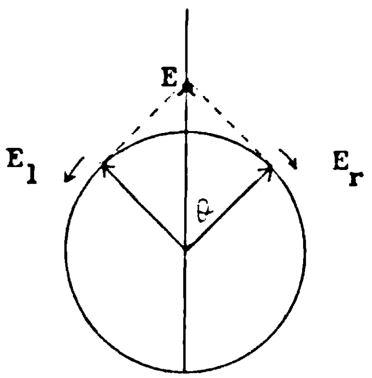
Bands in the ultraviolet spectra for phenanthrene, 4-fluorophenanthrene, and 4-nitrophenanthrene are given in table 8.

TABLE 8 ULTRAVIOLET ABSORPTION SPECTRA OF SOME PHENANTHRENES

	phenanthrene[33]		4-fluorophenanthrene[34]		4-nitrophenanthrene[34]	
	λ_{max} (Å)	log ε_{max}	λ_{max} (Å)	log ε_{max}	λ_{max} (Å)	log ε_{max}
Group I	3450	2.07	3480	3.11		
	3380	2.29	3415	2.64		
	3300	2.31	3320	3.04		
	3240	2.29	3260	2.66		
	3160	2.24	3180	2.70		
	3080	2.18				
Group II	2910	4.51	2965	4.27	2985	3.98
	2800	4.09	2850	4.11	2780	4.09
	2740	4.21	2740	4.03		
Group III	2500	4.85	2675	4.04	2400	4.62
	(2450)	(4.76)	2475	4.96	2210	4.37

OPTICAL ACTIVITY

Plane polarised light may be regarded as being made up of equal components of left-handed and right-handed circularly polarised light, where the electric field vector traces out a left-handed and a right-handed helix respectively.

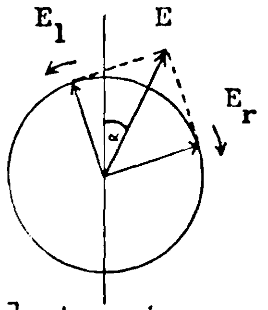


E_l - left-handed electric field vector.

E_r - right-handed electric field vector

E - resultant electric field vector of plane polarised light.

An optically active medium will have different refractive indices n_l for left- and n_r for right-handed polarised light, i.e. it is circularly birefringent. Thus, if n_l is greater than n_r, the left-handed component of the circularly polarised light will be retarded with respect to the right-handed component, and the plane of the emergent light will have been rotated through an angle α dependent on the differences between n_l and n_r and the path length. The concentration and solvent (when a solution is being considered), the wavelength and the temperature also influence the value of the angle of rotation.



The specific rotation $[\alpha]$ at a given wavelength and temperature for a particular solvent is defined by Biot's Law; $[\alpha] = \frac{\alpha \times 100}{l \times c}$ where α is the observed angle, l is the path length in decimetres and c is the concentration in g./100 ml. of solution.

The molecular rotation $[\phi]$ is given by $[\phi] = \frac{M[\alpha]}{100}$ where M is molecular weight.

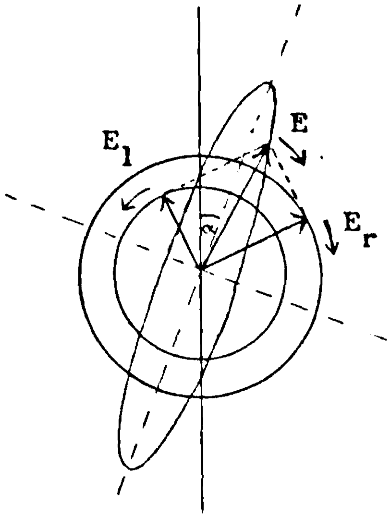
The dependence of $[\alpha]$ on temperature may be due to:

1) change in volume of the solution,

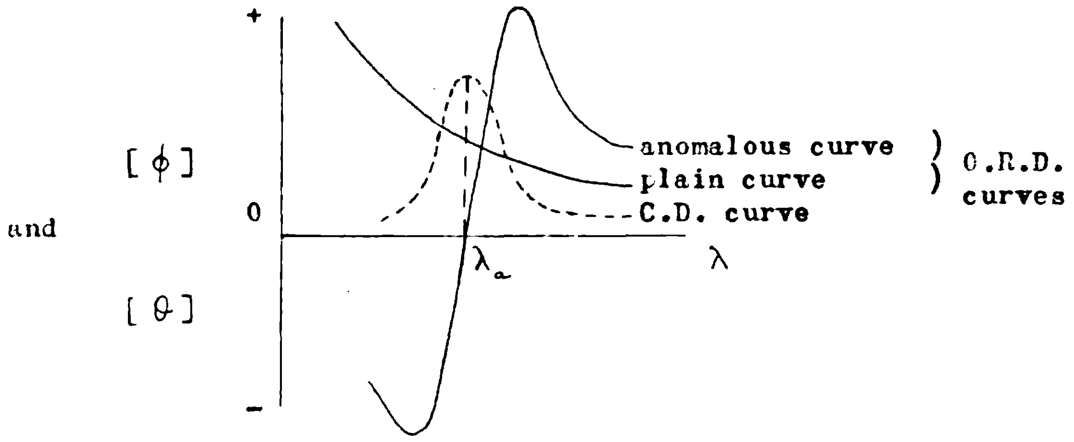
2) change in association,

3) change in the population of different conformations.

Further, the absorption coefficient will depend on the chirality of the light, and this will mean that one component will be absorbed more than the other, and the emergent light will be elliptically polarised.



This phenomenon is known as circular dichroism (C.D.). The difference in extinction coefficients is expressed by specific ellipticity [Ψ] or molecular ellipticity [θ] = 3300 ($\varepsilon_l - \varepsilon_r$). If the specific rotation is plotted against wavelength, a graph of the optical rotatory dispersion (O.R.D.) is obtained.



Positive C.D. and O.R.D. curves

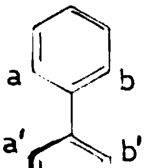
If the absorption band is at low wavelength, only the end part of the curve is observed, owing to limitations of the instruments, and the curve is called a plain curve. At an absorption band, an S-shaped O.R.D. curve is obtained, which is the derivative of the C.D. curve, and this is called a Cotton Effect. If the extremum on the longer wavelength side is more positive than the second extremum, the curve is called positive. C.D. curves are less complicated than O.R.D. curves, but they cannot be measured to such a low wavelength. Comparison of O.R.D., C.D. and U.V. curves are useful to elucidate information on structure, configuration and conformation.

OPTICAL ACTIVITY IN BIPHENYLS

A biphenyl substituted in such a way that it is non-superposable on its mirror image fulfils the conditions required for optical activity, but the enantioners cannot be separated unless there is enough hindrance to rotation for them to retain configuration through the resolution. If there are large groups in the ortho position, or the biphenyl rings are held out of coplanarity by a bridge, it is likely that the molecule may be prepared in optically active forms.

The absolute configuration of a molecule can be found by chemically relating the compound to another of known absolute configuration, without disturbing the asymmetric centre.

The notation R (rectus or right) and S (sinister or left) was devised by Cahn, Ingold and Prelog[36]. According to whether the sequence of the groups or atoms, when ordered following certain rules, results in a right-handed or left-handed pattern, the element of asymmetry is called R or S. When considering biphenyls, axial asymmetry is operating, and the substituents in the rings must be considered.



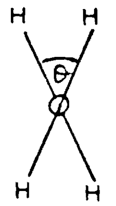
R configuration if the pair a - a' either precede or follow the pair b - b' in the order of priority.

Substituents a and b must be different, but it is possible for a = a' and b = b'. If there is a meta substituent giving asymmetry, then a and b can be the same.

Mislow and his co-workers have put forward a rule[26], for use with bridged biphenyls, where the rings are held in a <u>cis</u> conformation ($\theta < 90°$). The long-wave Cotton Effect is found to be positive for 6,6'-dimethyl, 6,6'-dichloro-derivatives and 1,1'-binaphthyl and negative for 6,6'-dinitro derivatives when these molecules have the R configuration.

They also report[23] that the sign of the Cotton Effect at the conjugation band frequency, which reflects the sense of twist, or chirality, of the π electron system is positive for the R configuration of symmetrically substituted bridged biphenyls ($\theta < 90°$)

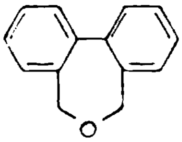
The Cotton Effect centred at the biphenyl conjugation band changes position with change of angle, as shown in the bridged biphenyls, and Mislow[26] and his colleagues consider that this provides an experimental demonstration of the inherently dissymmetric biphenyl chromophore. They suggest that the configuration of biphenyl



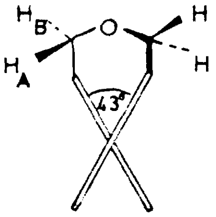
with θ <u>ca</u>. 45 will have a positive Cotton Effect centred at 2400–2500 Å

<u>ACTIVATION ENERGY TO INVERSION OF CONFIGURATION</u>

The energy required to twist the molecule into the other enantiomer, the activation energy, E, for inversion of configuration can be measured by studying polarimetrically the rate of racemisation of the resolved compound, which must be sufficiently optically stable, or by studying the nuclear magnetic resonance spectrum of the compound at different temperatures, providing the molecule contains protons which exist in different magnetic environments in the two enantiomers, e.g. 2,7,-dihydro-3,4:5,6-dibenzoxepin



Looking down the line of the 1,1' bond, this can be drawn



It is obvious that the environments of protons A and B are considerably different, and so when the temperature is low, and the conversion from one enantiomer to the other is slow, signals for the protons will be received and resolved into a multiplet. However, at higher temperatures, these coalesce and only one peak is obtained. By considering the change in intensity, or of separation of the absorption lines with temperature, E, the potential energy for the equilibrating motion can be calculated. The energy can also be calculated from measurements of changes in line width with temperature, but the values are considered less reliable.

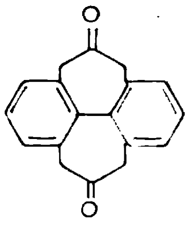
It may be noted that the energy barrier to an equilibrating process, e.g. rotation round a bond, may be calculated in any molecule which contains magnetically non-equivalent protons which exchange environment during that process, and which provide a suitable N.M.R. spectrum. The molecule need not be optically active. Hence activation energies of inversion of configuration may be obtained without a resolved sample. As yet, the N.M.R. method has not been applied to compounds whose inversion rates have also been measured by the conventional polarimetric method.

There are two conditions for magnetic equivalence:

1) rapid interchange of the disymmetric environment of the proton.
2) very small differences in the chemical shifts of the two protons or spin coupling constant effects.

Because of this latter condition apparent magnetic equivalence may exist together with steric non-equivalence.

Mislow and his co-workers[23] found that



and

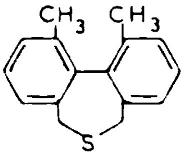
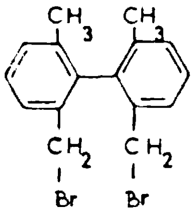
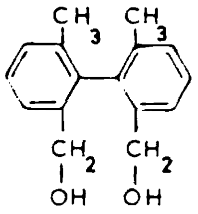


exhibit sharp single signals in the methylene region which would indicate conformational lability, although the compounds had been prepared optically active and are optically stable. They found that the proton resonances for the bridged compounds they studied changed regularly with dielectric constant, except for the ketones, where there is no discernable trend; in all cases, benzene gave anomalous results. They suggested that this solvent dependent behaviour is due to change in the dihedral angle.

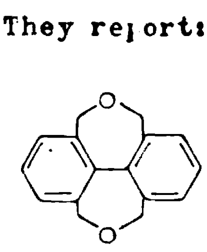
Another example of misleading N.M.R. data is the spectrum for 6,6'-dimethyl-2,2'-bisbromomethyl biphenyl



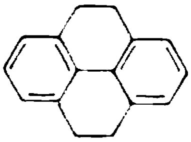


Both this and the hydroxy compound, shown above, are optically active and optically stable so in neither compound are the methylene protons magnetically equivalent because of rapid exchange. The diol exhibits the expected methylene pattern but the bisbromomethyl compound only a single sharp peak. Conclusions about the conformative lability drawn from N.M.R. measurements may therefore be misleading.

Oki, Iwamura and Hayakawa[37] have investigated the rates of inversion of *o*,*o*'-bridged biphenyls by N.M.R. spectra. They report:

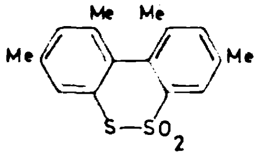


has a slow inversion rate and a lower limit to the activation energy can be calculated.

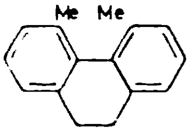


retains a singlet to a low temperature and is likely to have a fast inversion rate.

The higher limit of the energy of activation can be deduced. They found E_{act} to be < 9 Kcal. by assuming log A = 12, (see page 30) since they state, referring to Hall & Harris's survey[38], that, for o,o'-bridged biphenyls this is the average value. In fact, for singly bridged biphenyls, this is not so. The average value is over 13, and only one compound is quoted at a value less than 12. Two other compounds whose values have been measured [39, 75] since the publication of Hall & Harris's paper are



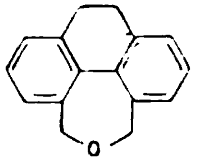
log A 13.2 and



log A 12.8

For the doubly bridged compounds which are comparable, the value of log A is approximately 12 for the oxepin and thiepin (see page 34) but the diketone and the oxathiepin have higher values[23].

For the compound



two signals are obtained at room temperature, corresponding to the methylene protons on the $-CH_2CH_2-$ and $-CH_2OCH_2-$ bridges. As the temperature decreases, the proton signals from the $-CH_2OCH_2-$ methylene groups are resolved, but not from the other bridge. Thus, as might be expected from the proximity of the methylene groups in the $-CH_2CH_2-$ bridge, spin coupling causes magnetic equivalence down to a lower temperature. The activation energy is calculated by these authors[37] from the change in behaviour of the $-CH_2OCH_2-$ protons and results in a value of E_{act} 10.5 ±0.5 Kcal. and log A 12.6 ± 0.4. In some compounds the equilibration motion may not be the same as inversion of configuration and thus the activation energy calculated may be for a different process.

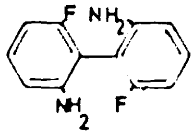
FACTORS AFFECTING THE OPTICAL STABILITY OF BIPHENYLS

The optical stability of a biphenyl is largely dependent on the ortho substituents.

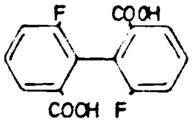
When comparisons of the effect of ortho substituents on the optical stability are made, it is considered that steric effects are most important, and that electrical effects are likely to be small[41]. It is found that biphenyls tetrasubstituted with fluorine or methoxyl groups are not resolvable; with polar substituents nitro- or chloro-, they are very resistant to racemisation, and with the non-polar group methyl, which is of comparable size to chloro-, also resistant to racemisation.

When considering the steric effects, Adams and Yuan[41] calculated 'interference values' for certain pairs of atoms or groups, by comparing the 'internuclear distance' (the distance from the nucleus of the ortho carbon atom to the centre of the group atom) with the 1,1'- carbon bond length, which they took as 2.90 Å. They considered that when the total internuclear distance for the 2,2'- substituents was greater than the 1,1'-bond length, then the compound should be capable of resolution. Their 'internuclear distances' follow the order

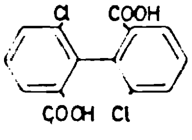
$I > Br > NO_2 > Cl > CH_3 > NH_2 = COOH > OH > F$



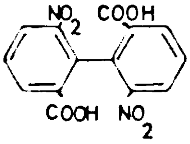
I



II



III



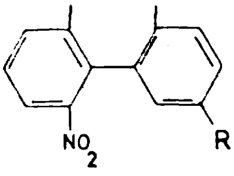
IV

They found that I with substituents F and NH_2 passing, and II with F and COOH passing during racemisation, should be able to be resolved, but easily racemised, whereas III with Cl and COOH passing or IV with NO_2 and COOH passing should be resolvable and quite stable. These predictions were proved correct in practice. Williamson and Rosebush[15] give the interference of the groups in the order

$SO_3Na > NO_2 > Cl > CH_3 > COOH > NH_2 > OH > OCH_3$

This is estimated from the van der Waals's radii and corresponds well with Adams and Yuan's order.

If, however, one considers the racemisation data of compounds such as



Where R = H, and X = CH_3, NO_2, COOH, OCH_3; and also where R = CH_3 and X = Br, Cl and F, the stability is found to decrease in the order[42]

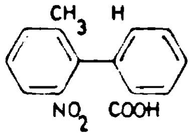
$$Br \gg CH_3 > Cl > NO_2 > COOH \gg OCH_3 > F$$

The carboxyl group is smaller than the nitro- group, and so, in the racemisation, the group X will pass the carboxyl group. Apart from NO_2, Cl and CH_3, the order reproduces the other two given, and parallels the order of size, whereas there is no relation with polar properties.

There are difficulties in attributing the optical stability entirely to steric factors, since the order listed above gives

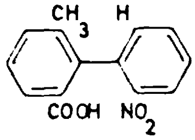
$$CH_3 > NO_2 > COOH$$

and optical stability follows the order



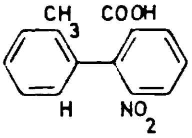
I

$>$



II

$>$



III

although the expected order is III $>$ II = I

When groups are in the 3,3'- positions, they can prevent the ortho substituents from bending away from each other in the plane of the ring, and they thereby increase optical stability. This is called a 'buttressing' effect, and is demonstrated in the following table[42], which gives half-lives in minutes at 25° of compounds substituted in 3,4 or 5 positions.

Table 9

Half-lives in minute at 25° of some substituted biphenyls

position of substituent	solvent	nitro-	bromo-	chloro-	methyl-	methoxy-
3	EtOH	1905	827	711	331	98
4	Acetone	115	25	12	2.6	3.6
5	EtOH	35	32	31	11.5	10.8

This shows the effectiveness for buttressing to be in the order

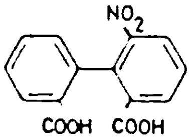
$$NO_2 > Br > Cl > CH_3 > OCH_3$$

Thus the buttressing capacity differs from the ortho interference. The order approximately parallels that for polarity, and thus both size and polarity may be responsible for this effect.

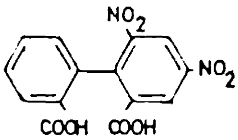
The optical stability is not only governed by the activation energy. The frequency factor A, in going to the transition state in the racemisation process must also be considered. The rate of racemisation follows first order kinetics and is given by the Arrhenius equation

$$K_{rac} = A \exp (-E/RT)$$

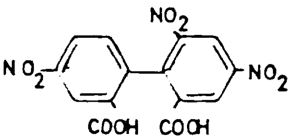
The dependence of optical stability on A as well as E is demonstrated in the following example



(a)



(b)



(c)

The activation energy for these compounds[43] is found to be 22.6 Kcal/mole (in 2N Na_2CO_3), but there is a marked increase in optical stability on addition of the nitro- groups in the <u>para</u> position. This is due to the frequency factors, which are

(a) $10^{10.6}$ sec.$^{-1}$

(b) $10^{10.1}$ sec.$^{-1}$

(c) $10^{9.7}$ sec.$^{-1}$

Thus, by comparing rates of racemisation, different results may be obtained from those by comparisons of E_{act}.

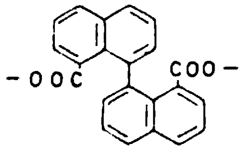
The Glasstone, Laidler and Eyring absolute reaction rate equation[44,45] gives the transition-state-theory functions.

$$k_{rac} = \kappa\ (kT/h)\ \exp(-\Delta H^{\ddagger}/RT)\ \exp(\Delta S^{\ddagger}/R)$$

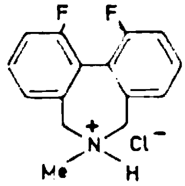
where $\Delta H^{\dagger}$ is the change in enthalpy accompanying the formation of the transition state in the racemisation process; κ = transmission coefficient (taken as 1) and k = Boltzmann constant. The change in entropy in going to the transition state in the racemisation process, $\Delta S^{\dagger}$, may be calculated from

$$\Delta S^{\dagger} = 4.576 \log k_{rac}/T + E/T - 49.2$$

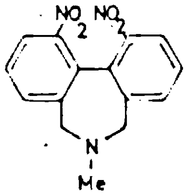
Values of A greater than 10^{13} sec.$^{-1}$ correspond to positive values of $\Delta S^{\ddagger}$ although this is somewhat dependent on temperature. These positive entropy factors are, with only one exception so far, found in bridged biphenyls. The exception is the binaphthyl[46]



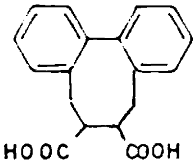
This does not mean that bridged biphenyls have only positive values of $\Delta S^{\ddagger}$.



has $\Delta S^{\ddagger}$ -2.9 (E = 27.8; log A 12.7)[38,47]



has $\Delta S^{\ddagger}$ -8.3 (E = 30.0; log A 11.5)[38,47]

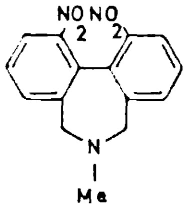


has $\Delta S^{\ddagger}$ -3.5 (E = 22.8; log A 12.5)[38,48]

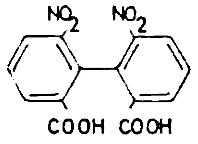
while the ion has $\Delta S^{\ddagger}$ + 5.8 (E = 25.4; log A 14.5).

Entropies of activation for bridged biphenyls appear to have small negative or positive values[49], and seem to lie within the range -8.3 to +8.6 e.u.

Bridging a molecule leads to decrease in optical stability. This is demonstrated in the following examples:



<



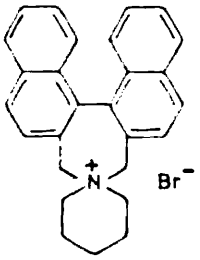
$t_{\frac{1}{2}}$ 16 hours at 125°

E_{act} 30.0 Kcal/mole

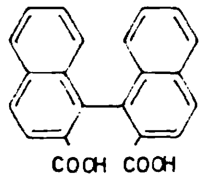
log A 11.5 in C_6H_6 [47].

Decrease of 22% activity[50]

after 60 hours at 140°-160°



<



$t_{\frac{1}{2}}$ 26 hours at 172°

in ethylene glycol[51]

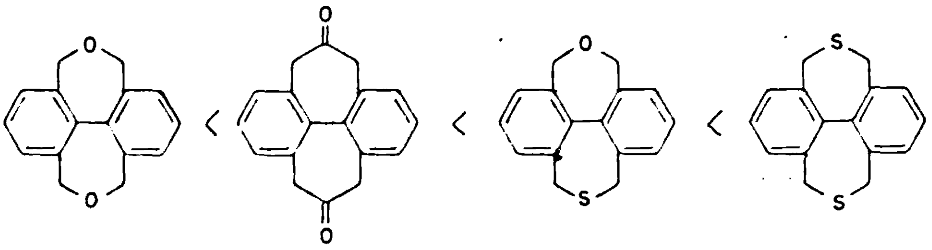
No change[51] after 8 hours

at 175°

although the -COOH group is not strictly comparable with the $-CH_2-$ group and there is the possibility that the compound racemises by the alternative route.

The decrease in activation energy can be explained by the fact that the change in dihedral angle in attaining the planar conformation will be less for the bridged compounds and therefore the molecular strain will also be less, provided that the deformations are equal in number and the force constants are similar. Mislow and his colleagues have found this to be so with doubly bridged compounds[23], thus:

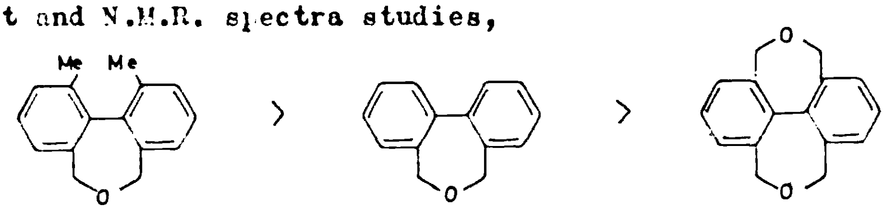
Dihedral angle (Calc)



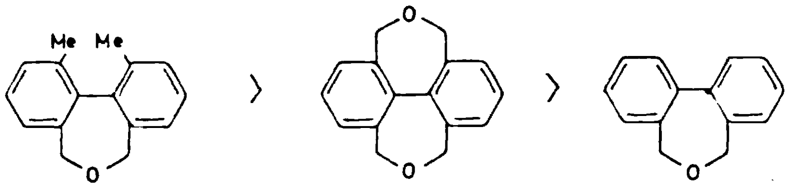
E_{act}	20.4	31.2	30.6	35.0
log A	12.1	14.5	13.5	12.2

N.M.R. studies for singly bridged biphenyls show a similar trend: the thiepin has the largest ground state angle and also shows the greatest conformational stability.

In the oxepin series, the order for dihedral angle is, from ultraviolet and N.M.R. spectra studies,



but optical stability runs

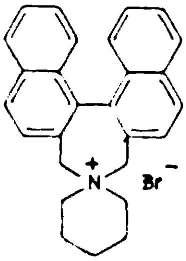


E_{act} 20	E_{act} 20.4	E_{act} 9.2
N.M.R. measurement[37*]	ref. 53	N.M.R. measurement[54]
		No optical stability at room temperature.

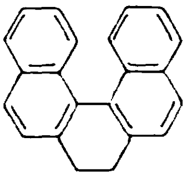
(* The E_{act} value quoted is considerably less than expected, and is unlikely to be the same as the doubly bridged oxepin which is much less optically stable)

This is because the numbers and kinds of deformation are different for singly and doubly bridged compounds.

As expected, it is found that lengthening the bridge from two to three atoms leads to considerable increase in optical stability, thus:



>



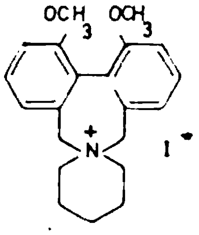
$t_{\frac{1}{2}}$ 26 hours at 172°[52]

$t_{\frac{1}{2}}$ 158 mins. at 110.5°[52]
E_{act} 30.8 Kcal/mole
log A 13.4 sec^{-1}
in dioxan, PhMe and PhEt

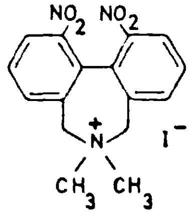
It seems that the interference of 6,6'- ortho substituents in biphenyls with a three atom 2,2' bridge follows the order

$$OCH_3 > NO_2 > F$$

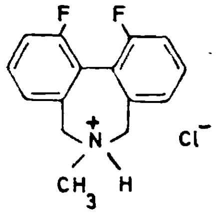
Since optical stability follows the order:



>



>



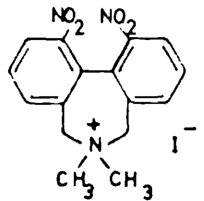
partly racemised after 8 hours at 160°[23]

$t_{\frac{1}{2}}$ 4.75 hours at 145°[47]

$t_{\frac{1}{2}}$ 6.5 hours at 80°[47]
E_{act} 27.8 Kcal/mole
log A 12.7 sec^{-1}
in aqueous HCl.

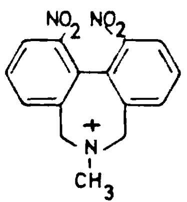
The dinitro-spiropiperidinium compound has been prepared by Mislow, Fitts and Siegel[55], but they give no racemisation data.

Hall and Ahmed~~[49]~~[41] found that the quaternary nitrogen compound is more stable than the corresponding tertiary compound:



$t_{\frac{1}{2}}$ 4.75 hours at 145°

>

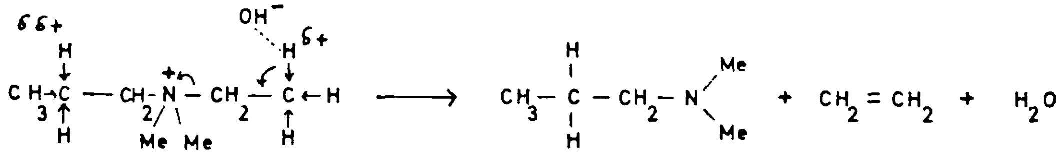


$t_{\frac{1}{2}}$ 16 hours at 125°

E_{act} = 30.0 Kcal/mole
log A 11.5 sec^{-1} in C_6H_6

HOFMANN DEGRADATION AND STEVENS'S REARRANGEMENT OF QUATERNARY AMMONIUM SALTS[56,57]

The conversion of a quaternary ammonium salt into an olefin, with the formation of a tertiary amine and water by elimination of the nitrogen atom and extraction of an adjoining hydrogen atom, was reported by Hofmann[57].



The general requirements for the Hofmann elimination reaction to occur in these compounds are:

1) a moderately strong base

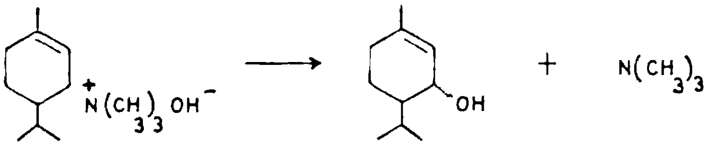
2) a β -hydrogen atom

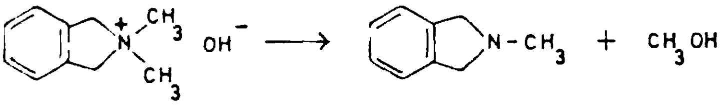
3) a positively charged nitrogen centre

The reaction proceeds normally if there are no α-hydrogen atoms, so these are not involved[58].

Side reactions competing with this elimination are:

1) a displacement reaction at the α-carbon atom by hydroxyl ion to form an alcohol and a tertiary amine.



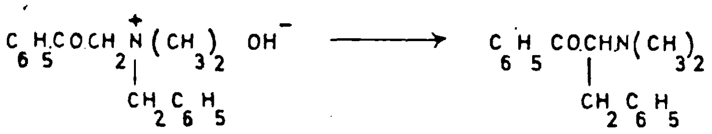


When anions less basic than hydroxide or alkoxide are used, e.g. carbonate, the displacement reaction increases in importance; therefore, to reduce this reaction, the solution should be protected from carbon dioxide.

2) in addition to alcohol formation, other hydroxyl groups may be alkylated to produce ethers.

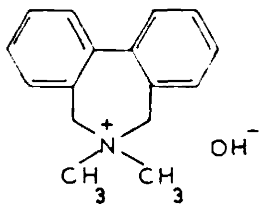
3) occasionally an allylic shift occurs in the olefin in order to give a conjugated unsaturated system.

4) molecular rearrangements may occur. When the normal elimination reaction cannot take place, e.g. there are no β-hydrogen atoms, Stevens's rearrangement is often observed.



$$C_6H_5COCH_2\overset{+}{N}(CH_3)_2(CH_2C_6H_5)\;OH^- \longrightarrow C_6H_5COCH(CH_2C_6H_5)N(CH_3)_2$$

This rearrangement has been shown to be intramolecular[59], and to take place in alkaline, but not neutral solutions. Hall and Poole[24] have investigated the degradation of some quaternary ephedrinium compounds and also 2,7-dihydro-1,1-dimethyl-3,4:5,6-dibenzazepinium hydroxide



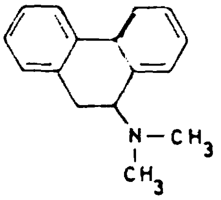
To test the effectiveness of the hydroxide ion in the Hofmann degradation of the last compound, they carried out the reaction under the following conditions:

<u>Expt. I</u> In an atmosphere of nitrogen, keeping the temperature lower than 135°.

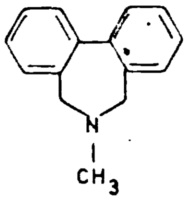
<u>Expt. II</u> Under similar conditions to expt. I, with added hydroxide.

Expt. I gave 9-dimethylamino-9,10-dihydrophenanthrene
2,7-dihydro-1-methyl-3,4:6-dibenzazepine (the result of OH$^-$ attack at the methyl α-carbon atom)
phenanthrene in 32-40% yield.

Expt. II gave 9-dimethylamino-9,10-dihydrophenanthrene
33% phenanthrene
no azepine.



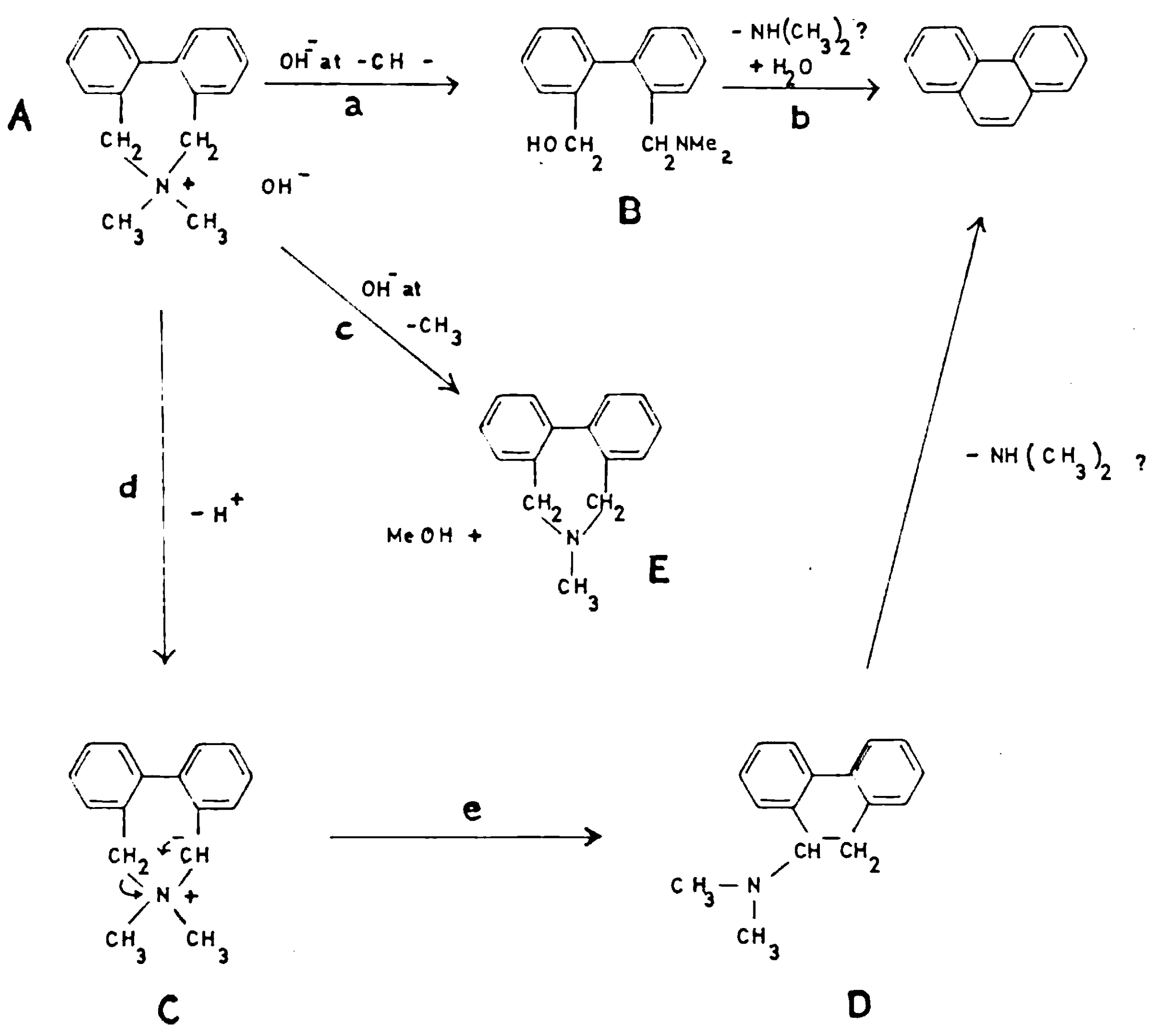
9-dimethylamino-9,10-dihydrophenanthrene



2,7-dihydro-1-methyl-3,4:5,6-dibenzazepine

Thus, the Stevens' rearrangement (which gives the aminodihydrophenanthrene) is favoured by high concentration of hydroxide ion, and, they found, also by high temperature. The amount of phenanthrene is unaffected and so may be expected to be formed by some method not dependent on the Stevens' rearrangement.

Azepinium hydrogen carbonate is formed from the hydroxide during working up, and this, when kept at 210° for 40 minutes gave 9-dimethylamino-9,10-dihydrophenanthrene. Hall and Poole thus found that the hydroxide ion from the decomposition of the hydrogen carbonate is a strong enough base to bring about Stevens' rearrangement at this temperature. However, although they isolated no phenanthrene or azepine, alkaline fumes were evolved and when heated for 3 hours, a


A
OH⁻ at -CH -
a
- NH(CH3)2 ?
+ H2O
b
HOCH2
CH2NMe2
B
OH⁻
OH⁻ at
-CH3
c
d
- H⁺
MeOH +
E
- NH(CH3)2 ?
e
C
D

non-basic fraction, amounting to 15% of the hydrogen carbonate was isolated, but not identified; there was sufficient only for an infrared spectrum. This is occurring at a much higher temperature than that used in the degradation.

Proposed mechanisms are given on the facing page. d,e represents the Stevens' rearrangement following removal of a proton. c is the competing hydroxide attack at the methyl α-carbon atom to form the tertiary amine and methyl alcohol.

The method of formation of the phenanthrene is far from clear. It is suggested that the proposed route a,b does not seem likely since the hydroxyamine B is unknown and the corresponding diol is stable to hot alkali. No oxepin was reported among the neutral products.

Elimination of dimethylamine appears to be involved, since an alkaline gas was evolved during the reaction, but the authors were unable to isolate it. The aminodihydrophenanthrene was found to be stable to heat and to alkali. Thus, the phenanthrene does not seem to arise from the Stevens' rearrangement product or intermediate, or from the competing hydroxide displacement reaction, but where the Hofmann elimination reaction cannot function, it has been found[60] that the nitrogen atom removes the shared electrons from a group without the help of a carbanion, and this group, having so formed a positive ion can then unite with a negative ion, in this case, hydroxide.

The products and relative proportions of the products seem to be delicately balanced, and concentration of carbon dioxide, pressure, temperature and concentration of reactants may be important.

After chlorinating 2,2'-bishydroxymethylbiphenyl, converting the mixture to the bisbromomethyl compounds and quaternising them with dimethylamine, a Hofmann degradation on the hydroxides yielded a mixture of phenanthrene, 1-2- and 3-chlorophenanthrenes (about 15%)[60]. This reaction is therefore a possible route to substituted phenanthrenes.

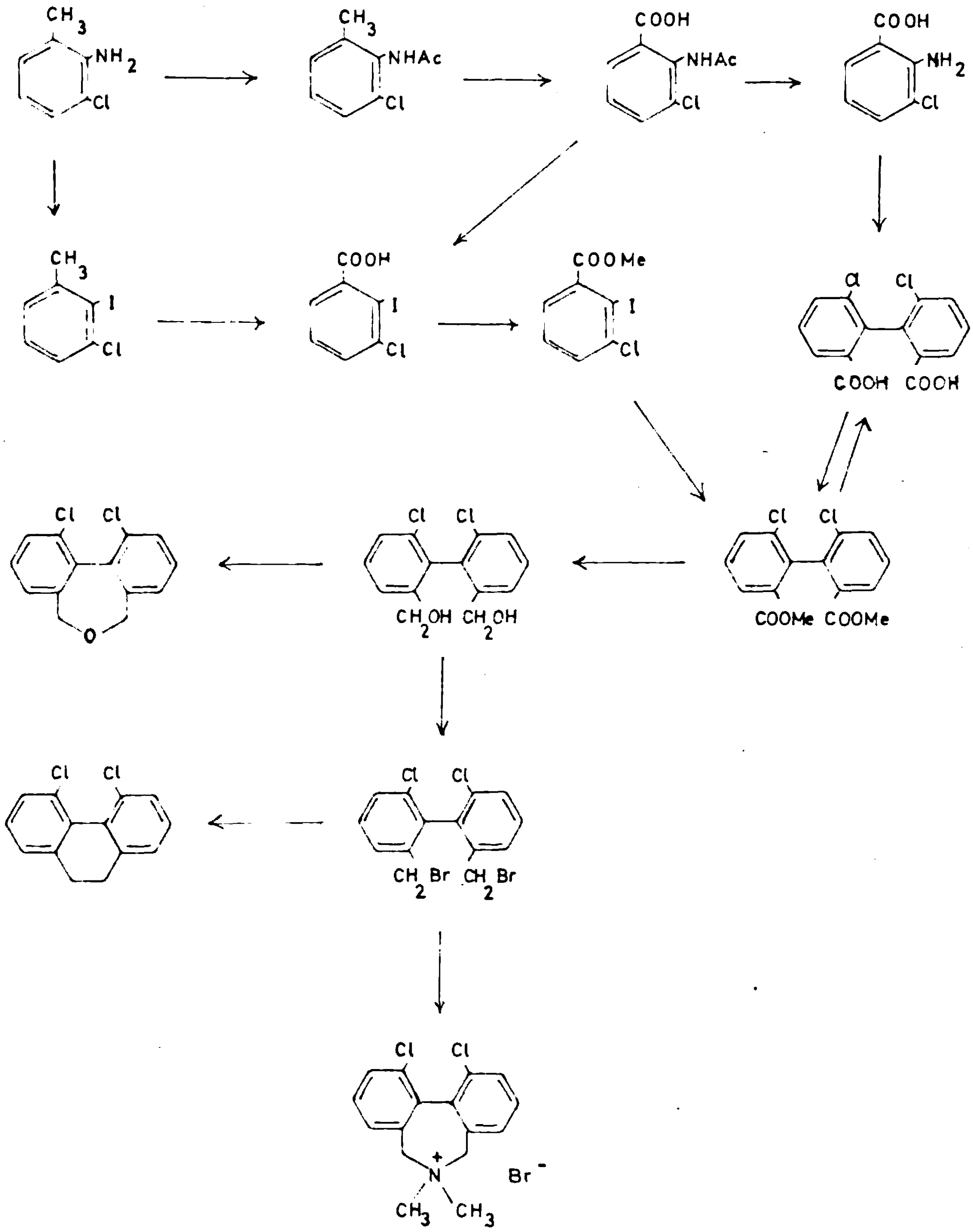
OBJECT OF THIS WORK

To prepare 6,6'-dichloro-2,2'-diphenic acid by a more convenient route than that of Christie, James and Kenner[61], and from this, to prepare and study some bridged biphenyls, substituted in the 6,6' positions with chlorine, and with 2- and 3- membered bridges. Preparation of optically active compounds, where possible, and determination of the Arrhenius parameters for their racemisation was intended. These, together with ultraviolet spectra and, where relevant, circular dichroism curves, would be compared with each other, and with those of differently substituted compounds.

A study of the infrared spectra of the compounds was made in the hope of revealing the position of the C-Cl stretching frequency in these compounds and to confirm, or otherwise, general assignments made for these types of compound.

It was hoped to confirm the results of Hall and Poole[24] obtained by decomposing 2,7-dihydro-1,1-dimethyl-3,4:5,6-dibenzazepinium hydroxide under Hofmann conditions, when a considerable yield of phenanthrene was obtained, and to investigate the possibility of using this as a preparative method for obtaining 4,5-substituted phenanthrenes, particularly 4,5-dichlorophenanthrene.

SCHEME OF REACTIONS



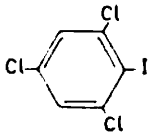
DISCUSSION

PREPARATION OF COMPOUNDS

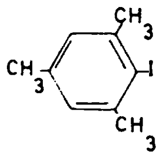
3-Chloro-2-iodo-toluene was prepared by diazotisation of the 2-amino- compound and addition of the diazo solution to warm potassium iodide solution. With cold iodide solution, a red intermediate was formed, which decomposed, sometimes explosively: when warm, the decomposition took place smoothly. The intermediate is possibly the diazonium iodide. Yields of up to 78% were obtained and altogether 565 g. of the compound were prepared. This compound has previously been prepared by Fieser and Cason[62] from 3-amino-2-iodo-toluene. They refer to a paper by Long and Dains[63] who report the preparation of the dihalide. From the evidence available, it seems likely that Long and Dains had not, in fact, obtained the pure dihalide.

The dihalogeno-toluene was oxidised to the acid with neutral potassium permanganate solution. The mixture was refluxed for ca. 33 hours, but little more than half the starting material had reacted. The product was separated from the starting material via the sodium salt. When the quantities of the reagents were increased, no more acid was produced than previously and the yields went down. Addition of hydrated magnesium sulphate had no effect. The greatest yield obtained was 45% and, in all 28 g. of the acid were prepared by this method. Christie, James and Kenner[61] have previously prepared this compound, but from 3-amino-2-iodo-benzoic acid. Because so little of the acid could be prepared in each reaction, i.e. up to 3 g., this method was abandoned, and alternative routes were tried. Attempts were made to prepare dichloroditolyl with a view to bromination by N-bromosuccinimide in order to obtain 6,6'-dichloro-2,2'-bisbromomethylbiphenyl. Another route to the 3-chloro-2-iodo-benzoic acid entailed making the acid before the introduction of the iodo- group by diazotisation, and thus the amino- group had to be protected by acetylation. (See scheme of reactions on page 44)

The Ullmann reaction on 3-chloro-2-iodo-toluene has not been included by Fanta[64] in his list of Ullmann reactions reported up to 1944, which is included in his survey of Ullmann synthesis of biaryls. The Ullmann reaction on this compound was unsuccessful. The reaction mixture was kept at ca.250° for two days and after distilling the extracted material under reduced pressure, oils and some solid were obtained. The oils appeared to be mixtures and all attempts to separate pure material from these failed. An attempt was made to purify the solid by crystallisation and column chromatography, but the product had a low melting point and melted over a range. A low yield of impure material indicates that this route is not preparatively useful. The reaction would be expected to be difficult, since the ortho chloro and methyl group will hinder the reaction sterically, thus:



gives 52.5% biaryl



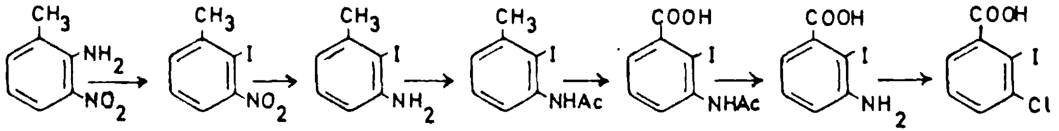
very poor yield

Also, the methyl group is not activating for the reaction. However, if pure material could easily have been obtained, even with a poor yield, this route might have proved more economical both in time and material than the many-stage scheme. Another method of making the dichloroditolyl was attempted, this time by a Grignard reaction and coupling of the Grignard reagent using anhydrous cobalt or cupric chloride. On fractionally distilling the products under reduced pressure, gums were obtained which were shown to be mixtures by thin layer chromatography. Recrystallisations were unsuccessful, and on further distillation, decomposition occurred, giving iodine vapour, showing that iodine had been retained in the molecule and that reaction had not been complete. The idea of a 'short cut' to the dichloro-bisbromomethyl compound was not pursued further, but the alternative route to the 3-chloro-2-iodo-benzoic acid was tried out and proved satisfactory. The acetylation of 2-amino-3-chloro-toluene gave yields of up to 92%. Bamberger[65] first reported this compound which he also prepared by acetylation of the amine. 1280G of acetylated amine were made.

Oxidation of the acetamido- compound by neutral potassium permanganate solution was fairly rapid and did not take longer than two hours. After the acid had been separated from the starting material via the sodium salt, yields of up to 80% were recorded, and altogether 830 g. were prepared. Bamberger[66] has previously prepared this compound by this method.

The hydrolysis was carried out with 35% sulphuric acid, since with 70% acid the sulphate precipitated and caused bumping. The 3-chloro-anthranilic acid was isolated using the method described by Baker, Schaub, Joseph, McEvoy and Williams[67], i.e. by bringing the solution to pH 4 and collecting the precipitate. They prepared the compound from 7-chloroisatin. It has also been reported by Hüber and Weiss[68] who reduced the nitro- compound, but they give melting point 148° compared with 190°. More recently, Dokunikhin[69] has reported its isolation as one of the products from the action of aluminium chloride on 2-chlorophenylisocyanate. The hydrolysis gave yields of up to 85% and 497 g. were prepared in all.

In order to prepare the 2-iodo compound, the 3-chloroanthranilic acid was diazotised by the method used by Wittig and Petri[70] for 2-amino-3-methoxy-benzoic acid. The diazo solution was added to hot potassium iodide solution, because then the decomposition took place rapidly and smoothly, without separation of any intermediate. Yields of up to 89% were recorded and 445 g. of the dihalogeno-acid were prepared. This compound has been prepared by Christie, James and Kenner[61] by the scheme:



and from this they also prepared the ester.

The methyl ester was prepared by refluxing the acid with methanol and concentrated sulphuric acid. A total of 404 g. was prepared and yields of 94% were obtained. A portion of the ester solidified on keeping, and, if required, more could be obtained solid by seeding, although solidification was rather slow. This compound has not previously been reported as a solid. The melting point is 35-36°.

The biphenyl was made by an Ullmann reaction similar to that by Christie, James and Kenner[61], but at a lower temperature. A total of 192 g. were prepared with yields of 90%. This high yield means that there can be little steric hindrance to the reaction, and also shows the activation by the COOMe group.

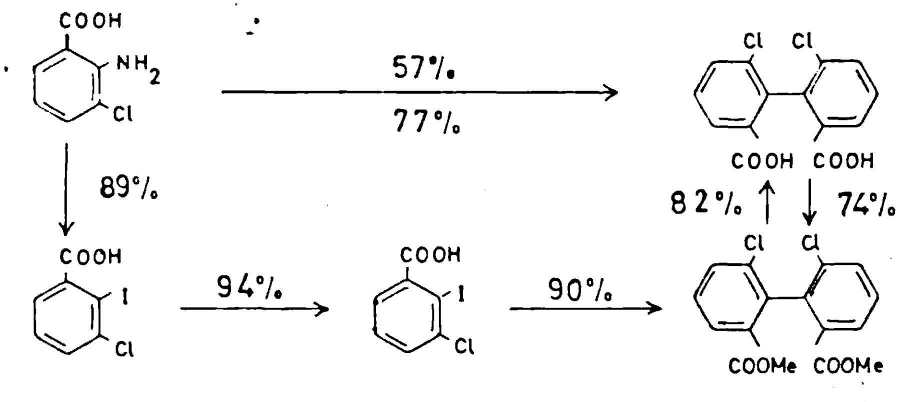
Hydrolysis of the di-ester gave an 82% yield of the diphenic acid, but most of the di-ester was used to prepare 6,6'-dichloro-2,2'-bishydroxymethylbiphenyl. When preparing the diphenic acid, it was possible that a shorter and more economical route could be by reduction of diazotised 3-chloro-anthranilic acid, so this was tried. The diazotisation was performed in the normal way and also by Wittig and Petri's method for 2-amino-3-methoxy-benzoic acid. Different reducing agents were used and the work closely followed that of Atkinson, Lawler, Heath, Kimball and Read[71] for diphenic acid. The results are shown in table 10. Atkinson and his co-workers also found that ammoniacal solutions of cuproammonium ion

Table 10

Expt.	Diazotisation	Catalyst	Product	Yield
1.	normal	Cuproammonium complex formed by reduction with sodium metabisulphite	Dichlorodiphenic acid	22%
2	"	More catalyst than 1	"	20%
3	Wittig & Petri	"	"	44%
4	normal	Cuproammonium ion formed by reduction with hydroxylamine	"	57%
5	" but with more water	Cuprous salts formed by reduction by hydroxylamine	mixture of dichlorodiphenic acid and 2,3-dichlorobenzoic acid	
	Method 4 was later repeated and gave a best yield of 77%			

are better reducing agents than those of cuprous ion in dilute hydroxylamine; and that the best method of forming these is by reduction with hydroxylamine. When they used solutions of cuprous ion in dilute hydroxylamine the yield of diphenic acid fell to 70% and they also obtained the Sandmeyer type product, but there seems a greater tendency to form this product with the 3-chloroanthranilic acid. A total of 32 g. of dichlorodiphenic acid was prepared by this method. Christie, James and Kenner[61] prepared the 6,6'-dichloro-2,2'-diphenic acid from the dimethyl ester; Fitts, Siegel and Mislow[72][55] have prepared it similarly. The dimethyl ester was prepared from the acid in 74% yield by refluxing with methanol and concentrated sulphuric acid. Fitts, Siegel and Mislow[55] have prepared the (-) ester from the (-) acid using ethereal diazomethane.

Yields for the steps in each route are as follows:



The overall yield in the 4-stage route to the diphenic acid is 62%, which is thus better than the 57% yield in the 1-step route, but not as good as the subsequent 77% yield. When preparing the dimethyl ester, the route using the Ullmann reaction is superior (75%).

6,6'-Dichloro-2,2'-bishydroxymethylbiphenyl was prepared from the dimethyl ester by reduction with lithium aluminium hydride and has been similarly prepared by Siegel and Mislow^{72}. Yields were up to 95% and 66 g. were prepared altogether.

The bishydroxymethyl compound was used to prepare the bisbromomethyl compound and the 2,2'-bridged compound 4',1",-dichloro-2,7-dihydro-3,4:5,6-dibenzoxepin. The oxepin was easily prepared by dehydration with concentrated sulphuric acid at a yield of 53% and 0.25 g. was prepared.

The bisbromomethyl compound was prepared using the method adopted by McGinn, Lazarus, Siegel, Ricci and Mislow^{73} for the (+) compound, and 61 g. were prepared with yields of up to 92%.

The dichloro-bisbromomethyl compound was treated with dimethylamine, giving the corresponding azepinium bromide. The first attempt gave a product which was considerably contaminated with dimethylammonium bromide. In subsequent preparations the product was dissolved in water and potassium hydroxide added to decompose the dimethylammonium bromide and precipitate the azepinium bromide. This procedure gave an improved product. The bisbromomethyl compound had a bad analysis and the azepinium bromide melted over a range, so the 4',1"-dichloro-2,7-dihydro-3,4:5,6-dibenzazepinium-1-<u>spiro</u>-1'"-piperidinium bromide was prepared because this has a known sharp melting point. The bisbromomethyl compound was treated with piperidine to give the spiro-piperidinium bromide, the method used by Fitts, Siegel and Mislow[55]. This had a good melting point and a subsequent analysis of the bisbromomethyl compound was very satisfactory. The analysis of the azepinium bromide closely agrees to that calculated for one molecule of water of crystallisation, and it seems likely that it dissolves in its water of crystallisation on heating, causing the wide-range melting point.

The azepinium bromide was sent away for biological testing and showed some in vitro antimicrobial activity against Staphylococcus Aureus.

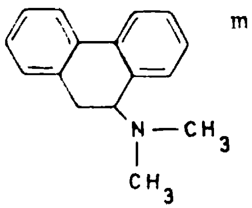
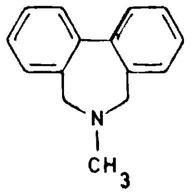
The bisbromomethyl- compound was also used to prepare 4,5-dichloro-9,10-dihydrophenanthrene, using phenyl-lithium. When equi-molecular proportions were used, a low yield of 12% resulted. Hall and Turner[74] obtained a similar yield when preparing the 4,5-dimethoxy- compound. The reaction is obviously sterically hindered since the unsubstituted compound gives dihydrophenanthrene in 80% yield. Another preparation using 1½ mols. of phenyl lithium gave a yield of 22%. Yet Mislow & Hopps[75], using optically active material and equimolecular proportions of reagents, prepared 4,5-dimethyl-9,10-dihydrophenanthrene in 30% yield. They maintained a temperature of 0–5° for a reaction time of one hour. Bergmann and Lelchowicz[76] have also prepared the dimethyl-dihydrophenanthrene using phenyl lithium and they report an 80% yield.

HOFMANN DEGRADATIONS OF THE AZEPINIUM COMPOUNDS

Before the dichloro-azepinium bromide was converted into the hydroxide and submitted to the conditions of Hofmann degradation, the work of Hall and Poole[24.] on the unsubstituted azepinium bromide was repeated. Starting with 2,2'-bishydroxymethylbiphenyl prepared by Poole, the bisbromomethyl compound and azepinium bromide were prepared. The azepinium bromide was converted into the hydroxide and the solution distilled under reduced pressure in an atmosphere of nitrogen. The products were separated into a water soluble fraction, a neutral ether soluble fraction and a basic ether soluble fraction. Attempts were made to separate the bases in the latter fraction by crystallisation of the picrates. Table 11, p.55 summarises the results. Out of the two experiments, one resulted in a little less, and the other in about the same yield of phenanthrene, the greater yield being 39%, (or 50% when calculated on the material which has reacted and considering the residue obtained from the aqueous solution to be the bicarbonate.) The infrared spectrum of the residue from evaporation of the aqueous solution differs from that obtained by Hall and Poole, but the compound was not identified. The aqueous residue from the dichloro- compound gave the azepinium bromide with effervescence when treated with hydrobromic acid. In both these and Hall and Poole's experiments, approximately the same yield of basic material was obtained, but a much greater proportion of the dimethylaminodihydrophenanthrene, 29%;

Table 11 COMPARISON WITH RESULTS OBTAINED BY D. M. HALL & T. M. POOLE

EXPERIMENT	WEIGHT OF AZEPINIUM BROMIDE	NEUTRAL ETHEREAL RESIDUE	BASES	PICRATES	PICRATES I	PICRATES II
D.M.HALL and T.M.POOLE						
1.	4.25 g.	0.989 g. 40%	1.320g.	2.155 g.	1.185g.	0.5795g.
2.	2.25 g.	0.438 g. 33%				
1.	5.00 g.	0.814 g. 22%	1.725g.	3.011 g.	2.16g.	trace
2.	5.00 g.	1.141 g. 39%	1.657g.	3.025 g.	2.19g.	
Residue from aqueous solution in expt. 2 1.063 g.		(50% on material which has reacted)				

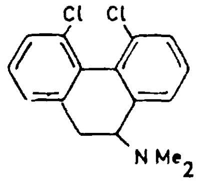
I picrate of  m.p. 175°-176° II picrate of  m.p.159°-161°

or calculating the yield on material which has, in fact, reacted, and not on the amount of azepinium bromide used, 38%, as against the 19% obtained by Hall and Poole. When Hall and Poole added potassium hydroxide, they obtained a 34% yield of phenanthrene and 38% yield of dimethylaminodihydrophenanthrene. The difference in the results obtained can be due to two factors: exclusion of carbon dioxide is known to reduce the displacement reaction[58] which gives the azepine product. Because the balance of the competing reactions may be easily disturbed, less carbon dioxide in the system may cause the greater ratio of dimethylaminodihydrophenanthrene to azepine (Hall and Poole's ratio 2:1; these results indicate a ratio of the order of at least 4:1). An alternative, or additional, reason could possibly be insufficient washing of the silver oxide in the preparation of the azepinium hydroxide and this would introduce hydroxide into the system. An indication of at least one other base was given: manual separation of two kinds of crystal found in one of the picrate crops gave products with only slightly different melting points, but a depressed mixed melting point. Not enough of either picrate was obtained for analysis. As with Hall and Poole's experiments, dimethylamine appears to have been evolved, for, on dismantling the apparatus, a smell similar to that of this gas was noticed.

The action of heat on 4',1"-dichloro-2,7-dihydro-1,1-dimethyl-3,4:5,6-dibenzazepinium hydroxide gave a much lower yield

Table 12 PRODUCTS OF HOFMANN DEGRADATION OF DICHLORO-AZEPINIUM HYDROXIDE

EXIT.	WT.USED	CONDITIONS PRESS. Temp. Time	AQUEOUS RESIDUE	WT REACTED	NEUTRAL ETHEREAL	BASES	SOLID AMINE	TOTAL PICRATE	PICRATES I	PICRATES II
1	5.006	23mm. 130-135° 15min	1.33	3.60	0.13	2.74	1.15	2.03	044	0.15
2	4.725	21mm. 140-145° 1 hr.	0.829	3.85	0.20	2.81	1.9	1.64	0.32	0.16
3a	5.421	13mm. 130-135° 1 hr.	4.16	1.04	0.02	0.21		0.6		0.12
3b	2.025	15mm. then 13mm. 140-145° 1 hr.	0.52	1.48	0.04	0.91		1.85	appeared mainly low-melting	

I 

picrate m.p. 212-213°

II unbridged biphenyl picrate m.p. 227-228°

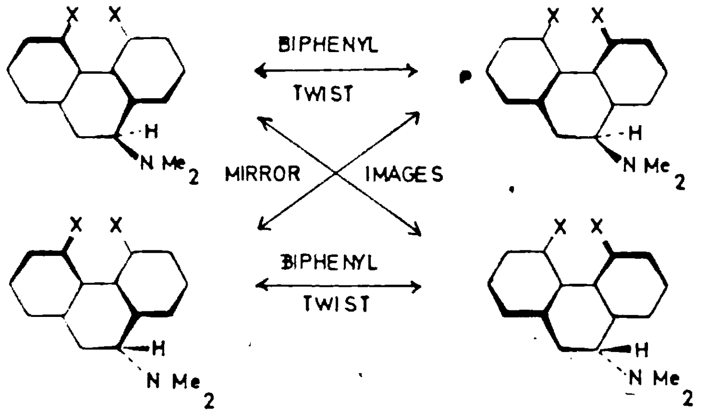
N.B. In 1 and 2, not all the base was turned into the picrate. The picrate of the amine that was obtained solid has m.p. 212-213°

The wt. reacted column is the actual weight of azepinium bromide that has reacted of the phenanthrene product (about 5%). As with the preparation of the dihydrophenanthrene, a lower yield would be expected, since the steric effect of the ortho chloro- groups would hinder the rings approaching closer to planarity to form the strained product. Poole[60] attempted to prepare substituted phenanthrenes by this method, and used a mixture of partially chlorinated material. Phenanthrene, 1-,2-, and 3-chlorophenanthrenes were obtained in about 15% yield. The substitution of chlorine into the aromatic nucleus would therefore appear to affect the yield of the phenanthrene product even though not in the sterically hindering 4,5-positions.

The neutral ethereal extract from the second Hofmann degradation of the dichloroazepinium compound was purified by column chromatography and gave 9 mg. of a second product, an oil. The infrared spectrum of this proved to be different from the phenanthrene, the starting material and the oxepin. The aromatic bands near 1610 cm.$^{-1}$(6.2μ) and 1590 cm.$^{-1}$(6.3μ) are very weak, if indeed present, and there are no strong bands lower than 1000 cm.$^{-1}$ (10.0μ) although less intense bands do occur in the 1000-650 cm.$^{-1}$(10.0-15.4μ) region. This, together with the fact that there is no band in the aromatic C-H stretching region suggests that the compound is aliphatic; the C-H stretching bands are close to the region for $-CH_2-$ stretching. There are bands in those positions assigned to $-CH_2-$ scissors, CH_3 CH asymmetric and symmetric bending, and methyl rock. A strong band at 1712 cm.$^{-1}$ (5.86μ) indicates the possibility of a carbonyl group.

Part of the basic material which was separated from the reaction products went solid, but proved to be a mixture. A specimen of one amine was separated and had m.p.101-102°; the other could not be obtained pure but the melting point is indicated to be in the region of 118°. The major amine product proved, from the ultra violet spectrum of the picrate (I), to be the 6-membered ring amine, 4,5-dichloro-9-dimethylamino-9,10-dihydrophenanthrene, picrate melting point 212-213°.

9-Dimethylamino-9,10-dihydrophenanthrene has a centre of asymmetry at the 9-carbon atom, therefore there are four possible isomers. This possibility does not arise with the symmetrically bridged azepine,

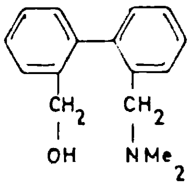


In the unsubstituted compound, the molecule will readily twist and the isomers will not be able to be isolated. Mislow and Joshua[77] have found that reaction of (+)S-4',1"-dimethyl-2,7-dihydro-3,4:5,6-dibenzazepinium ion with phenyl-lithium resulted in either (+)-S or (-)-R 4,5-dimethyl-9-dimethylamino-9,10-dihydrophenanthrene from second order asymmetric transformation. When the azepinium compound is treated with potassium hydroxide, the identical product is obtained[77]. They concluded that the reaction is highly stereospecific with respect to the configuration at C-9, although the sign of this had not been fixed, and consider the configuration at this position to be an important factor in the Stevens Rearrangement. The contribution of C-9 to the rotation was found to be negligible and the twist of the biphenyl the essential factor. When they treated 4',1"-dimethyl-azepinium compound with the strong base potassium amide in liquid ammonia[77], the phenanthrene and dihydrophenanthrene were produced; the former gradually being converted to the latter, which is eventually the sole product. As yet, no mechanism has been suggested for this. No dihydrophenanthrene has been isolated in the reaction with hydroxyl ions.

The second amine obtained in the Hofmann degradation of the dichloro- compound was shown by the ultraviolet spectrum to be an unbridged biphenyl (see page 153). The base was prepared from the picrate (II) as an oil, and could not be induced to solidify. The picrates of the bases also provided a very small amount of a higher melting picrate (III): m.p. 232-240° compared with 212-213° of dichloro-9-dimethylaminodihydrophenanthrene picrate (I) and m.p. 227-228° of the unbridged biphenyl picrate (II). Not enough of the higher melting amine (m.p. ca.118) was obtained to prepare the picrate for comparison, nor was there enough of the higher melting picrate (III) to purify and identify it. The infrared spectrum of this picrate (III) confirmed that it was different from the lower melting picrates, although, as expected, the spectrum showed a great many similarities; there are also two weak bands in the OH stretching region. Yet another very small crop of picrates had m.p. 146-185°, and although obviously impure, had a different infrared spectrum from the three picrates previously mentioned, nor did it appear to be mixtures of them. A subsequent reaction gave a picrate (IV) with m.p. 157-158° and it is possible that the picrate with m.p. 148-185° is a mixture of this and a higher melting picrate. Thus, besides the two main amine products, there are small amounts of at least two others, and this makes the separation of the picrates difficult. The isomers of the 9-dimethylamino- compound are very similar and if the other picrates are due to these, this would also hinder separation.

The first experiment gave a 40% yield of solid amine; predominately the 9-dimethylaminodihydrophenanthrene, for when the picrate of this was prepared, a good yield of pure picrate of m.p. 212-213° was easily obtained.

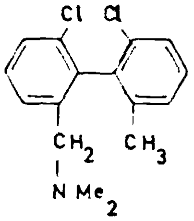
Similarly, the second reaction gave 63% yield of solid amine. It proved very difficult to separate the remaining bases by fractional crystallisation, but the dichlorodimethylaminodihydrophenanthrene appeared to predominate. This has the more soluble picrate, and although a greater amount of the pure unbridged amine was separated, the major component of the crops of mixed picrates remaining appeared to be the 9-dimethylamino- compound. This preponderance of the 9-dimethylaminodihydrophenanthrene, as in the reaction on the unsubstituted compound, may be the result of a high degree of success in elimination of carbon dioxide from the reaction or else, (or in addition), inclusion of potassium hydroxide through insufficient washing of the silver oxide during the preparation of the azepinium hydroxide, although this usually leads to the production of the azepine and thence to the 1-monomethyl azepinium picrate. It is possible that the steric effect of the chlorine atoms keeps the phenyl rings twisted after an attack on one of the bridging ring atoms, since no unbridged product was isolated in the reaction on the unsubstituted product. However, the 6-membered ring compound, the dimethylaminodihydrophenanthrene has been formed in considerable yield. Apart from an increase in strain in forming a 6-membered ring, the bridging ring may be distorted so that ease of attack in the different positions is altered. Attack of OH^- at one of the $-CH_2-$ groups has been envisaged as a primary step in the formation of phenanthrene. The product, an hydroxyamine,



has not been isolated and its participation in the reaction is yet to be proved. However, it is the only unbridged structure which has been put forward in the proposed modes of attack in this reaction[24].

The unbridged amine picrate isolated from the action of heat on the dichloro-azepinium hydroxide shows no bands in the infrared spectrum which can be assigned to -OH stretching. The analysis of the picrate agrees well with a formula of $C_{22}H_{20}Cl_2N_4O_7$: found C, 50.3; H,3.8; Cl,13.65; N, 10.5; O (by subtraction) 21.75; $C_{22}H_{20}Cl_2N_4O_7$ required C, 50.5; H, 3.85; Cl, 13.55; N, 10.7; O, 21.4. The hydroxyamine, with a formula of $C_{22}H_{20}Cl_2N_4O_8$ would require C, 49.0; H, 3.7; Cl, 13.15; N, 10.4; O, 23.7.

Taking the formula of the picrate as $C_{22}H_{20}Cl_2N_4O_7$, the amine would have the formula $C_{16}H_{17}Cl_2N$ and the most obvious compound is one with the structure



The process whereby such a compound could be formed is far from clear, but it is possible that the reaction path competes with that to the azepine, since none of this was isolated (or if so, only in quantities too small for identification). Thus, the facts known about the compound are: the amine picrate has m.p. 227-228°. The free base can be liberated from the picrate and neither the hydrochloride made from this, nor the picrate, show a conjugation band in the ultraviolet spectrum. Thus, the amine would appear to be an unbridged biphenyl. The infrared spectrum shows no bands in the OH stretching region and the analysis agrees well with the formula $C_{16}H_{17}Cl_2N$ for the amine; therefore it cannot be the hydroxyamine proposed as an intermediate in phenanthrene formation. In the complicated picrate infrared spectrum it is possible to pick out bands which could be due to methyl CH stretching vibration, but these cannot be categorically assigned to such vibrations. The suggested structure has not been proved and the mechanism of its formation obscure.

The second experiment was carried out at a higher temperature (140-145° instead of 130-135°) and increased temperature is considered to favour the Stevens rearrangement. Hall and Poole obtained solely the 9-dimethylamino-compound when they decomposed the unsubstituted quaternary hydrogen carbonate at 210°, even though the presence of carbon dioxide usually increases the nucleophilic displacement reaction at the methyl carbon atom to give the azepine, and, at lower temperatures, effectively reduces the concentration of hydroxyl ion. Neither did they detect any phenanthrene, which indicates (together with the fact that increased hydroxyl concentration does not increase the yield of phenanthrene) that for the azepinium compounds, the phenanthrene is not being produced by the same route as the 9-dimethylamino-compound, i.e. proton loss at the benzyl α-carbon atom. Mechanisms proposed by Hall and Poole have been given on page 40 and they suggest nucleophilic displacement at the benzyl α-carbon by hydroxyl ion to give a hydroxyamine, followed by elimination of dimethylamine as the route to the phenanthrene product. However, increased hydroxyl ion should also increase the displacement. A lower temperature might be expected to increase formation of phenanthrene, since a high temperature favours the competing Stevens rearrangement. The temperature differences in the reactions on the dichloro- compounds seem to have made little difference in the proportions of the products.

Optically Active Compounds

Resolution of the 6,6'-dichlorodiphenic acid was easily carried out by fractional crystallisation of the brucine salt and a good yield was obtained. At first, readings were taken in a non-jacketed tube at room temperature (in 0.1 NaOH). After crystallisation of the regenerated acid, the rotation was lower, and so readings were taken in a jacketed tube to determine whether racemisation was occurring. When readings were taken at a lower temperature, higher values were obtained, showing that the rotation is highly temperature dependent, (see Table 13 , Graph 1 , pages 200 and 201). The rotation changes sign at about 57°, At room temperature, the specific rotation changes approximately 1° fpr every degree in temperature (about 4% change). However, there is not a straight line relationship between the two. It is obviously important to know the temperature of the solution when measuring the rotation in order to determine the optical purity of the compound.

(+)-R-6,6'-dichloro-2,2'-bishydroxymethylbiphenyl was prepared by the method used for the racemic compound. A gum resulted, even after retreatment with lithium aluminium hydride, and this was eventually induced to solidify. Mislow and Siegel[72] have also prepared this compound and the values of the melting point and rotation agree well with theirs (m.p. 104.5-106; $[\alpha]^{20.2}_{5461}$ + 175, c 0.54 in benzene). Readings at different temperatures showed that the rotation (in benzene) was temperature dependent (Table 14, Graph 2 , pages 202 and 203,) and that when the solution is heated, the rotation does not decrease as much as would be expected if the only effect were expansion of the solvent. At room temperature, the specific rotation changes about a degree for every degree change in temperature (about 0.5% of the total value). There appears to be a straight line relationship between the two, but there is a change in the slope close to 40°C, the gradient above 40° being about half that below 40°. Dependence of specific rotation on temperature can be due to change in association and to change in the populations of different conformations. In these cases, it may be that a change in hydrogen bonding is causing a change in the dihedral angle of the biphenyls. Attempts were made to measure the circular dichroism spectrum of the diol at different temperatures in order to elucidate this effect. However, it was found that the compound is unsuited to this type of measurement, since it absorbs too strongly to enable meaningful deflections to be observed or the appropriate wavelength range to be covered. Changes in the association would show up in the OH stretching frequency in the infrared region and measurements of this spectrum at different temperatures could give useful information.

The oxepin was made from the diol and easily solidified. Rotations were measured at different temperatures and the solution in benzene was not found to be temperature dependent apart from the normal slight alteration due to expansion of the solvent. The specific rotation was $[\alpha]_{5461}^{16.2}$-391° (benzene,c 0.77), $[\alpha]_{5461}^{18.2}$-369° (2-phenylethanol, c0.60) and the latter solvent was used when recemising the oxepin. The C.D. spectrum confirmed the R configuration for the compound[23,26].

The optically active bisbromomethyl compound was also made from the diol by the method used for the racemic compound, except that the reaction was carried out on a water bath to avoid racemisation. The reaction was incomplete, and the resulting gum was retreated with hydrobromic acid giving a good yield of the bromo- compound. The melting point and rotation (m.p. 70-71°; $[\alpha]_{5461}^{20.0}$+93°,c 0.99 in benzene) agree well with those quoted in the literature[73]. The compound was shown to have a temperature-dependent rotation (in benzene) the observed value being slightly higher than that expected when the temperature is increased.

A small amount of the bisbromomethyl- compound was used in an unsuccessful attempt to prepare active 4,5-dichloro-9,10-dihydrophenanthrene. However, there was an indication of some material with a negative rotation besides the dextrorotatory dibromide. Work on separating the products is still in progress.

The rest of the dichlorobisbromomethyl compound was used to prepare the azepinium bromide, which, like the oxepin, has a negative rotation at room temperature and at the wavelength of the mercury green line; $[\alpha]^{20.2}_{5461}$ -160° (c 0.972 in chloroform) and $[\alpha]^{18.5}_{5461}$-300° (c 0.965 in 2-phenylethanol). The rotation of the solution in chloroform was found to be temperature dependent to an extent slightly less than that of the diol in benzene, but the rotations are nearer zero than expected when the temperature is increased. Thus, the ion of the diphenic acid has a lower positive rotation, the diol and dibromide a higher positive rotation, and the ionic azepinium bromide a smaller negative rotation than expected when the temperature is raised. The temperature dependence of rotation found in these compounds is expected to be due to changes in association, hydrogen bonding and conformation of the biphenyl. It is interesting that the rotation of the azepinium bromide also shows temperature dependence in spite of the fact that the dihedral angle of the biphenyl skeleton is maintained at a fairly constant angle by the bridge. That this compound is ionic may explain the temperature dependence of rotation as compared to that of the oxepin. The rotation of the diphenic acid is measured on the ionised compound and this shows strongly temperature-dependent behaviour. The diol is hydrogen bonded, and the bisbromomethyl compound also contains an electronegative element. The solvent is also likely to enter into this temperature dependent effect.

The (-) oxepin and (-) azepinium bromide were racemised in 2-phenylethanol. This has a high boiling point, 219-221°, but turns yellow when heated in air. The racemisations had, therefore, to be carried out under an atmosphere of nitrogen. The two bridged compounds turned out to have high rotations in this solvent and this was another advantage. The activation energy was calculated from the log k and $10^3/T$ values, using the method of least squares and graphically from the log k vs. $10^3/T$ plot. The results obtained are shown below:

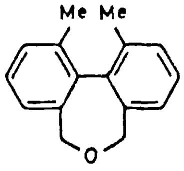
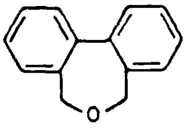
	E(Kcal.mole^{-1})		log A sec.$^{-1}$)	$\Delta S^{\ddagger}$ (e.u.)
	Calc.	Graphically		
oxepin	34.8±0.1	34.8	13.3	-0.5
azepinium bromide	38.3±0.2	38.3	13.5	+0.4

Error given is in log k vs. $10^3/T$ plot

The increase in activation energy in going from the oxepin to the azepinium bromide reflects the increase in dihedral angle , as found by Mislow and his co-workers[23]. There is little difference in the frequency factors, which are in the expected range for singly bridged biphenyls (12 - 15). The entropy changes in going to the transition state are very slight.

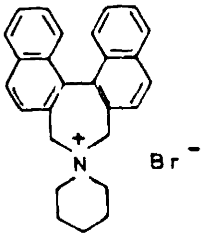
The most similar compound to the dichloro-azepinium bromide whose racemisation data have been measured is the difluoro-azepinium chloride[47] (p.32). The ring is slightly different, since there is only one methyl group attached to the quaternary nitrogen. Values given are E_{act} 27.8 Kcal./mole, log A 12.7 sec.$^{-1}$ and $\Delta S^{\ddagger}$ -2.9 e.u., measured in dilute hydrochloric acid. There is therefore a considerably greater activation energy and a noticeable increase in frequency factor in the dichloro- compound. The former leads to increase in stability and the latter to decrease of stability. It is conceivable that the greater mesomeric effect of the chlorine would be more favourable to a planar conformation of the biphenyl skeleton, thus tending to facilitate racemisation.

Apart from Mislow's doubly bridged oxepin, the only reports of racemisation data on such compounds are concerning the unsubstituted compound and the dimethyl oxepin. Both of these have been submitted to N.M.R. spectrum analysis only, although a value for the activation energy of the unsubstituted compound has been calculated and is in agreement with that obtained by the N.M.R. method.

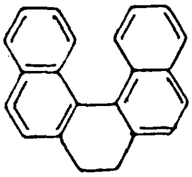
	E_{act}	log A	$\Delta S^{\ddagger}$	ref.
	20			37
	Not racemised < 100°			
	9.6		2.5	37
	9.3 calc.			54

The value of 20 Kcal./mole for the dimethyl oxepin seems unlikely and is presumably the lower limit for the activation energy. If this is calculated using a value of 12 for log A, the limit may well be higher, since the average value of log A for singly bridged biphenyls is closer to 13. In any case, assuming a normal frequency factor, an activation energy of 20 Kcal/mole seems low for a compound which is so optically stable.

It is found that lengthening the bridge leads to an increase in optical stability, e.g.[52, 51]



>



$t_{\frac{1}{2}}$ 26 hours at 172°
in ethylene glycol

$t_{\frac{1}{2}}$ 158 mins at 110.5°
E_{act} 30.8 Kcal/mole log A 13.4 sec^{-1}

The dimethyl oxepin is at least as stable as the 2-atom bridged binathphyl, since it is not racemised below 100°. The dimethyl-dihydrophenanthrene has an activation energy of 23.1 Kcal/mole and log A 12.8 sec^{-1} and it is more than likely that the oxepin, which is certainly more optically stable than the dihydrophenanthrene, will have a greater activation energy.

In unbridged biphenyls, it is found that the methyl group confers greater optical stability than the chloro- group[42] (see p. 28). But stability of substituted biphenyls with a three membered bridge need not be the same as an unbridged biphenyl.

e.g. bridged $OCH_3 > NO_2 > F$

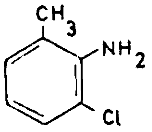
unbridged $NO_2 \gg OCH_3 > F$

One ortho nitro group in the oxepin gives a compound which is well suited to N.M.R. spectrum analysis at different temperatures. Oki, Iwamura and Hayakawa[37] have made measurements on this compound and give an activation energy of 16.5 ± 0.7 Kcal/mole and log A 12.8 ± 0.4 sec^{-1}. The dimethyl compound would be expected to be considerably more optically stable, with a higher activation energy. Thus the suggested value of 20 Kcal./mole would appear, from most considerations, to be rather low, and it is assumed that this is the lower limit. However, there is no evidence that the dimethyl bridged biphenyls should be more stable that the dichloro analogues, as is the case with unbridged compounds. The N.M.R. measurements were made in carbon disulphide and variations due to solvent are usually slight, although they can sometimes be large.

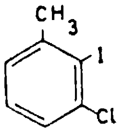
In this case, the N.M.R. data cannot be giving the activation energy for inversion of configuration and the protons may attain magnetic equivalence by some other process.

COMPOUNDS

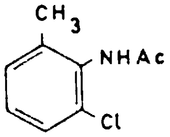
B 1



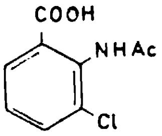
B 2



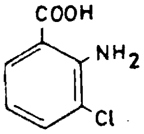
B 3



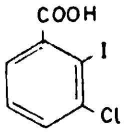
B4



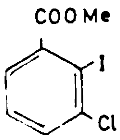
B 5



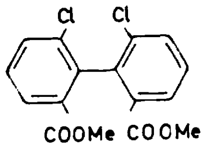
B 6



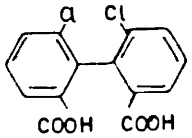
B 7



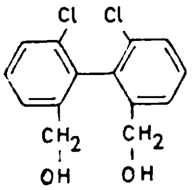
B P 1



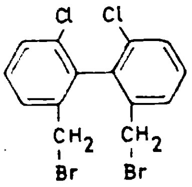
BP2



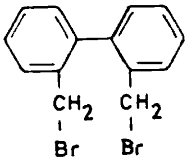
BP 3



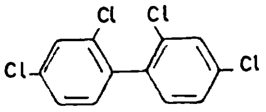
BP4



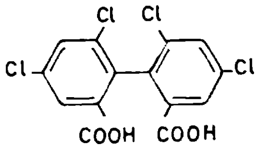
BP5



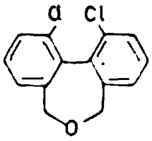
BP 6



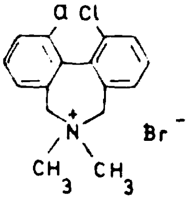
B P 7



BB 1

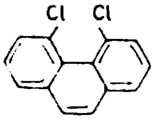


BB 2

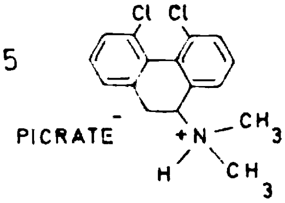


BB 3 " PICRATE⁻

BB 4

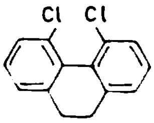


BB 5

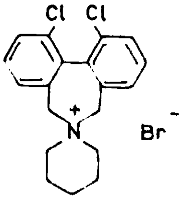


BB6 UNBRIDGED BIPHENYLAMINE PICRATE

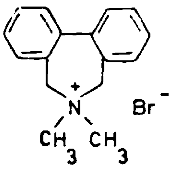
BB 7



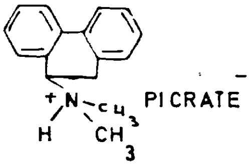
BB 8



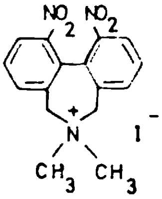
BB 9



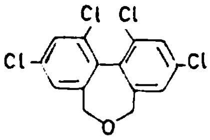
BB 10



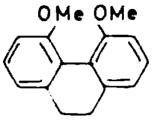
BB 11



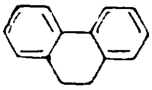
BB 12



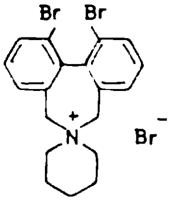
BB 13



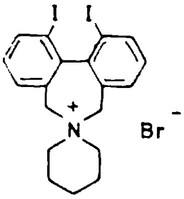
BB 14



BB 15



BB 16



INFRARED SPECTRA

The assignments of the infrared absorption bands have been made with reference to "The Infrared Spectra of Complex Molecules" by L. J. Bellamy, "Chemical Applications of Infrared Spectroscopy" by C. N. R. Rao, and R. N. Jones and C. Sandorfy's chapter on "The Applications of Infrared and Raman Spectra to the Elucidation of Molecular Structure" in "Techniques of Organic Chemistry" Vol. IX, chapter IV. General assignments have been made which correspond with the ranges given by these authors and by Cross ("Introduction to Practical Infrared Spectroscopy"), together with supplementary references where necessary. Points of interest or bands occurring outside the given ranges are noted.

Since many of the compounds prepared had Cl in similar environments, it was conceivable that the position of the C-Cl stretching frequency could be elucidated. Unfortunately, this position overlaps those of the substitution pattern in the 810-680 cm.$^{-1}$ region and some of the compounds also show absorption here due to other groups. Two bands are expected for the aromatic CH deformation pattern in vicinal tri-substituted benzene compounds and one for the C-Cl stretch. Some spectra did not show enough bands in the regions quoted in the literature and therefore a wider range, or superposition of two or more bands must be considered. The spectra of differently substituted and unsubstituted compounds were run for comparison.

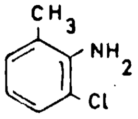
Compounds prepared by other workers have been noted at the end of this section.

Compounds have been grouped into three types, and given letters to designate the group, namely substituted benzenes, (B), biphenyls (BP) and bridged biphenyls (BB). The compounds are numbered within these groups. Optically active compounds are shown by the sign of the rotation at the frequency of the mercury green line.

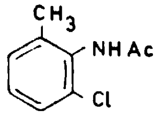
The spectra were measured on a Grubb-Parsons G S 2A double beam recording spectrophotometer and are linear in wavelength. The positions of the bands are given as the frequency in cm.$^{-1}$; the wavelength in μ is given in brackets. The spectrum of B1 was measured on the liquid; the rest of the compounds were examined as mulls in Nujol and hexachlorobutadiene. The spectra shown in the diagrams at the end of this section are composite spectra, with the hexachlorobutadiene measurement inserted in the Nujol absorption regions. Also at the end of this section are tables of bands, with their probable assignments, and of unassigned bands of strong to medium intensity. Strong, medium or weak bands are indicated by s, m or w and shoulder is abbreviated to sh.

$C\text{-}CH_3$ group

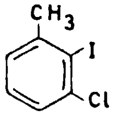
C-H stretch



B1



B3

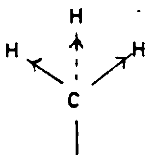


B2

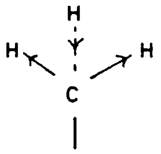
In this region there are bands at:-

2967 (3.37) w	2950 (3.39) w	2976 (3.36) w.
2924 (3.42) m		2950 (3.39) w
2915 (3.43) m	2915 (3.43) w	2915 (3.43) w
sh.2890 (3.46)		
2849 (3.51) w	2845 (3.515) v.w.	2849 (3.51) v.w.
	2813 (3.555) w	

There are, here, four bands in the methyl-C-H stretching region of 3000-2800 cm.$^{-1}$. Four bands might be expected in the case of B3, where there are two methyl groups in different environments, but the bands in the spectra of B1 and B2 should be due only to methyl together with any overtones or combination bands, since the aromatic C-H stretching usually occurs at a higher frequency. Bands occur in all three compounds at 2915 (3.43) and near 2849 (3.51). It is possible that these are due to the asymmetrical and symmetrical C-H stretching vibration;



symmetrical stretch



asymmetrical stretch

Jones and Sandorfy give 2930-2920 cm.$^{-1}$ (3.415-3.425 μ) and 2880-2860 cm.$^{-1}$ (3.47-3.50 μ) for the asymmetrical and symmetrical stretching respectively of a methyl group attached to a benzene ring in liquid alkylbenzenes and the frequency is likely to be slightly lower for the solid. Fox and Martin[78] have found that the lower frequency band is split when a double band is adjacent to the methyl group. They also noted two weaker intermediate bands in some of the hydrocarbons they studied.

Friedman[79] shows that most monomethyl- and dimethyl-naphthalenes show five bands in the methyl CH stretching regions close to:

2975 cm^{-1}	(3.36 μ)
2945	(3.395)
2925	(3.42)
2865	(3.49)
2735	(3.66)

These bands are in the same general positions as those in B1, B2 and B3. A weak band close to 2735 cm^{-1} (3.66μ) also occurs in the spectra of these compounds, as in many of the others studied here.

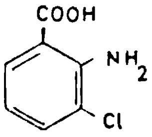
CH_3 deformations

B1	B3	B2
sh 1473 (6.79)	1468 (6.83) m	sh 1462 (6.84)
1468 (6.81) vs	1456 (6.87) m	
1441 (6.94) s	1443 (6.93) m	1445 (6.92) vs
1433 (6.98) s		
		1393 (7,18) w
1376 (7.27) w	1370 (7.30) m	1376 (7.27) w

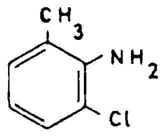
These bands occur close to the methyl deformation absorption region;

1470-1420 cm.$^{-1}$ (6.80-7.04 μ) for the asymmetric bending mode and 1385-1375 cm.$^{-1}$ (7.22-7.27 μ) for the symmetrical vibration. The 1445 cm.$^{-1}$ (6.92 μ) band in B2, which is assigned to the asymmetric bending vibration, is much stronger than the 1376 cm.$^{-1}$ (7.27 μ) symmetric bending absorption although the reverse is expected. Bands occur in similar positions in the other compounds at 1441 cm.$^{-1}$(6.94 μ) and 1443 cm.$^{-1}$ (6.93 μ). The symmetrical vibration appears at 1376 and 1370 cm.$^{-1}$ (7.27 and 7.30 μ). One of the higher frequency bands (near 1460 or 1470cm^{-1}) is likely to be due to a c=c in-plane vibration and the shoulder at 1473 cm.$^{-1}$ (6.79 μ) has tentatively been assigned to this.

-NH$_2$ group



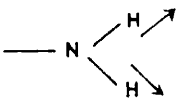
B5



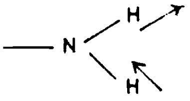
B1

The -NH$_2$ group gives rise to two absorption bands in the NH stretching region, 3500-3300 cm.$^{-1}$ (3.03-2.86 μ), due to the symmetric and asymmetric stretching.

symmetrical stretching



asymmetrical stretching



In B5, these occur at 3480 and 3365 cm.$^{-1}$ (2.87 and 2.97 μ) and in B1 at 3475 and 3380 cm.$^{-1}$ (2.88 and 2.96 μ), well within the given region. Anthranilic acid [80] absorbs at 3497 and 3390 cm.$^{-1}$(2.86 and 2.95 μ). The asymmetric stretching gives rise to the band of higher frequency.

Associated N–H absorbs in the region 3400–3100 cm.$^{-1}$ (2.94–3.23 μ). The compound B1 does show two weak bands at 3226 and 3195 cm.$^{-1}$ (3.10 and 3.13 μ) which may be attributed to such association. These bands cannot be distinguished in B5 because they come in the –OH stretching region of the –COOH group.

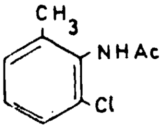
The NH scissors bending mode 1650–1580 cm.$^{-1}$ (6.06–6.33 μ) is a moderately strong band but the correlation is based on a limited range and, in some compounds, is hidden beneath the aromatic ring vibration near 1600 cm.$^{-1}$. It seems likely that the bands at 1616 cm.$^{-1}$ (6.19 μ) in B1 and 1610 cm.$^{-1}$ (6.21 μ) in B5 are due to the NH deformations. Anthranilic acid is assigned a band at 1618 cm.$^{-1}$ (6.18 μ) for this vibration, very close to both of these.

The C–N stretching mode for a primary aromatic amine gives rise to a strong band in the region 1340–1250 cm.$^{-1}$ (7.46–8.00 μ), but this cannot be assigned in these compounds since there are three strong bands:

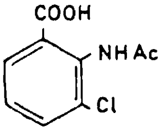
B5	B1
1312 (7.62)	1307 (7.65)
1272 (7.86)	1280 (7.81)
1250 (8.00)	1247 (8.02)

in this region in both compounds.

-NHAc group



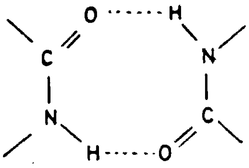
B3



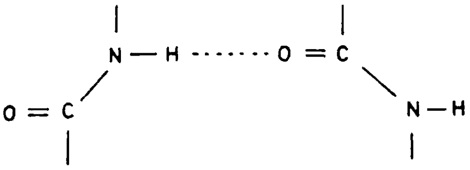
B4

The NH stretching frequency in amido acids shows up as a medium band in the region 3390-3260 cm.$^{-1}$ (2.95-3.07 μ). The range is lower than in secondary amides with a free NH because of hydrogen bonding, and is closer to the NH stretch in associated amides. Secondary amides absorb in the following regions:

Free NH	cis	3440-3420 cm.$^{-1}$	(2.91-2.93 μ)	strong
	trans	3460-3440 cm.$^{-1}$	(2.89-2.91 μ)	strong
Bonded NH	trans	3320-3270 cm.$^{-1}$	(3.01-3.06 μ)	medium
	cis	3180-3140 cm.$^{-1}$	(3.15-3.19 μ)	medium
cis and trans		3100-3070 cm.$^{-1}$	(3.23-3.26 μ)	weak



cis linked



trans linked

B4 has bands at 3257 cm.$^{-1}$ (3.07 μ) and B3 at 3226 cm.$^{-1}$ (3.10 μ)s

sh 3226 (3.10 μ) sh 3185 (3.14 μ)

3165 (3.16 μ) w 3115 (3.21 μ)w

3106 (3.22 μ) w

It seems likely that the three bands in B3 can be attributed to the differently bonded NH stretching vibration, although the outer bands are closer together than the given ranges. B3 is therefore predominantly trans-linked.

The situation in the N-acetyl-3-chloroanthranilic acid, B4, is complicated by the fact that there are two C=0 in the molecule which can be used for hydrogen bonding. However, it seems likely that the strong band, which comes at the lower end of the range given for amido acids, is due to intramolecular hydrogen bonding with the -COOH group, while the other three bands are due to the absorptions of the NH hydrogen bonded with the amido group of another molecule.

For most amido acids, weak bands occur at 2640-2360 cm.$^{-1}$ (3.79-4.24 μ) and 1945-1835 cm.$^{-1}$ (5.14-5.45 μ), however, the spectra of only a limited number of compounds have been analysed. Two flat topped bands, possibly unresolved doublets, occur at 2639-2611 cm.$^{-1}$ (3.79-3.83 μ) and 2506-2480 cm.$^{-1}$ (3.99-4.03 μ) in the high frequency region, but only the weak substitution pattern shows in the lower frequency region given. The 3-chloroanthranilic acid also shows bands close to this region, although weaker than the amido acid. These occur at 2710 and 2625 cm.$^{-1}$ (3.69 and 3.81 μ) with two very weak bands at 2558 and 2532 cm.$^{-1}$ (3.91 and 3.95 μ).

The C=0 stretching frequency of the carboxyl group at 1698 cm.$^{-1}$ (5.89 μ) is within the range given; 1724-1695 cm.$^{-1}$ (5.80-5.90 μ).

The amide band I, C=O stretch of the amido group, at 1634 cm.$^{-1}$ (6.12 μ) and the band II (NH deformation) at 1531 cm.$^{-1}$ (6.53 μ) are also within the quoted ranges.

There is often a strong band at, or near, 1225 cm.$^{-1}$ (8.16 μ) due to a -COOH vibration and this may be the band at 1208 cm.$^{-1}$ (8.28 μ), although the frequency is somewhat low.

Amides are reported to have bands as follows:

I	1680-1630 cm.$^{-1}$	(5.95-6.14 μ)	s.	C=O stretch
II	1570-1515 cm.$^{-1}$	(6.37-6.60 μ)	s.	NH deformation
III	1305-1200 cm.$^{-1}$	(7.67-8.33 μ)	m.	combination band of NH deformation and CN stretch
IV	770-620 cm.$^{-1}$	(13.00-16.13 μ)	m.	
V	ca.700 cm.$^{-1}$	(ca. 14.3 μ)		
VI	630-530 cm.$^{-1}$	(15.87-18.87 μ)	s.	

In the N-acetyl-3-chloro-toluidine ,B3, spectrum the probable assignments of these bands are as follows:-

I 1667 cm.$^{-1}$ (6.00 μ) vs.

II 1536 cm.$^{-1}$ (6.51 μ) s.

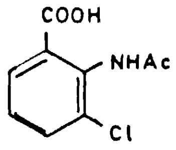
III 1297 cm.$^{-1}$ (7.71 μ) s. or 1269 cm.$^{-1}$ (7.88 μ) w. are possibilities.

IV 680 cm.$^{-1}$ (14.71 μ) m. seems most likely.

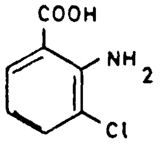
V Broad band at 698 cm.$^{-1}$ (14.32 μ)

VI 611 cm.$^{-1}$ (16.36 μ) m. or 588 cm.$^{-1}$ (17.02 μ) m.

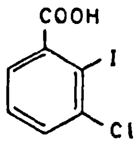
C-COOH group



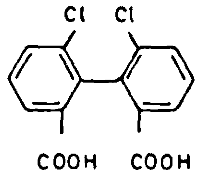
B4



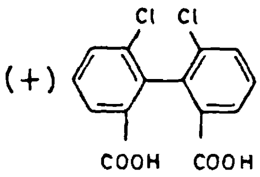
B5



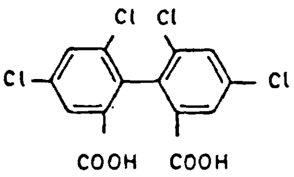
B6



BP2



+BP2



BP7

There is a broad region of absorption extending from about 3330 cm.$^{-1}$ (3.00 μ) to approximately 2380 cm.$^{-1}$ (4.20 μ), due to the very strong hydrogen bonding which occurs in carboxylic acids and distorts the -OH stretching vibrations. Flett[81] has observed that most carboxylic acids show one to three bands between 2500 and 2700 cm.$^{-1}$ (4.00-3.70 μ). Bands which overlie the main broad absorption band can be picked out in all of these compounds in the ranges 2680-2610 cm.$^{-1}$ (3.73-3.83 μ), 2550-2500 cm.$^{-1}$ (3.92-4.00 μ) and about 2325 cm.$^{-1}$ (4.3 μ); however, it is a region of many sub-maxima.

The C=O stretching frequency band occurs at 1700-1680 cm.$^{-1}$ (5.88-5.95μ) for the dimer and at 1680-1650 cm.$^{-1}$ (5.95-6.06μ) for intramolecularly hydrogen bonded carboxylic acid. B5 is expected to show strong intramolecular hydrogen bonding with the amine group, and has a band at 1669 cm.$^{-1}$ (5.99μ), which is in the latter range. B6 also absorbs in this position (1667 cm.$^{-1}$ 6.00μ) although expected to be intermolecularly hydrogen bonded to give the dimer. B5 and B6 have barely discernable shoulders in the dimeric region, i.e. near 1685 cm.$^{-1}$ (5.93μ), and also near 1720 cm.$^{-1}$ (5.81μ) which is in the region expected if any monomer were present.

Bands in the spectra of the dicarboxylic acids are found at 1689 cm.$^{-1}$ (5.92μ) for BP2 and +BP2 and 1695 cm.$^{-1}$ (5.90μ) in BP7 and these occur in the dimeric acid region. BP2 also has a band due to the monomer at 1745 cm.$^{-1}$ (5.73μ) and the other dicarboxylic acids have shoulders in this region.

Generally, there is a strong band in the 1320-1210 cm.$^{-1}$ (7.57-8.26μ) region and a weak one in 1440-1395 cm.$^{-1}$ (6.49-7.17μ) region which are assigned to strongly coupled C-O stretching and O-H deformation vibrations. There are, in some compounds, two bands reported in the lower frequency region, one near 1300 cm.$^{-1}$ (7.69μ) and one near 1200 cm.$^{-1}$ (8.33μ) (usually above 1240 cm.$^{-1}$ in aromatic acids[81]), and the 1300 cm.$^{-1}$ band has been assigned to the coupled CO and OH vibrations, while the 1200 cm.$^{-1}$ band has been associated with a CO vibration. Conjugation is reported to raise the frequency of these bands. B5 and +BP2 exhibit three bands (in +BP2 one is split) and B6, BP2 and BP7 two strong bands between 1312 and 1240 cm.$^{-1}$, while B4 has four bands in this region. The strongest band in this frequency range is at 1252-1250 cm.$^{-1}$ (7.99-8.00μ) in compounds B4, B5 and B6 and since a band occurs here in the ester B7, this may be due to CO stretching. B4 and B5 both have bands at 1312 cm.$^{-1}$ (7.62μ) and this may be the CO and OH coupled vibration although there is only a slight shoulder in B6. The diphenic acids and the ester absorb in the following positions:

BP2	+BP2	BP7	BP1
sh 1309 cm.$^{-1}$			
1280	1295 cm.$^{-1}$	1282 cm.$^{-1}$	1282 cm.$^{-1}$
1261	1267 1264	1269	1263
	1245	sh1247	
		1233	

The alternatives which present themselves are:

1) the 1269-1261 cm.$^{-1}$ band is the CO band whose frequency has been raised due to attachment of the carboxyl group to the aromatic system and the shoulder at 1309 cm.-1 band in BP2 is due to coupled CO/OH vibrations but for some reason does not show up in +BP2 and BP7,

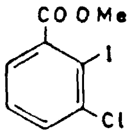
or 2) the bands in +BP2 and BP7 are shifted to slightly lower frequency and so the 1261, 1241, 1247 and 1263 cm.$^{-1}$ bands in BP2, +BP2, BP7 and BP1 respectively are due to the CO vibration, possibly also the 1280, 1267 and 1264, 1269 and 1282 cm.$^{-1}$ bands, while the higher frequency bands sh1309, 1295 and 1282 cm.$^{-1}$ are the ones due to CO/OH coupled vibrations.

The 1269-1261 cm.$^{-1}$ band seems the most reasonable for the CO absorption. It is possible that different vibrations give rise to the 1280-1295 cm.$^{-1}$ band in the acids and the 1282 cm.$^{-1}$ band in the ester, in which case, this could be the acid 1300 cm.$^{-1}$ band.

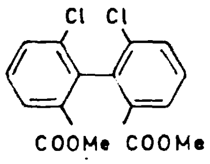
In compounds B4-6, the higher frequency band is likely to be that between 1410 and 1420 cm.$^{-1}$ (7.09 and 7.04μ), although only in B4 is the band weak. For the biphenyls BP2, +BP2 and BP7, the band probably occurs between 1429 and 1420 cm.$^{-1}$ (7.00 and 7.04μ) or 1403 and 1404 cm.$^{-1}$ (7.12 and 7.13μ).

The O-H out-of-plane deformation frequency is reported as a broad band of variable intensity between 955 and 890 cm.$^{-1}$ (10.47 and 11.24μ). Broad bands appear in the spectrum of B6 at 885 cm.$^{-1}$ (11.30μ), of B5 at 892 cm.$^{-1}$ (11.21μ) and of B4 at 904 cm.$^{-1}$(11.07μ). BP7 has a weak but sharp band at 909 cm.$^{-1}$(10.99μ). In this region, BP2 has two bands and +BP2 three bands, which are close together; 927 and 917 cm.$^{-1}$ (10.78 and 10.90μ) and 925, 911 and 896 cm.$^{-1}$ (10.81, 10.97 and 11.16μ).

-COOCH$_3$ Group



B7



BP1

The C=O stretching absorption occurs at 1724 cm.$^{-1}$ (5.80μ) and 1727 cm.$^{-1}$ (5.79μ) in B7 and BP1 respectively. The C–O stretching region is quoted by Bellamy as 1310–1250 cm.$^{-1}$ (7.63–8.00 μ) and 1150–1100 cm.$^{-1}$ (8.70–9.09μ) and by Jones and Sandorfy as 1280–1150 cm.$^{-1}$ (7.81–8.70μ) with one or more in the region 1300–1000 cm.$^{-1}$ (7.69–10.00μ). Bands arising from this vibration may be at 1250 or 1290 cm.$^{-1}$ (8.00 or 7.75μ) for B7 and 1263 or 1286 cm.$^{-1}$ (7.92 or 7.80μ) for BP1, while other bands appear at 1149 cm.$^{-1}$ (8.70μ) in both compounds and also at 1133 cm.$^{-1}$ (8.83μ) in B7 and 1125 cm.$^{-1}$ (8.89μ) in BP1. A band near 1150 cm.$^{-1}$ (8.7μ) occurs in all the compounds and is considered to be due to an aromatic CH in-plane deformation vibration.

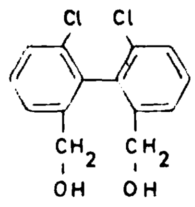
It seems likely that the 2950 and 2959 cm.$^{-1}$ (3.39 and 3.38μ) bands, for B7 and BP1 respectively, are due to the asymmetric stretching vibration of -CH$_3$. There is a weak intermediate band at 2899 cm.$^{-1}$ (3.45μ) for B7 and 2907 cm.$^{-1}$ (3.44μ) for BP1.

Comparison of the spectra of the acids and esters leads to the conclusion that the band near 1430 cm.$^{-1}$ (6.99μ) in the esters is possibly due to a methyl bending vibration. There is also an extra shoulder at 1460 cm.$^{-1}$ (6.85μ). When the methyl group is attached to an oxygen atom, the frequency of the methyl deformation vibration is increased from the normal values of 1470-1420 cm.$^{-1}$ (6.80-7.04μ) m for the asymmetric vibration and 1385-1375 cm.$^{-1}$ (7.22-7.27μ) s for the symmetric vibration; it therefore seems possible that the asymmetrical bending vibration occurs at 1460 cm.$^{-1}$ (6.85μ) and the symmetrical vibration at 1432 cm.$^{-1}$ (6.98μ). The intensity of the symmetrical mode is greater than that of the asymmetrical mode as expected.

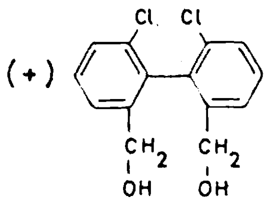
This is an increase in the symmetrical vibration frequency only. A band occurs near 1400 cm.$^{-1}$ in both the acids and esters.

There is a noticeable band near 970 cm.$^{-1}$ (10.3μ) which is present in the esters and not in the acids. A band close to 1000 cm.$^{-1}$ (10.0μ) also occurs in the substituted toluenes.

-CH$_2$OH group

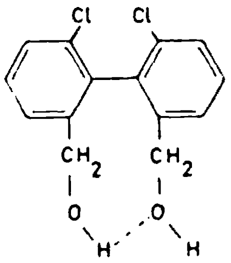


BP3

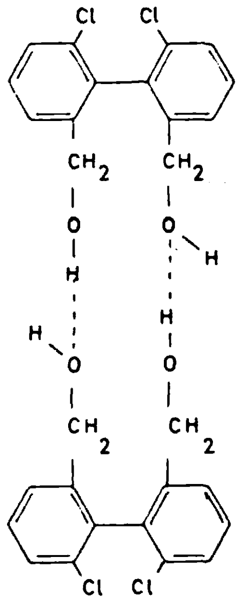


+BP3

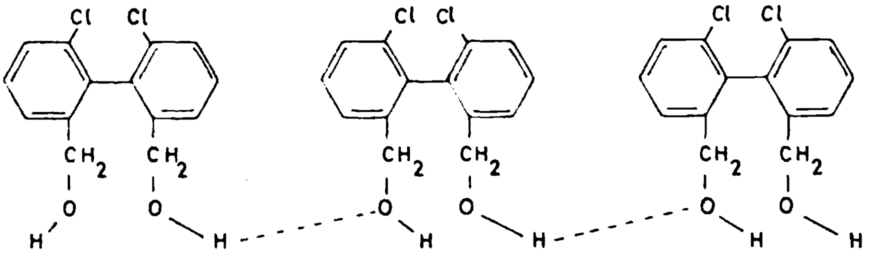
The (+) and racemic diols show spectra with points of interest, and many of the bands appear to be split. The crystal structures are different and the infrared spectra display marked differences in the -OH stretching region, in particular, showing hydrogen bonding of different types. In a diol, there arises the possibility of intramolecular hydrogen bonding, as well as intermolecular dimers and polymers.



intramolecular bonding



dimeric bonding



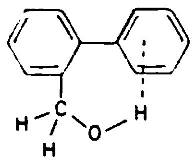
Example of polymeric bonding

The racemic compound shows a strong broad band at 3247 cm.$^{-1}$ (3.08μ) with a shoulder at 3215 cm.$^{-1}$ (3.11μ) and this band also occurs in the active compound at 3333 cm.$^{-1}$ (3.00μ) with a shoulder at 3279 cm.$^{-1}$ (3.05μ). Bellamy gives the range 3400-3200 cm.$^{-1}$ (2.94-3.10μ) as the range for polymeric associated -OH stretching absorption, and the values of the diols are well within the region.

The (+) diol has, in addition, two sharp peaks at 3610 and 3559 cm.$^{-1}$ (2.77 and 2.81μ), the former having a shoulder. These are assigned to a free -OH, together with a dimeric or intramolecularly hydrogen bonded -OH. It may be that the shoulder is due to the intramolecular hydrogen bond and the band at 3559 cm.$^{-1}$ (2.81μ) to dimeric association.

Work on solutions of 6,6'-dichloro-2,2'-bishydroxymethylbiphenyl in carbontetrachloride has been included by Baitinger jr., Schleyer and Mislow[82] in their hydrogen bonding studies. They report bands at

3632 cm.$^{-1}$ sh	due to free OH
3613	due to OH.....π bonding
3472	due to OH.....O bonding



OH.....π bonding

From their work, they conclude that perpendicular conformations favour OH.....π and OH.....O bondings although interactions due to the latter also occur in cis conformations. They consider that it is easier to make the intramolecular bond than to increase the entropy and make the intermolecular bond. In the solid, the situation is different; the rigid structure holds the molecule in a set conformation and strong intermolecular hydrogen bonding occurs. The racemic diol BP3 is a racemic compound with no free -OH or intramolecularly bonded -OH. The situation in the optically active diol will be closer to that of the racemic compound in solution where the compound will behave as separate molecules of the (+) diol and the (-) diol. The 3610 cm.$^{-1}$ (2.77μ) band could correspond to Mislow's 3632 cm.$^{-1}$ free -OH band and its shoulder perhaps to his 3613 cm.$^{-1}$ band.

Two bands have been observed in primary alchols; one near 1050 cm.$^{-1}$ (9.52μ) s and the other in the range 1350-1260 cm.$^{-1}$ (7.41-7.94μ) s. There is some uncertainty over the -OH bending, the C-O stretching and the C-OH stretching frequencies, but it seems likely[83] that the -OH bending gives rise to the higher frequency band. Hydrogen bonding will increase the frequency of this band, which varies considerably and has not been the subject of a systematic study. Bands occurring between 1350 and 1260 cm.$^{-1}$ in the active and inactive diols are listed below:

BP3			+BP3		
			1370 cm.$^{-1}$	(7.30μ)	w
1323 cm.$^{-1}$	(7.56μ)	m	1353 cm.$^{-1}$	(7.39)	m
1279	(7.82)	w	1280	(7.81)	w
1261	(7.93)	vw	1263	(7.92)	w

It is possible that the 1280 cm.$^{-1}$ (7.81μ) or 1261 cm.$^{-1}$ (7.93μ) band is due to the –OH deformation, but the 1261 cm.$^{-1}$ band is very weak in the racemic compound. Alternatively, the –OH deformation could give rise to the 1323 cm.$^{-1}$ (7.56μ) band in the racemic compound, and bands at 1370 and 1353 cm.$^{-1}$ (7.30 and 7,39μ) in the active compound be due to differently bonded –OH and free –OH. The argument against this is that the active compound also contains polymerically associated molecules, and thus a band due to this would be expected to occur in both spectra. Either this band is much weaker than expected, or it occurs outside the reported wavelength range.

The C–O stretching vibration is quoted as being responsible for a strong band near 1050 cm.$^{-1}$ (9.52μ). The frequency of this band will also be increased slightly by hydrogen bonding. Bands occurring in the 1100-1000 cm.$^{-1}$ (9.09-10.00μ) region are listed:

BP3			+BP3		
1094 cm.$^{-1}$	(9.14μ)	w	1096 cm.$^{-1}$	(9.12μ)	w
1075	(9.30)	w	1078	(9.28)	w
			1042	(9.60)	
1017	(9.84)		1017	(9.84)	
			1004	(9.96)	
998	(10.02)		998	(10.02)	

The first two bands are only weak and so can be rejected. This leaves two bands in the spectrum of BP3 and these are at a rather lower frequency than expected. Since the frequency is raised by hydrogen bonding, the 1017 cm.$^{-1}$ band is the more likely. In this case, the 1004 cm.$^{-1}$ band of +BP3 is possibly due to the free -OH, while that at 1042 cm.$^{-1}$ caused by dimeric or intramolecular hydrogen bonding. Poole[60] has assigned a band at 1033 cm.$^{-1}$ (9.68 μ) to the C-O stretching frequency of the $-CH_2OH$ group in 2,2'-bis-hydroxymethylbiphenyl.

A band close to 1010 cm.$^{-1}$ (9.90 μ) is considered by Beaven and Johnson[19] to be diagnostic of a biphenyl skeleton (see p.108)

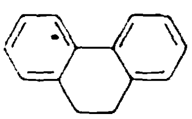
$-CH_2-$ group

The diols BP3 and +BP3 have at least four bands in the region 3000-2840 cm.$^{-1}$ (3.30-3.52 μ), while the 6,6'-dichloro-substituted bisbromomethyl-compounds have three and the unsubstituted bisbromo-methyl- compound possibly two bands. However, the bromo- compounds give a poor spectrum in this region and any shoulders or other very weak bands there may be are not discernable. These bands occur near to the following positions:

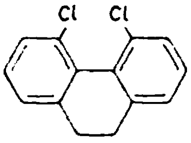
2960 cm.$^{-1}$	(3.38 μ)	occurs in	BP3vw, +BP3w, BP4w, +BP4vw, BP5w.
2930	(3.41)	" "	BP3w, +BP3m, BP4w, +BP4vw
2890	(3.46)	" "	BP3w, +BP3w.
2850	(3.51)	" "	BP3vw, +BP3w, BP4vw, +BP4vw.

The ranges quoted for the methylene stretching vibration are 2940-2915 cm.$^{-1}$ (3.40-3.45 μ) for the asymmetrical and 2870-2915 cm^{-1}

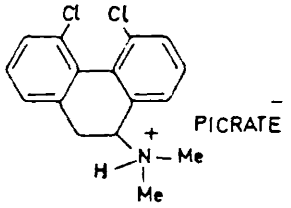
(3.49-3.52μ) for the symmetrical stretching mode. These cover the second and fourth bands given above. The spectra may be expected to be complicated by the presence of the oxygen and bromine atoms. However, when 9,10-dihydrophenanthrene (BB14), 4,5-dichloro-9,10-dihydrophenanthrene (BB7) and 9-dimethylamino-4,5-dichloro-9,10-dihydrophenanthrene picrate (BB5) are included in the survey, it is found that they also show bands in approximately the same positions, although they may, in some cases, be only very weak or shoulders. Positions of the bands are given below.



BB14



BB7



BB5

				2976 cm.$^{-1}$	(3.36μ) m
sh 2950 cm.$^{-1}$	(3.39μ)	2955 cm.$^{-1}$	(3.385μ)m	sh2967 cm.$^{-1}$	(3.37)
2933	(3.41)m	2903	(3.445)w	sh2924	(3.42)
2890	(3.46w)w	sh2890	(3.46)	sh2890	(3.46)
		2861	(3.495)vw		
2833	(3.53)w	2833	(3.53)w	2850	(3.51)vw

These three compounds have the -CH$_2$- group in a six-membered ring, with no hetero-atoms adjacent, and might be expected to show differences from the diols and di-bromo- compounds, especially in the case of the 9-dimethylamino- compound, which has only one-CH$_2$- group. The -CH- group in this compound is next to the centre of positive charge and this would have a considerable effect on the -CH- stretching frequency.

Thus the band at 2890 cm.$^{-1}$ (3.46μ) which is the normal position for -CH- stretching vibration, and which also occurs in BP3, +BP3, BB15 and BB8, is more likely to arise from the same vibration as in those compounds.

Hall and Poole[24] suggest bands close to 2922 cm.$^{-1}$ (3.42μ) for $-CH_2-$ groups in dihydrophenanthrene (BB14) melt and 2,7-dihydro-1-methyl-3,4:5,6-dibenzazepine. The closest band in BB14 and BB5 to their value is the 2933 cm.$^{-1}$ (3.41μ) band which also occurs in the unbridged compounds but does not occur here in the dichlorodihydrophenanthrene BB7. As can be seen from the table, BB7 is the only compound discussed here which has no band near 2933 cm.$^{-1}$, but has one at 2903 cm.$^{-1}$. Bands in this region in the spectrum of the melt of BB14 are at 2819, 2874 and 2921 cm.$^{-1}$ (3.55, 3.48 and 3.42μ). The solution spectrum of dihydrophenanthrene in carbon tetrachloride is given in the D.M.S. collection of spectra (No 11353) and was also measured by Hall and Poole. The bands in this region occur at 2930 and 2885 cm.$^{-1}$ (3.41 and 3.47μ). This result suggests that the 2890 cm.$^{-1}$ (2.46μ) band is due to the symmetrical stretching vibration.

The $-CH_2-$ scissoring deformation is likely to give a band near 1460 cm.$^{-1}$ (6.85μ). An aromatic C=C in-plane vibration also occurs in this region and gives rise to the absorption near 1450 cm.$^{-1}$ (6.9μ) in the benzene compounds. In the 1470-1420 cm.$^{-1}$ (6.80-7.04μ) region, the dichlorobisbromo- compounds BP4 and +BP4 show two absorption bands:

at 1443 cm.$^{-1}$ (6.93μ) and 1425 cm.$^{-1}$ (7.02μ) for BP4, and 1447 cm.$^{-1}$ (6.91μ) and 1429 cm.$^{-1}$ (7.00μ) for +BP4. One of these will be due to the $-CH_2-$ scissoring vibration and the other to the aromatic C=C in-plane vibration. The compounds BP1 and BP2 also absorb between 1420 and 1435 cm.$^{-1}$, and these bands are attributed to a methyl vibration and acid vibration respectively, but the compounds do absorb near 1450 cm.$^{-1}$ and these bands are assigned to the aromatic C=C in-plane vibration. The other biphenyls BP3 and +BP3 absorb near 1460, 1440 and 1430 cm.$^{-1}$, while BP5 absorbs near 1450, 1440 and 1430 cm.$^{-1}$.

Double bonds or oxygen atoms next to methylene groups lower the scissoring frequency of the latter and the bromine atoms would be expected to have a similar, but lesser, effect. It is unlikely that there will be much change in the position of the aromatic C=C vibration, therefore this one is more likely to give rise to the band close to 1440 cm.$^{-1}$, and the higher frequency of the two bands in BP4 and +BP4.

Since adjacent oxygen atoms lower the scissoring frequency from the value of 1460 cm.$^{-1}$ found in hydrocarbons, the bands at 1458 cm.$^{-1}$ in the diols are unlikely to be due to this. The band which remains in both the diols and bisbromomethyl- compounds is one close to 1430 cm.$^{-1}$ and this is possibly the one arising from the $-CH_2-$ scissoring vibration.

-C-O-C grouping

The stretching mode gives rise to a strong band at 1063 cm.$^{-1}$ (9.41 μ) in the (-) dichloro- (-BB1) and tetrachloro- (BB12) oxepins and at 1057 cm.$^{-1}$ (9.46 μ) in the racemic dichloro-oxepin (BB1). The optically active and racemic oxepins have different crystal structures and show slight differences in spectra.

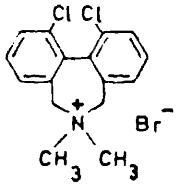
Mislow[53,23] has prepared an oxathiepin which has a strong CO peak at 1065 cm.$^{-1}$ (9.39 μ) and Poole[60] reports a doublet at 1081 and 1072 cm.$^{-1}$ (9.25 and 9.33 μ) for the -C-O-C-stretching frequency of the unsubstituted oxepin. Poole also reports bands at 901 and 888 cm.$^{-1}$ (11.10 and 11.26 μ) as characteristic of the oxepin spectrum. Bands are present in this region at the following positions:

BB1		-BB1		BB12	
909 cm.$^{-1}$	(11.00 μ)	905 cm.$^{-1}$	(11.06 μ)	902 cm.$^{-1}$	(11.09 μ)
		896	(11.16)		
884	(11.32)	888	(11.26)	881	(11.35)
870	(11.49)	867	(11.53)	868	(11.52)

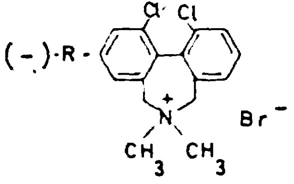
The bands in the 905-909 cm.$^{-1}$ and 881-888 cm.$^{-1}$ ranges are those which correspond to the values given by Poole.

Water of Crystallisation

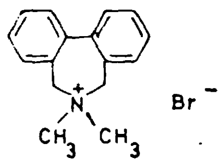
Water of crystallisation in hydrated inorganic salts usually gives rise to a broad hydrogen-bonded -OH stretching absorption in the region 3600-3100 cm.-1 (2.78-3.23 μ) but no extensive study has been made with organic salts. The -OH symmetrical and asymmetrical stretching vibration bands in the hydrated azepinium compounds are partially resolved and the spectra show more than two bands in the region. It seems likely that these are due to two water molecules in different environments, and that the unit cell of the crystal contains two molecules each of the azepinium bromide and water for the BB2 and BB10 compounds. The analysis of -BB2 shows that it contains two molecules of water of crystallisation. -BB2 has a similar infrared spectrum to BB2 and is likely to have the same crystal structure. The expected fourth peak in -BB2 may be hidden under the 3436 cm.$^{-1}$ (2.91 μ) band, and indeed, there may be a shoulder at 3448 cm.$^{-1}$ (2.90 μ). Peaks in the region are given below.



BB2



-BB2



BB9

				3571 cm.$^{-1}$	(2.80 μ)
3484 cm.$^{-1}$	(2.87 μ)	3491 cm.$^{-1}$	(2.865 μ)	3484	(2.87)
		?sh3448	(2.90)		
sh3430	(2.915)	3436	(2.91)		
3413	(2.93)			3413	(2.93)
3322	(3.01)	3365	(2.97)		

The fourth band of the unsubstituted azepinium bromide (BB9) also appears to be very close to the 3484 cm.$^{-1}$ (2.87 μ) band and this would account for the enhanced intensity of this band.

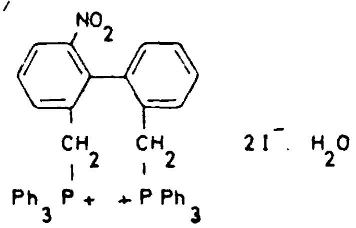
It is interesting to note that two of the bands correspond to those arising in the spectrum of water in the liquid or crystalline state, where the molecules are disturbed by hydrogen bonding. The water spectrum has a broad band with three maxima arising from the symmetrical and asymmetrical stretching vibrations and the first overtone of the deformation vibration. It is unlikely that the overtone band would show up in the azepinium compounds because the fundamental is weak.

The -OH stretching bands of water occur at 3480 ± 20 cm.$^{-1}$ ($2.857-2.890\,\mu$) (asymmetric) and 3425 ± 10 cm.$^{-1}$($2.919-2.929\,\mu$)(symmetric).[84] Hydrogen bonding tends to lower the frequency of the stretching vibration and raise that of the deformation vibration. The bromides appear to have one water molecule bonded to the same extent as in water, and one which, in the substituted bromides is more strongly bound, but in the unsubstituted bromide is less strongly bonded. Bands in the -OH deformation region are:

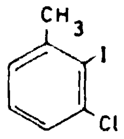
BB2		-BB2		BB9	
1647 cm.$^{-1}$	($6.07\,\mu$)	sh1616 cm.$^{-1}$	($6.19\,\mu$)		
1610	(6.21)	1610	(6.21)	1610 cm.$^{-1}$	($6.21\,\mu$)
				sh1603	(6.24)

The values for the -OH stretch are near the high frequency end of the range and this would indicate that the water molecules are only loosely held.

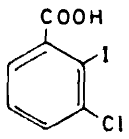
Presumably the ionic nature of the molecule or the weak nature of the hydrogen bond is the cause of the discrete absorption bands. Hall and Prakobsantisukh[86] have prepared a phosphonium iodide containing water of crystallisation which absorbs at 3646 cm.$^{-1}$ (2.75 μ) and 3410 cm.$^{-1}$ (2.93 μ).



-C-I group



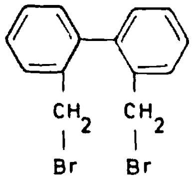
B2



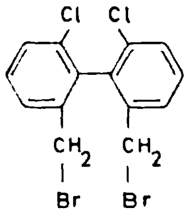
B6

In compounds B2 and B6 the C-I stretching frequency occurs at 539 cm.$^{-1}$ (18.55 μ) and 573 cm.$^{-1}$ (17.44 μ) respectively. The lower frequency in B2 may be due to the +I inductive effect of the methyl group compared to the -I inductive effect of the carboxyl group, or to steric hindrance, both of which cause a longer C-I bond length in the methyl compound.

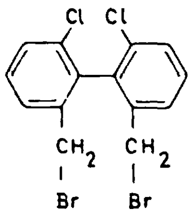
-C-Br group



BP5



BP4



+BP4

In the spectrum of BP5, strong bands occur at 602 cm.$^{-1}$ (16.60μ) and 537 cm.$^{-1}$ (18.62μ). Mortimer, Blodgett and Daniels[87] consider that, in benzyl bromide, the benzene ring interacts with the bromine atom and that this will result in only one C-Br stretching vibration. They assign the three bands in the benzyl bromide spectrum thus:

691 cm.$^{-1}$	(14.47μ)	ring vibration
612	(16.34)	ring vibration
550	(18.18)	C-Br stretch

It therefore seems likely that in BP5 the 537 cm.$^{-1}$ (18.62μ) band would be due to the C-Br stretching mode while the 602 (16.60μ) band could be due to a ring vibration. However, there is no band corresponding to the 691 cm.$^{-1}$ (14.47μ) but this may be due to the different substitution or the biphenyl skeleton.

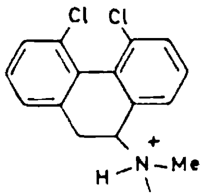
The dichloro-biphenyls absorb in this region at the following frequencies:

BP5		BP4		+BP4	
		632 cm.$^{-1}$	(15.82μ)		
		sh626	(15.98)	624 cm.$^{-1}$	(15.96μ)
602 cm.$^{-1}$	(16.60μ)	558	(17.02)	591	(16.92)
				572	(17.48)
		560	(17.86)	561	(17.82)
537	(18.62)	548	(18.26)	545	(18.35)

The bands at 548 cm.$^{-1}$ (18.26μ) and 545 cm.$^{-1}$ (18.35μ) are likely to be due to the C-Br stretching vibration, while the others may be ring vibrations, by analogy with benzyl bromide.

$\overset{+}{\mathrm{N}}$-H group

The $\overset{+}{\mathrm{N}}$-H stretching absorption is reported to occur in the range 2820-2730 cm.$^{-1}$ (3.55-3.66μ). This grouping occurs in two of the compounds, namely BB5 and BB10 and possibly in the unbridged biphenyl amine picrate

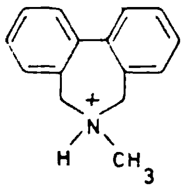


picrate

BB5

unbridged biphenyl picrate

BB6



picrate

BB10

Bands in these compounds occur at the following frequencies:

BB5	BB6	BB10
sh 2778 cm.$^{-1}$ (3.60μ)	2825 cm.$^{-1}$(3.54μ)	
2743 (3.645)	2747 (3.64)	sh2743 cm.$^{-1}$ (3.645μ)
2725 (3.67)	2717 (3.68)	2710 (3.69)

Most of the compounds studied had a weak band close to 2717 cm.$^{-1}$ (3.68μ) but only in the unsubstituted azepinium picrate BB10 was this band noticeably intense. Apart from a weak band in the region of 2600-2450 cm.$^{-1}$ (4.08-3.05μ) in BB5 and BB6 there are no distinguishable bands below this until the substitution pattern at 2000-1650 cm.$^{-1}$ (5.00-6.06μ) although more are reported in the region 1800-2200 cm.$^{-1}$(4.55-5.56μ) when no other hetero-atom is near.

Bands in the region 1600-1540 cm.$^{-1}$

Aromatic compounds often show two bands in this region due to skeletal C=C in-plane stretching. The intensity of the lower frequency band is considered by Bellamy to be considerably enhanced by conjugation of the benzene ring, and, without this, to be usually undetectable. The benzene compounds studied here exhibit these two bands when they are not overlaid by other bands. They occur between 1597 and 1570 cm.$^{-1}$ (6.26-6.37μ) and 1582 and 1548 cm.$^{-1}$ (6.32-6.46μ). For vicinal tri-substituted and halogeno- compounds, a shift in the band position to lowerfrequency is reported. The 1587 cm.$^{-1}$ band occurs at the lower frequency end of the given region (1625-1575 cm.$^{-1}$), while the 1563 cm.$^{-1}$ band is outside the range quoted (1587-1575 cm.$^{-1}$), Except for BP5, all the biphenyls show the two bands and they occur between 1590-1575 cm.$^{-1}$ (6.29-6.35μ) and 1563-1548 cm.$^{-1}$(6.40-6.46μ); thus at a slightly lower frequency than in the benzene compounds and in a narrower range. The bridged biphenyls display the bands at a slightly higher frequency than the biphenyls: at 1605-1587 cm.$^{-1}$ (6.23-6.32μ) and 1565-1550 cm.$^{-1}$ (6.38-6.45μ). The bands are not easily picked out in BB4. In compound BB10 and BB5, which are picrates, there are two sets of peaks, presumably due to the two different benzene systems. The bands are near 1623 and1608 cm.$^{-1}$ (6.16 and 6.22μ) and 1563 and 1553 cm.$^{-1}$(6.40 and 6.44μ). In some compounds the first band is the more intense, in other, the second. On the whole, the frequency of these bands is lower than expected.

Absorption bands due to C=C skeletal vibrations are also reported near 1500 cm.$^{-1}$ and 1450 cm.$^{-1}$ M-s (6.67-6.90μ). The compounds studied in this work generally show no bands between 1540-1470 cm.$^{-1}$ (6.5-6.8μ) but vicinal tri-substitution is reported to lower the frequency and thus bring the position closer to the 1450 cm.$^{-1}$ region.

A band, usually of medium to strong intensity, does occur near 1450 cm.$^{-1}$ although the position is variable, and sometimes there are two bands in the region. The region is also complicated by the absorptions of substituent groups.

Substitution Patterns

2000-1650 cm.$^{-1}$ (5.00-6.06μ) region

3-Chlorotoluidine (B1) is a liquid and the spectrum was run on a film of this. As a result, the substitution pattern in the region 2000-1650 cm.$^{-1}$ shows up very clearly with the characteristic 1,2.3-substitution pattern. In many of the remaining compounds, the bands are usually rather weak and are not very noticeable. The pattern is often in narrower limits than the region given, and is usually between 1960 and 1755 cm.$^{-1}$ (5.10-5.70μ), sometimes being above 1820 cm.$^{-1}$ (below 5.50μ).

Compounds with unusual features are noted below:

Biphenyls

BP1 A fourth band at 1789 cm.$^{-1}$ (5.59μ)

BP3 The first two bands are doubled.

+BP3	Many weak bands.
BP4	There are four bands in the region.
+BP4	Very weak. There are at least four bands.
BP6	Definite pattern. The central band is doubled.
BP7	The pattern cannot be picked out.

Bridged Biphenyls

-BB1	Weak pattern. The bands are doubled.
BB4	No definite pattern.
BB5	No normal pattern distinguishable
BB7	Normal pattern, together with a fourth peak in this region.
BB8	Many very weak bands.
BB9	Very weak; there are slight differences from the normal pattern.
BB11	No peaks are distinguishable.
BB12	The normal pattern cannot be discerned.

Aromatic in-plane CH deformation

Compound B1 to B7 and BP1 to +BP4 all have bands in the region 1145–1160 cm.$^{-1}$ (8.73–8.62μ). All the biphenyls but BP4 and +BP4 have two bands in this region, the second band, in some cases, appearing as a shoulder. All have bands in the region 1075–1096 cm.$^{-1}$(9.30–9.12μ), there being a shoulder in B1 and two bands in the spectra of BP2, +BP2, BP3 and +BP3. These two absorptions, due to in-plane deformation vibrations, come in the given ranges of 1175–1125 cm.$^{-1}$ (8.51–8.89μ) and 1110–1070 cm.$^{-1}$(9.01–9.35μ) for 1,2,3- substituted benzenes, although they are not all weak, as reported.

A third region between 1070 and 1000 cm.$^{-1}$ (9.35 and 10.00μ) is reported to exhibit two bands due to this type of vibration. This may be the band reported by Beaven and Johnson[19,88] and mentioned below as the 1010 cm.$^{-1}$ biphenyl band.

Bands in this region are shown below.

B1	1030		(9.71)	BP1	1002	(9.98)
B2	1032	1014	(9.69, 9.86)	BP2	-	
B3	1037	1010	(9.64, 9.90)	+BP2	1002	(9.98)
B4		1011	(9.89)	BP3	-	
B5 sh	1029		(9.72)	+BP3	-	
B6		1017	(9.84)	BP4	1002	(9.98)
B7		1017	(9.84)	+BP4	1003	(9.97)

More bands between 1000 and 960 cm.$^{-1}$ are reported by Cross and Rao, but are either absent or too weak to be picked out.

1010 cm.$^{-1}$ Biphenyl band

This band has been reported by Beaven and Johnson[19,88] as being characteristic of the biphenyl skeleton in alkyl substituted biphenyls. Buck and Connor[89] have found that this band is not always present when there are other substituents, and this is confirmed in the following results.

Benzene compounds (table in previous section)

All the compounds except B1 and B5 show a band, in the region of

1010 cm.$^{-1}$(9.90μ). The intensity of this band varies from compound to compound. Thus, out of seven benzene compounds, six show a band in the region.

Biphenyl compounds Biphenyls BP1, +BP2, BP4 and +BP4 show only very weak bands close to 1000 cm.$^{-1}$(10.00 μ). The diols BP3 and +BP3 show a strong band at 1017 cm.$^{-1}$ (9.83μ) and, +BP3, in addition, another at 1004 cm.$^{-1}$ (9.96μ), but these compounds are expected to absorb in this region due to the C–O stretching mode. The unsubstituted bromide BP5 has a sharp band at 1005 cm.$^{-1}$ (9.95μ). Of the tetrachloro- substituted biphenyls, BP6 has a strong sharp peak at 1003 cm.$^{-1}$ (9.97μ) and BP7 has a very weak band at 1006 cm.$^{-1}$ (9.94μ). Thus, out of ten biphenyls, four show strong or medium intensity bands, while the rest show very weak or negligible absorption.

Bridged biphenyls

Out of the six bridged biphenyls studied, only five show any marked absorption near 1010 cm.$^{-1}$. This band is most likely to be an aromatic in-plane CH deformation as noted in the previous section.

830-660 cm.$^{-1}$ (12.0-15.0μ) region

The substitution pattern in this region is due to the out-of-plane deformation of the ring hydrogen atoms and is dependent on the number of adjacent hydrogen atoms. None of the 1,2-,1,2,4-, or 1,2,3,5-substituted compounds show abnormalities in this region. 1,2,3-tri-substituted compounds are discussed below.

1,2,3-trisubstitution and other absorptions in the region

The benzene compounds absorb in the regions 775-746 cm.$^{-1}$(12.9 and 13.4μ) and 735-704 cm.$^{-1}$(13.6-14.2μ). The first band is, perhaps, at slightly lower, and the second at slightly higher, frequency than expected.

The substitution pattern of the acids BP2 and +BP2 and of the methyl ester BP1 appear to be different from that of the active and racemic diols and bisbromomethyl compounds. The former have bands in the given regions near 817 cm.$^{-1}$ (12.25μ) and 759 cm.$^{-1}$ (13.18μ) and near 714 cm.$^{-1}$(14.00μ) and 704 cm.$^{-1}$(14.20μ), while the latter have bands close to 795, 746 and 690 cm.$^{-1}$(12.58, 13.40 and 14.50μ), some of these bands being doublets. Buck and Connor[89] have given the following ranges for 2,2',6,6'-substituted biphenyls i.e. trisubstitution with one of the substituents being another benzene ring. 783–811 cm.$^{-1}$m and 692-725 cm.$^{-1}$w (12.77-11.48 and 14.45-13.79μ). The 795 cm.$^{-1}$ (12.58μ) band of the diols and bromo- compounds must correspond to the stronger of the substitution bands, since it is the only one in this region and comes in the ranges for both biphenyls and benzenoid compounds. This band is strong, although reported by Buck and Connor as of medium intensity. The bands are possibly split because of interactions due to crystal structure, or because of Fermi resonance*, or else they are simply due to different vibration.

*(Fermi resonance is the coupling of vibrations of the same

symmetry when the frequency of these vibrations is close. This causes the two bands to be split into a doublet, one on either side of the original frequency. The intensity and position of the bands depends on the closeness of the perturbed frequencies.) The lower frequency substitution band, if it falls in the biphenyl range, will be that at 690 cm.$^{-1}$ (14.5μ) and it is tempting to assign the remaining band at 745 cm.$^{-1}$(13.4μ) to the $-CH_2-$ rock. A band close to this also occurs in the unsubstituted bisbromomethyl compound. However, the possibility that the strong 745 cm.$^{-1}$(13.4μ) band might be part of the substitution pattern should not be rejected. The 690 cm.$^{-1}$ (14.5μ) band would be too high for the $-CH_2-$ rock, and this vibration does not usually show up unless there are more than two $-CH_2-$ groups. As for the acids and ester, it is possible that, in fact, the substitution pattern follows that of the benzenoid compounds, at 760 cm.$^{-1}$(13.16μ) and 715 cm.$^{-1}$(14.0μ).

The bridged biphenyls will not necessarily have the same range of substitution pattern as that suggested for biphenyls. There are usually up to five bands between 830 and 665 cm.$^{-1}$(12.0-15.0μ) and this makes assignment difficult.

Both the chloro-substituted azepinium compounds, the unbridged biphenyl picrate and the substituted 9-dimethylamino-9,10-dihydrophenanthrene compound (BB5) have a distinct pattern of three bands between 740 and 645 cm.$^{-1}$(13.5 and 15.5μ). The intensity of these bands decreases regularly with decreasing wavelength. This does not occur in the unsubstituted compounds and is not obviously present in the dinitro- compound although it could have been distorted. A similar pattern exists in the disubstituted oxepins, but the lower frequency bands are closer together, and the central band is of lowest intensity. The higher frequency of these bands is considered to be part of the substitution pattern although the second also comes in the range given for unbridged biphenyls. The pattern might be caused by the azepinium ring, either directly, as a skeletal vibration, or indirectly, by holding the biphenyl in an otherwise unfavoured conformation. The former seems unlikely, since the substituted compounds exhibit this pattern, while it is absent in the unsubstituted compounds. The latter may be the case if the nitro- groups of the dinitro- substituted azepinium iodide can have an effect on the vibrations causing these bands, such as a change in the dihedral angle of the biphenyl. Since the oxepin also has a similar, but modified, pattern, this would appear likely. For unsubstituted compounds[18] the oxepin has a dihedral angle of 43° while the quaternary spiro-piperidinium compound has a dihedral angle of 47°. One would not, in this case, have expected the pattern to remain in the dimethylamino- compound, which has a six-membered ring. The pattern is not present in the dichlorodihydrophenanthrene. There is only one band at lower frequency than the substitution pattern in this region, and this at a frequency which is centred between the two lower bands of the pattern. This second band is not present in either the dihydrophenanthrene or dimethoxydihydrophenanthrene, and therefore should not be due to the dihydrophenanthrene skeleton or the substitution pattern. An alternative suggestion for the origin of these bands is that they are due to the C–Cl stretch, and that in the heterocyclic compounds, this band is split into two. The bands are not strong, as would be expected, but are, in most cases, medium and weak.

The seven-membered ring compounds also show two bands between 770 and 800 cm.$^{-1}$(12.5 and 13.0μ) one of which disappears on going to the six-membered ring compound. The remaining band could be due to –CH_2– rock.

It may be noted that there is a band between 905 and 913 cm.$^{-1}$ (10.95-11.05μ) in the substituted quaternary nitrogen compounds which is very strong in the bromides and moderate to strong in the other compounds. The band appears to be stronger in compounds which are disubstituted with methyl groups on the nitrogen than when there is only one. The unsubstituted azepinium compounds show bands close to this position, as do sodium picrate and picric acid. In the latter compounds this is possibly due to C–N stretch of the nitro-group. A band here would therefore be expected in the picrates, and in fact these compounds often display two bands close to 910 cm.$^{-1}$ (11.0μ). Although it seems likely that this band arises from vibrations connected with $\overset{+}{N}$–Me, there are weak bands here in several other compounds, notably the dichlorooxepin. Many of the bridged compounds give a pair of bands between 800 and 950 cm.$^{-1}$(10.5-12.5μ).

C-Cl stretching frequency

Bellamy gives the range 750-700 cm.$^{-1}$(13.3-14.3μ) for the C-Cl stretch, but indicates a higher frequency, of the order of 845 cm.$^{-1}$ (11.83μ) for chlorinated aromatic compounds. The tetra-chloro-compounds will have one of the strongest bands in the region for the C-Cl stretch, and a band occurring between 805 and 780 cm.$^{-1}$(12.4-12.8μ) in all these is a possible one (in BP6 at 787; BP7 at 805; BB12 at 801 cm.$^{-1}$). The tetrachloro-biphenyl BP6 shows no bands other than weak ones between 790 and 590 cm.$^{-1}$(12.7 and 17.0μ) and thus the C-Cl stretching frequency may be expected to be higher than 790 cm.$^{-1}$ in this compound.

The benzene compounds have bands between 848 and 794 cm.$^{-1}$ (11.8-12.6μ) and also between 758 and 633 cm.$^{-1}$(13.2 and 15.8μ) although the latter is usually close to 690 cm.$^{-1}$(14.5μ). Sometimes the only band in the range is the substitution band but it is possible that they occur very close together and are unresolved.

The substituted unbridged $-CH_2-$ containing compounds BP3, +BP3, BP4 and +BP4 have the bands near 800 and 740 cm.$^{-1}$(12.5 and 13.5μ) doubled. There is a band close to 690 cm.$^{-1}$(14.5μ) which is not present in the unsubstituted compounds, and this may be either the C-Cl stretch or the substitution pattern. There are also bands between 830 and 770 cm.$^{-1}$(12.0-13.0μ) in all the substituted biphenyls and the C-Cl stretch could be in either region.

The dichlorodihydrophenanthrene has a band near 680 cm.$^{-1}$ (14.7μ) and also a band near 813 cm.$^{-1}$(12.3μ) neither of which appear in the unsubstituted or dimethoxy- compound. The dimethylamino- compound also has bands in these regions at 700 and 662 cm.$^{-1}$ (14.3 and 15.1μ) and 855 and 794 cm.$^{-1}$(11.7 and 12.6μ). Thus, it is not possible to indicate with certainty the C–Cl stretching frequency in this complicated region. Two regions are most likely: near to 690 or near 830 cm.$^{-1}$(14.5 and 12.0μ).

The fact that there are also bands in the unsubstituted compounds between 800 and 770 cm.$^{-1}$(12.5 and 13.0 μ) suggests that in the quaternary ammonium compounds, these may be due to the $C-\overset{+}{N}$ stretch or to an $\overset{+}{N}$-Me vibration, but little work has been done on such compounds. This band is close to 780 cm.$^{-1}$(12.8μ) in most of the azepinium compounds, but in the picrates, can be obscured by a picrate peak. The spectra of mono- and dichloro- substituted benzenes were studied in the range 910–650 cm.$^{-1}$(11.0–15.38μ) but showed bands in both regions. Bands in this range other than the substitution pattern are shown below:

Chlorine at position:	1	682 cm.$^{-1}$ s. (14.66μ)		908 cm.$^{-1}$ w–m (11.01μ)
	1,2	660 m. (15.15)		823 s (12.17)
	1,3	sh670 (14.93)	784 or 774 (12.76)(12.92)	836 w–m (11.96)
	1,4	–		–

Some compounds prepared by Ahmed and Hall[27] were examined, since they might prove helpful in elucidating the position of the C–Cl stretching frequency. These are 4',1"-dihalogeno-2,7-dihydro-3,4:5,6-dibenzazepinium-1-spiro-1"'-piperidinium bromides with 4",1"-substituents chlorine, bromine or iodine (BB8,15 and 16). The region between 870 and 650 cm.$^{-1}$(11.5 and 15.4μ) was studied.

There are bands near 815, 850 and 860 cm.$^{-1}$(12.3, 11.8 and 11.6μ) in all three compounds and a band near 830 cm.$^{-1}$(12.0μ) in the dichloro- and dibromo- compounds. In the substitution pattern region, there are, for all, bands near 790, 775 and 730 cm.$^{-1}$(12.7, 12.9 and 13.7μ). The dichloro- compound shows the band pattern in the other dichloro-azepinium compounds, but this is not present in the other two, although a weak band is present close to 650 cm.$^{-1}$(15.4μ) in all of them. Therefore it seems that this band pertains to the ring.

The band at 694 cm.$^{-1}$(14.41μ) in the dichloro- compound is not present in the dibromo- or diiodo- compound although there is a double band in the dibromo- compound at 670 and 667 cm.$^{-1}$(14.92 and 14.98μ). This appears to uphold the 690 cm.$^{-1}$(14.5μ) region for the position of the C–Cl stretch in the bridged biphenyls.

The compounds below were already prepared by the workers listed:

BP6, BP7 and BB12	D. M. Hall and F. Minhaj[18]
BB15 and 16	S. Ahmed and D. M. Hall [27]
BB11	S. Ahmed and D. M. Hall[47]
BB13	D. M. Hall and E. E. Turner[74]
BB14	Specimen purified from material prepared by D.M. Hall, M. S. Lesslie and E. E. Turner[91]

The following tables are divided into two sets: firstly, those giving bands to which possible assignments have been made, together with the probable assignments, and secondly, those bands of medium to strong intensity which appear in the spectra, but to which no assignment has been made. Other, less intense, bands may be found by inspection of the spectra, which are given after the tables.

INFRARED BANDS WITH PROBABLE ASSIGNMENTS

B1	B2	Probable assignment
3475 cm.$^{-1}$ (2.88μ)		sym NH str.
3380 (2.96)		asym NH str.
3226 (3.10)		sym assoc. NH str.
3195 (3.13)		asym assoc. NH str.
2967 (3.37)	2976 (3.36)	? CH_3
2924 (3.42)	2950 (3.39)	? CH_3
2915 (3.43)	2915 (3.43)	? CH
2890 (3.46)		? CH_3
2849 (3.51)	2849 (3.51)	? CH_3
1890 (5.29)	1923 (5.20)	substitution pattern: overtone and combination tone vibration
1838 (5.44)	1845 (5.42)	
1779 (5.62)	1761 (5.68)	
1616 (6.19)		NH scissors
1587 (6.30)	1570 (6.37)	C=C i.p. vibr.
1572 (6.36)	1548 (6.46)	
1473 (6.79)	sh1462 (6.84)	? C=C i.p. vibr.
1441 (6.94)	1445 (6.92)	asym CH_3 bending def.
1376 (7.27)	1376 (7.27)	sym CH_3 bending def.
1147 (8.72)	1148 (8.71)	Ar CH i.p. def.
sh1091 (9.17)	1095 (9.13)	"
1030 (9.71)	1032 (9.69)	"
759 (13.18)	769 (13.00)	CH o.o.p. def.
721 (13.86)		CH o.o.p. def. or C–Cl str.
	711 (14.07)	CH o.o.p. def.
	692 (14.46)	? C–Cl str.
	530 (18.55)	C–I str.

B3		B4		Probable Assignment
		3257 cm.$^{-1}$	(3.07μ)	NH stretch intramol. bonded with -COOH
3226 cm.$^{-1}$	(3.10μ)	sh3226	(3.10)	NH str. Bonded with $COCH_3$.
sh3185	(3.14)	3165	(3.16)	"
3115	(3.21)	3106	(3.22)	"
2950	(3.39)			? CH_3
2915	(3.43)			? CH_3
2845	(3.515)			? CH_3
2813	(3.555)			? CH_3
1931	(5.18)	1934	(5.17))	subst. pattern: overtone
1862	(5.18)	1869	(5.35))	and combination tone
1786	(5.60)	1805	(5.54))	vibration
		1698	(5.89)	C=O str. acid
1667	(6.00)	1634	(6.12)	C=O str. amide band I
1597	(6.26)	1592	(6.28)	C=C i.p. vibr.
1575	(6.35)	1582	(6.32)	"
1536	(6.51)	1531	(6.53)	NH def. amide band II
1464	(6.83)	1466	(6.82)	? ArC=Ci.p. vibr.
or 1456	(6.87)			
1443	(6.93)	1437	(6.96)	asym. CH_3bending def.
		1416	(7.06)	CO str. and OH def. comb. band
1370	(7.30)	1376	(7.27)	sym. CH_3 bending def.
1297	(7.71)			comb. band of NH def. and
or1269	(7.88)			CN str.:amide band III

B3		B4		Probable assignment
		1312	(7.62)	? CO str. and OH def.
				comb band
		1252	(7.99)	? C–O vibration
1148	(8.71)	1149	(8.70)	ArCH i.p. def.
1082	(9.24)	1078	(9.28)	"
1037	(9.64)	1011	(9.29)	"
or 1010	(9.90)			
		904	(11.07)	OH o.o.p. def.
775	(12.91)	761	(13.14)	CH o.o.p. def.
		or 755	(13.25)	
733	(13.64)	704	(14.20)	CH o.o.p. def. or ? CCl str.
or sh720	(13.89)			
698	(14.32)			amide V band
680	(14.71)			amide IV band
611	(16.36)			amide VI band
or 588	(17.02)			

B5		B6		Probable assignment
3480	(2.87)			asym. NH str.
3365	(2.97)			sym. NH str.
1927	(5.19)	1961	(5.10))	substitution pattern:
1883	(5.31)	1894	(5.28))	overtone and combination
1842	(5.43)	1838	(5.44))	tone vibration.
sh1704	(5.87)	sh1721	(5.81)	monomer C=O str.
sh1685	(5.93)	sh1685	(5.93)	dimer C=O str.
1669	(5.99)	1667	(6.00)	assoc. C=O str.
1610	(6.21)			NH scissors
1587	(6.30)			C=C i.p. vibr.
1550	(6.45)	1563	(6.40)	"
1451	(6.89)	1441	(6.94)	? "
1420	(7.04)	1410	(7.09)	CO str. and OH def. comb. band
1312	(7.62)	sh1300	(7.7)	? "
1250	(8.00)	1250	(8.00)	? C–O str.
1161	(8.61)	1159	(8.63)	Ar i.p. CH def.
1089	(9.18)	1095	(9.13)	"
or1075	(9.30)			
sh1029	(9.72)	1017	(9.84)	"
892	(11.21)	885	(11.30)	OH o.o.p. def.
754	(13.27)	752	(13.30)	CH o.o.p. def.
708	(14.13)	719	(13.91)	CH o.o.p. def. or ?CCl str.
		677	(14.77)	? CCl str.
		573	(17.44)	CI str.

B7		BP1		Probable assignments
2950 cm.$^{-1}$	(3.39 μ)	2959 cm.$^{-1}$	(3.38)	asym CH_3 CH str.
1934	(5.17)	1957	(5.11)	subst. pattern: overtone
1880	(5.32)	1898	(5.27)	and combination tone
		1845	(5.42)	vibration
		1789	(5.59)	
1724	(5.80)	1727	(5.79)	C=0 str.
1572	(6.36)	1585	(6.31)	C=C i.p. def.
1553	(6.44)	1563	(6.40)	"
sh1443	(6.93)	1445	(6.92)	? "
sh1458	(6.86)	sh1460	(6.85)	? asym CH_3 str.
or1431	(6.99)	or1433	(6.98)	
1397	(7.16)	1416	(7.06)	? sym CH_3 str.
1290	(7.75)	1286	(7.80)	CO str.
or1250	(8.00)	or1263	(7.92)	
1133	(8.83)	1125	(8.89)	"
1149	(8.70)	sh1159	(8.63)	Ar CH i.p. def.
		or1149	(8.70)	"
1088	(9.19)	1092	(9.16)	"
1017	(9.84)	? 1002	(9.98)	"
754	(13.26)	759	(13.18)	CH o.o.p. def.
731	(13.68)	739	(13.53)	"
		or729	(13.72)	
683	(14.58)	716	(13.99)	? CCl str.

BP2		+BP2		Probable assignment
sh1745 cm.$^{-1}$	(5.73)	sh1742 cm.$^{-1}$	(5.74)	monomeric C=0 str.
1689	(5.92)	1689	(5.92)	dimeric C=0 str.
1587	(6.30)	1587	(6.30)	C=C i.p. vibr.
1560	(6.41)	1560	(6.41)	"
1451	(6.89)	1449	(6.90)	? "
1425	(7.02)	1420	(7.04)	? CO str. and OH def.
or1403	(7.13)	or1404	(7.12)	comb. band
sh1309	(7.64)	1295	(7.72)	? "
or1280	(7.81)			
1261	(7.93)	1267	(7.89))	? C–0 vibration
		1264	(7.91))	
		or1245	(8.03)	
1153	(8.67)	1157	(8.64)	Ar CH i.p. def.
or sh1147	(8.72)	or1152	(8.68)	
1096	(9.12)	1092	(9.16)	"
		1002	(9.98)	? "
927	(10.78)	925	(10.81))	
917	(10.90)	911	(10.97))	? OH o.o.p. def.
		896	(11.16))	
759	(13.18)	755	(13.24)	CH o.o.p. def.
713	(14.02)	714	(14.01)	"
705	(14.19)	704	(14.20)	CCl str.

These two spectra show great similarity

BP3		+BP3		Probable assignments
		3610 cm.$^{-1}$	(2.77μ)	free OH str.
		sh3597	(2.78)	intramol. bonded OH str.
		3559	(2.81)	dimeric OH str.
3247	(3.08)	3333	(3.00)	polymeric OH str.
sh3215	(3.11)	sh3279	(3.05)	"
2930	(3.41)	2930	(3.41)	CH_2 asym. str.
2890	(3.46)	2890	(3.46)	CH_2 sym. str.
or2850	(3.51)	or2850	(3.51)	
1585	(6.31)	1590	(6.29)	C=C i.p. vibr.
1560	(6.40)	1563	(6.40)	"
sh1458	(6.86)	sh1458	(6.86)	"
orsh1435	(6.97)	or sh1445	(6.92)	? "
1427	(7.01	1427	(7.01)	? CH_2 scissors
1147	(8.72)	1147	(8.72)	Ar CH i.p. def.
or1139	(8.78)	or1139	(8.78)	
1094	(9.14)	1096	(9.12)	"
1017	(9.84)	1017	(9.84)	? assoc. CO str.
		1004	(9.96)	free "
		1042	(9.60)	dimeric "
795	(12.58)	797	(12.58)	CH o.o.p. def.
789	(12.67)	782	(12.78)	
753	(13.29)	748	(13.38)	"
745	(13.42)	739	(13.53)	"
693	(14.43)	696	(14.38)	CCl str.
		691	(14.48)	

BP4	+BP4	Probable assignments
2930 cm.$^{-1}$ (3.41μ)	2930 cm.$^{-1}$ (3.41μ)	asym. CH. str.
2856 (3.51)	2856 (3.51)	? sym. CH str.
1582 (6.32)	1590 (6.29)	C=C i.p. vibr.
1558 (6.42)	1563 (6.40)	"
1443 (6.93)	1447 (6.91)	C=C i.p. vibr.
1425 (7.02)	1429 (7.00)	? CH$_2$ scissors
1156 (8.65)	1151 (8.69)	Ar CH i.p. def.
1089 (9.18)	1087 (9.21)	"
1002 (9.98)	1003 (9.97)	? "
793 (12.61)	794 (12.59)	CH o.o.p. def.
	sh 789 (12.68)	
746 (13.40)	748 (13.38)	"
	731 (13.56	
690 (14.50)	687 (14.55)	CCl str.
632 (15.82)	624 (15.96)	? ring vibr.
sh 626 (15.98)	591 (16.92)	"
588 (17.02)	572 (17.48)	"
560 (17.86)	561 (17.82)	"
545 (18.35)	548 (18.26)	CBr str.

BP6		BP7		Probable Assignments
		sh1745	(5.73)	monomeric C=0 str.
		1695	(5.90)	dimeric C=0 str.
1585	(6.31)	1575	(6.35)	C=C i.p. vibr.
1548	(6.46)	1550	(6.45)	"
1445	(6.92)			"
		1429	(7.00)	? C=C i.p. vibr or -COOH vibration
		1429	(7.00)	coupled CO str. & OH def.
		or sh1403	(7.13)	"
		1282	(7.80)	? coupled CO str. & OH def.
		1269	(7.88)	? CO vibration.
		909	(10.99)	OH o.o.p. def.
867	(11.53)	875	(11.43)	CH o.o.p. def.
815	(12.70)			"
787	(12.70)	805	(12.42)	? CCl str.
		or 696	(14.36)	"

BP5		Assignments
sh1443	(6.93)	Ar CH i.p. def.
or sh1449	(6.90)	"
1431	(6.99)	? $-CH_2-$ scissors
769	(13.01)	CH o.o.p. def.
or 755	(13.24)	
602	(16.60)	ring vibr.
537	(18.62)	CBr str.

BB1		-BB1		Probable assignments
1590	(6.29)	1590	(6.29)	C=C i.p. vibr.
1563	(6.40)	1558	(6.42)	"
1057	(9.46)	1063	(9.41)	–C–O–C– str.
909	(11.00)	905	(11.06)	–C–O–C– vibr.
884	(11.32)	888	(11.26)	"
795	(12.57)	792	(12.62)	CH o.o.p. def.
730	(13.69)	767	(13.76)	"
686	(14.58)	686	(14.57)	CCl str.
BB2		-BB2		
3484	(2.87)	3491	(2.865)	asym OH str. of water
sh3430	(2.915)	?sh3448	(2.90)	OH str. of H_2O
3413	(2.93)	3436	(2.91)	"
3322	(3.01)	3365	(2.97)	sym. OH str. of H_2O
1647	(6.07)	sh1616	(6.19)	H_2O OH def.
1610	(6.21)	1610	(6.21)	"
1592	(6.28)	1590	(6.29)	C=C i.p. vibr.
1567	(6.38)	1565	(6.39)	"
910	(1o.98)	910	(10.98)	? $\overset{+}{N}$-Me vibr.
795	(12.58)	795	(12.58)	CH o.o.p. def.
or782	(12.78)	or781	(12.81)	
or775	(12.89)	or771	(12.96)	
730	(13.69)	730	(13.70)	"
695	(14.39)	696	(14.37)	CCl str.

BB4		BB7		Probable assignments
		2903	(3.445)	CH_2 asym. str.
		2833	(3.53)	? CH_2 sym. str.
		1590	(6.29)	C=C i.p. vibr.
		1558	(6.42)	"
		1453	(6.88)	CH_2 scissors
		or1433	(6.98)	
817	(12.24)			CH o.o.p. def.(2H)
753	(13.28)	777	(12.87)	CH o.o.p. def.(3H)
727	(13.76)	725	(13.80)	"
706	(14.17)	680	(14.70)	? CCl str.
or673	(14.85)			
BB8		**BB9**		
		3571	(2.80)	asym. OH str. of H_2O
		3484	(2.87)	OH str. of H_2O
		3413	(2.93)	sym OH str. of H_2O
		1610	(6.21)	H_2O def.
		sh1603	(6.24)	"
1592	(6.28)			C=C i.p. vibr.
1565	(6.39)			"
789	(12.68)	762	(13.12)	CH o.o.p. def.
or774	(12.92)			
729	(13.71)			"
694	(14.41)			CCl str.

BB12		BB14		Probable assignments
		2933	(3.41)	asym CH$_2$ str.
		2833	(3.53)	? sym CH$_2$ str.
1590	(6.29)	1605	(6.23)	C=C i.p. vibr.
1555	(6.43)	1585	(6.31)	"
		or1565	(6.39)	
		1451	(6.89)	CH$_2$ scissors
		or1441	(6.94)	
1063	(9.41)			-C-O-C- str.
902	(11.09)			-C-O-C- vibr.
881	(11.35)			-C-O-C- vibr.
801	(12.48)			CCl str.
or679	(14.73)			
738	(13.55)	745	(13.43)	CH o.o.p. def.

BB15		BB16		
1587	(6.30)	1582	(6.32)	C=C i.p. vibr.
1558	(6.42)	1550	(6.45)	"
786	(12.72)	798	(12.53)	CH o.o.p. def.
or771	(12.97)	or 779	(12.83)	
727	(13.75)	735	(13.61)	"
670	(14.92)			
&/or 667	(14.98)			CBr str.

UNASSIGNED BANDS OF MEDIUM TO STRONG INTENSITY

B1		B2		B3		B4	
		1176	8.50	1176	8.50		
1468	6.81	1014	9.86	874	11.46	1312	7.62
1280	7.81	854	11.71	sh858	11.52	1266	(7.90)
1247	8.02			847	11.81	1282	(7.80)
1192	8.39					1208	8.28
1076	9.29			533	18.75	806	12.41
992	10.09			513	19.48	668	14.97
847	11.81					603	16.59
826	12.10					662	17.80
630	15.86						

B5		B6		B7	
		1284	(7.79)		
		1198	8.35		
1272	7.86	811	12.33		
sh1217	8.22				
611	16.37			1199	8.34
572	17.47			964	10.38
548	18.26			841	11.88
456	21.92			799	12.52

BP1		BP2		+BP2	
978	10.23	1203	8.31	1203	8.31
845	11.83	818	12.23	1131	8.84
815	12.28			846	11.82
				817	12.25

BP3		+BP3		BP4		+BP4	
1323	7.56	1174	8.52	1209	8.27	1211	8.26
1218	8.21	998	10.02	1179	8.48	1178	8.49
1176	8.50	987	10.14	1111	9.00	1087	8.99
998	10.02	970	10.31	891	11.23	892	11.21
883	11.33	870	11.50	504	19.85	501	19.95
637	15.71	852	11.73	492	20.32	487	20.54
		633	15.8				
		626	15.95				
		ca593	ca16.9				
		567	17.65				
		560	17.85				

BP5		BP6		BP7	
1218	8.21	1515	6.60	1395	7.17
1193	8.38	1460	6.85	1381	7.24
1005	9.95	1381	7.24		
830	12.07	1366	7.32		
809	12.37	1138	8.79	1233	8.11
				1195	8.37
sh774	12.92	1103	9.07	1149	8.70
		1086	9.21	886	11.29
		1058	9.41		
		1503	9.97		
		574	17.43		

BB1		– BB1		BB2		– BB2	
1205	8.30	1178	8.49	1479	6.76	1475	6.78
1174	8.52	1135	8.81	1439	6.95	1441	6.94
1147	8.72	807	12.49	1179	8.48	1321	7.57
1135	8.81	764	13.09	1153	8.67	1208	8.28
870	11.49	676	14.84	1130	8.77	1199	8.34
Sh790	12.66			880	11.36	1175	8.51
768	13.02			822	12.17	1151	8.69
667	14.98					1139	8.78
602	16.61					880	11.36
						821	12.19
						658	15.20

BB4	
1195	8.37
1175	8.51
1110	9.01
948	10.55
862	11.60
803	12.45
771	12.96
761	13.14
667	15.00

BB8	
1412	7.08
1195	8.37
1129	8.86
950	10.53
890	11.24
813	12.30
757	13.21
605	16.54

BB9	
3040	3.29
3003	3.33
2959	3.38
2915	3.43
1464	6.83
1449	6.90
1172	8.53
1130	8.85
928	10.77
912	10.96
863	11.59
830	12.05
819	12.21
650	15.39
607	16.49

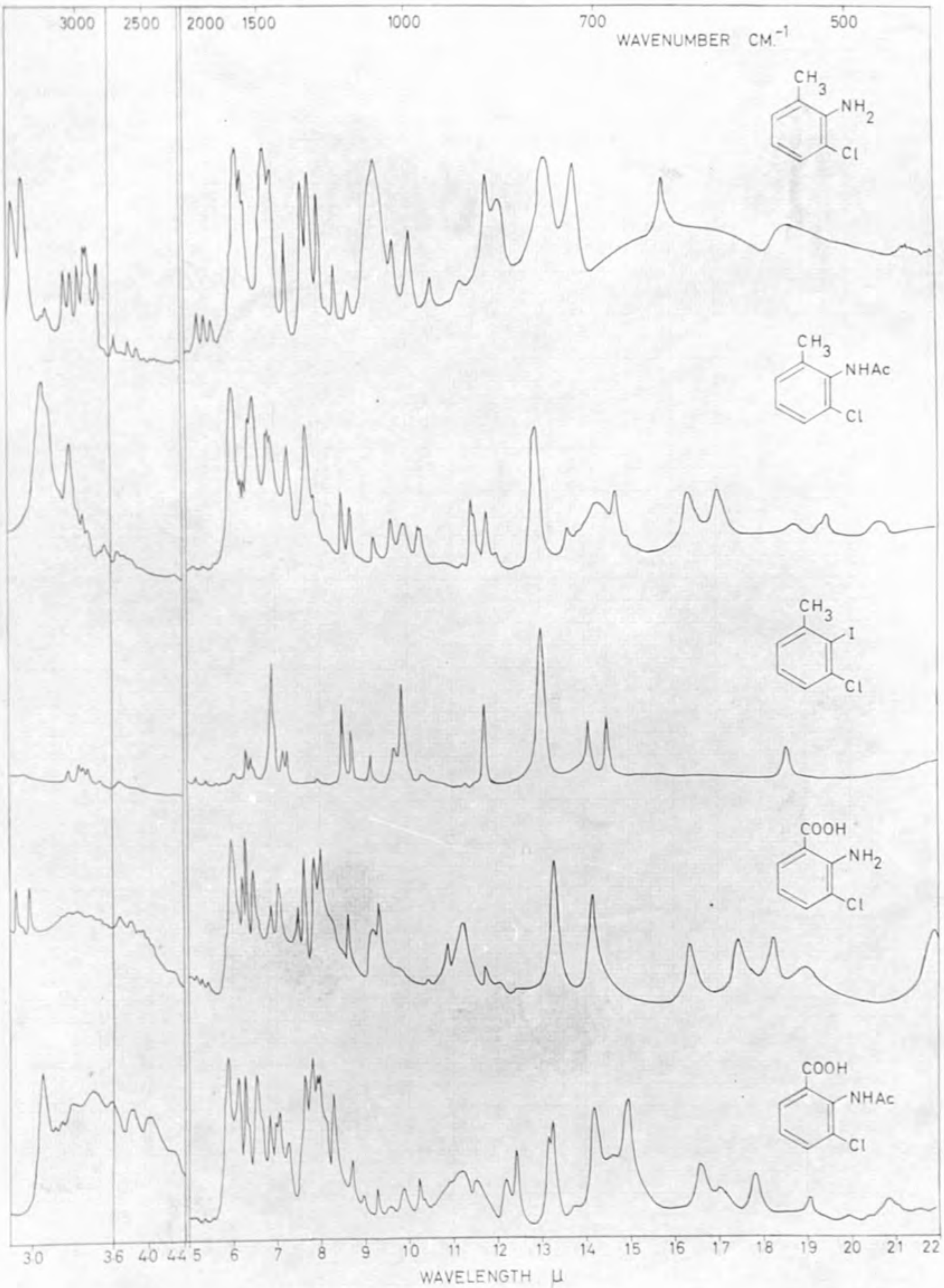
BB10	
1479	6.76
1453	6.88
1412	7.08
1202	8.32
987	10.13
947	10.56
920	10.87
806	11.17
783	13.77

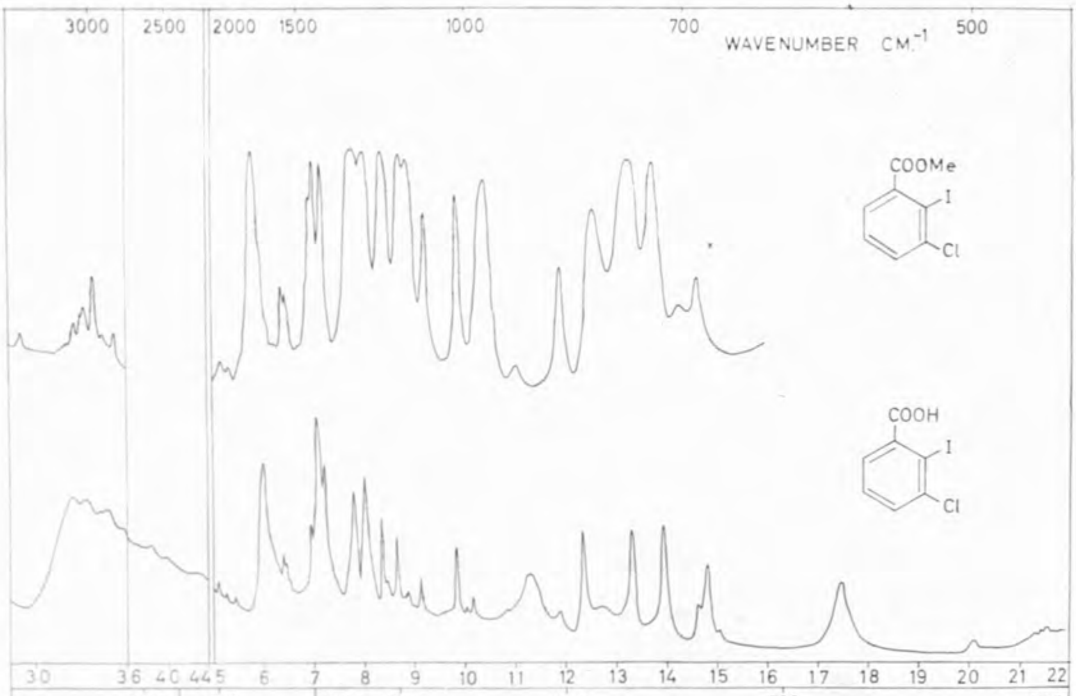
BB13	
2732	3.66
1464	6.83
1427	7.01
1370	7.30
1208	8.28
1172	8.53
1110	9.01
858	11.65
679	14.73

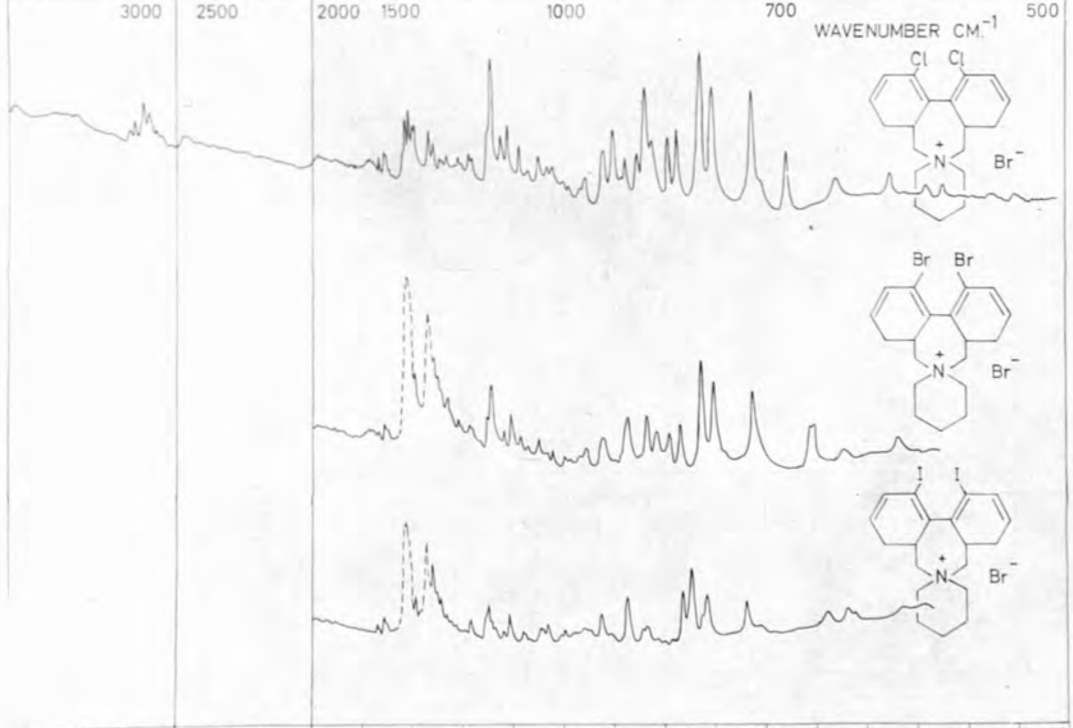
BB15	
3062	3.265
3030	3.30
3017	3.315
2890	3.46
1484	6.74
770	12.95
745	13.43
726	13.77
621	16.10
603	16.59

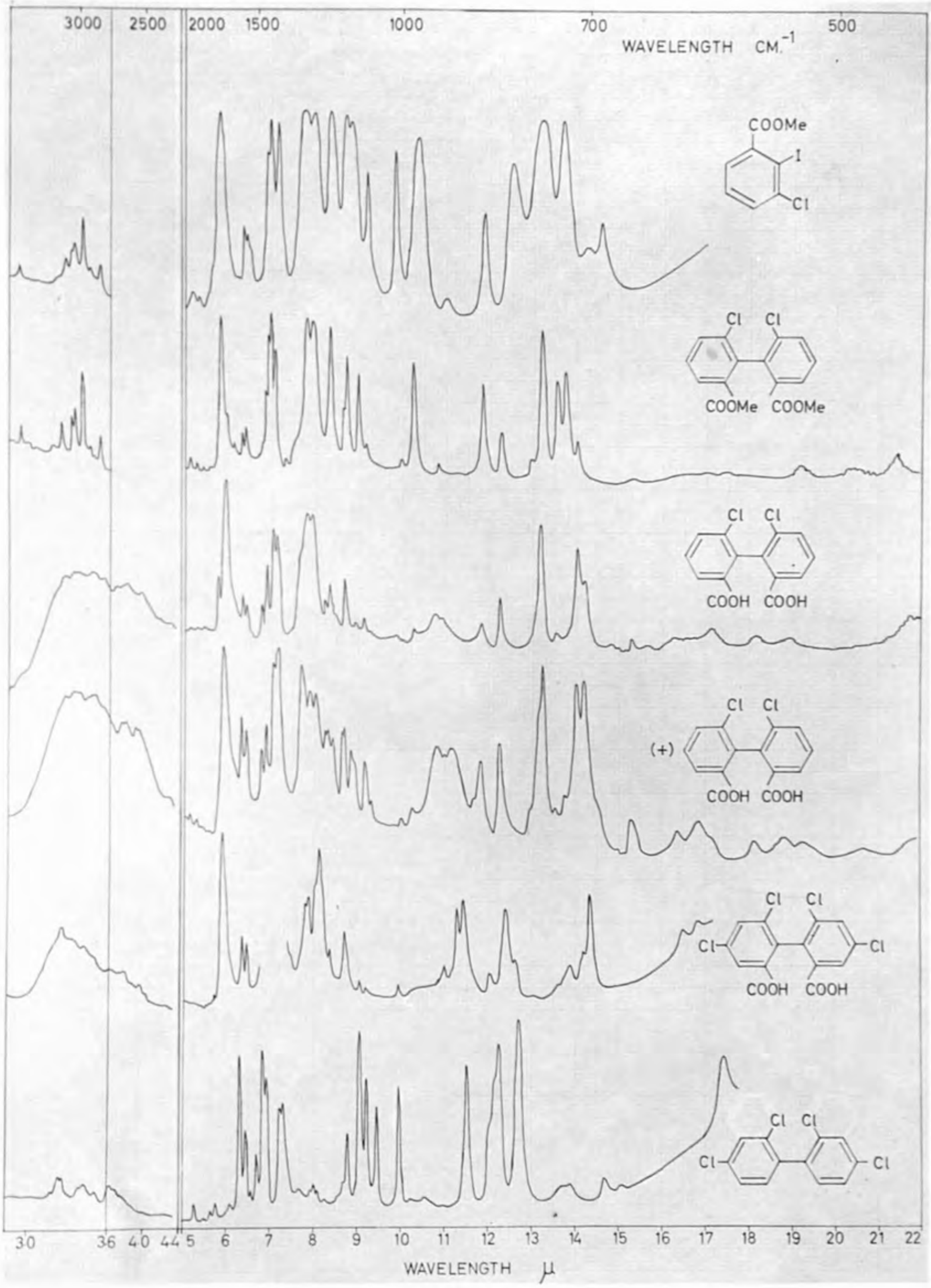
BB16	
1168	8.56
888	11.26
860	11.63
812	12.31

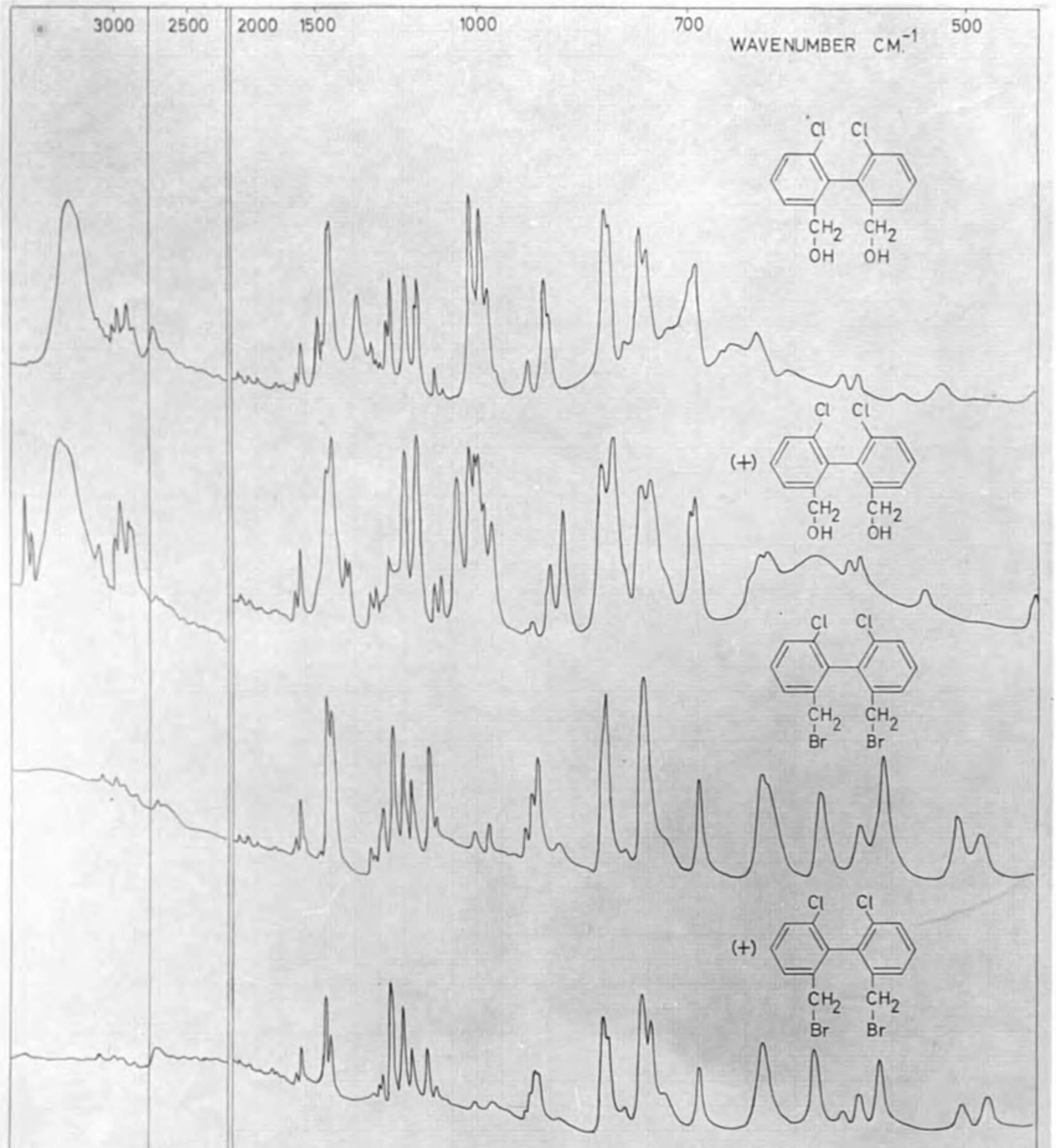
BB17	
1174	8.52
1120	8.93
930	10.75
889	11.25
810	12.35

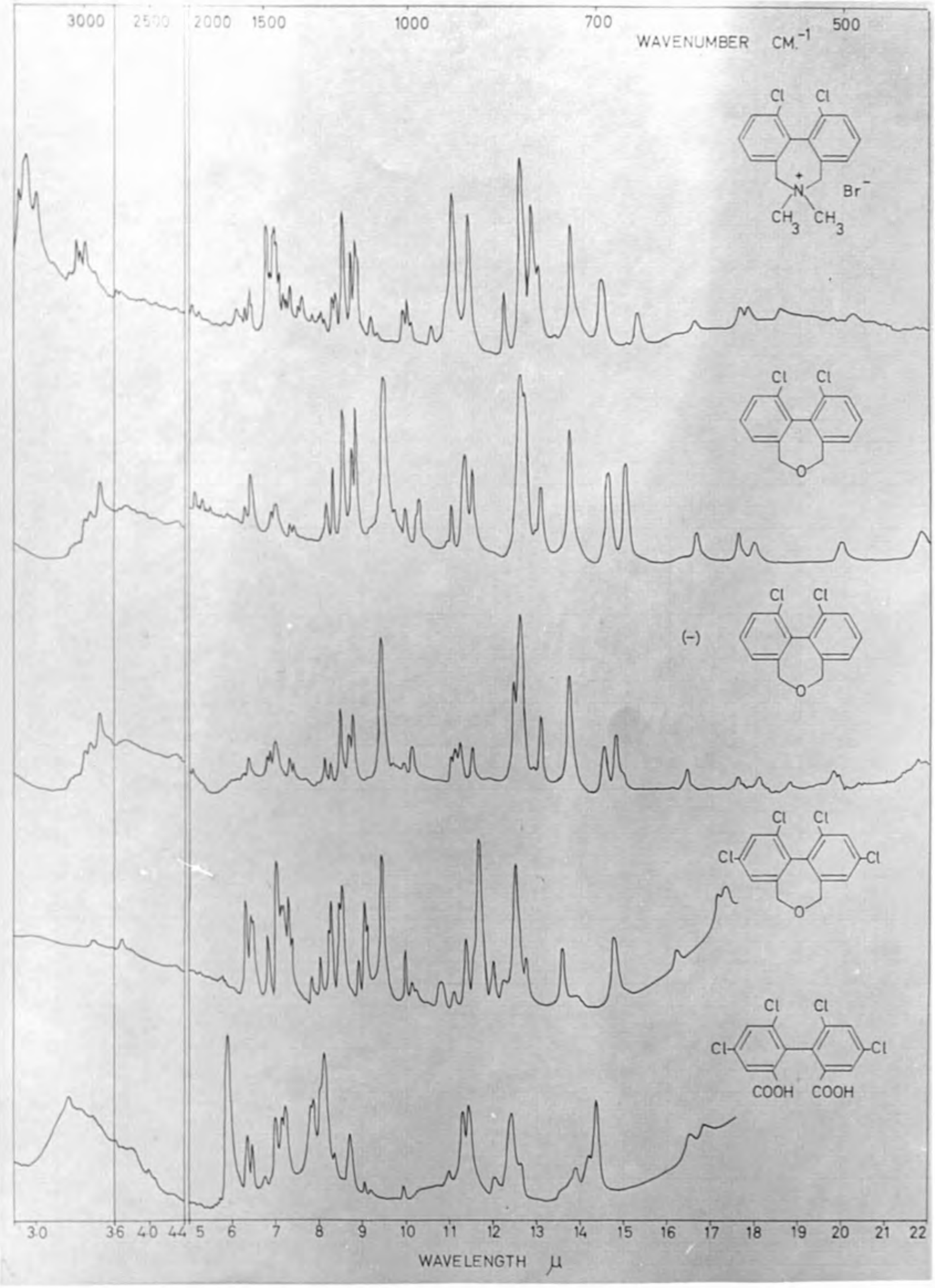

3000
2500
2000
1500
1000
700
500
WAVENUMBER CM.-1
CH3
NH2
Cl
CH3
NHAc
Cl
CH3
I
Cl
COOH
NH2
Cl
COOH
NHAc
Cl
3.0
3.6
4.0
4.4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
WAVELENGTH μ

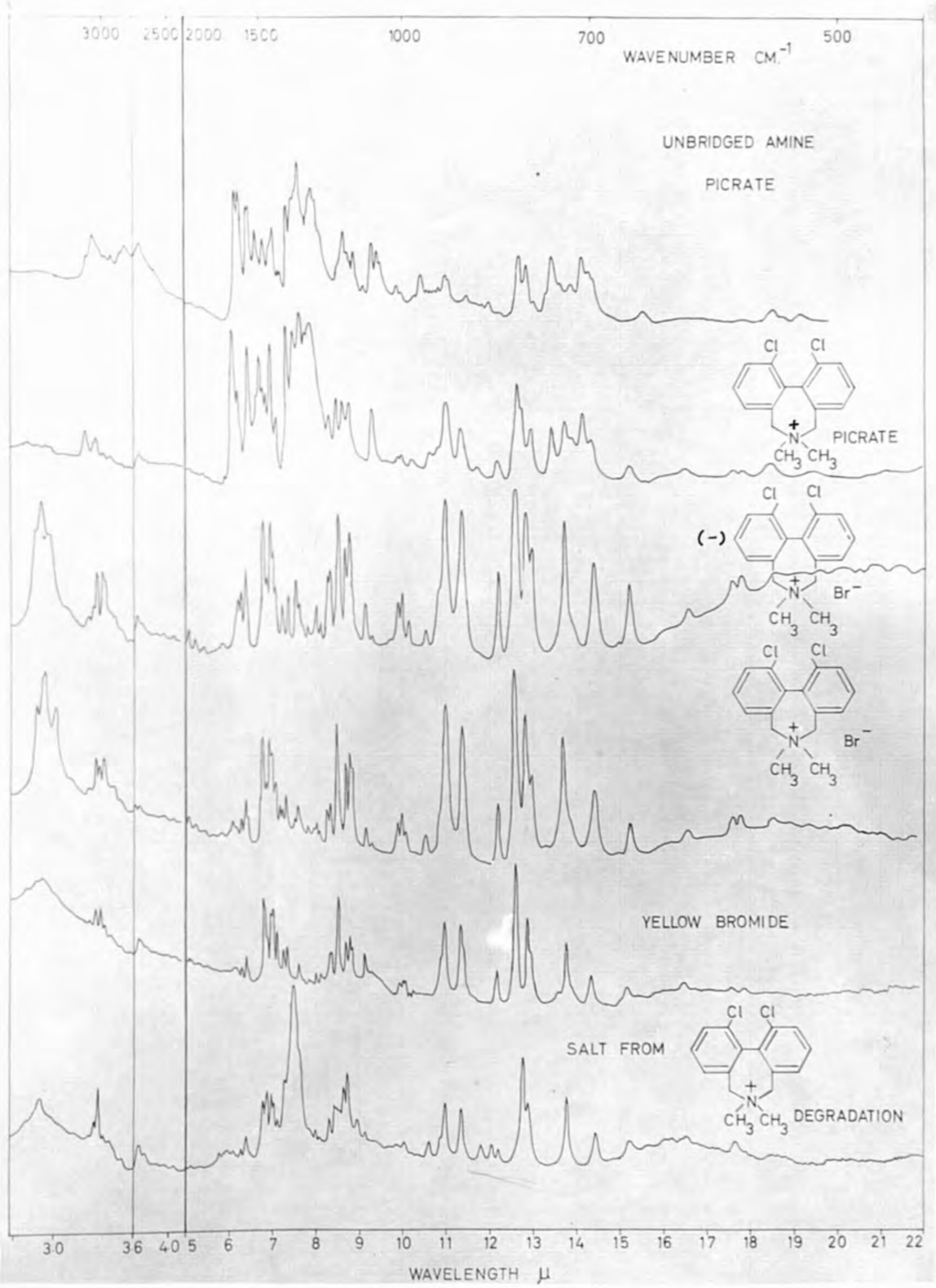

3000
2500
2000
1500
1000
700
WAVENUMBER CM.-1
500
COOMe
I
Cl
COOH
I
Cl
3.0
3.6
4.0
4.4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22

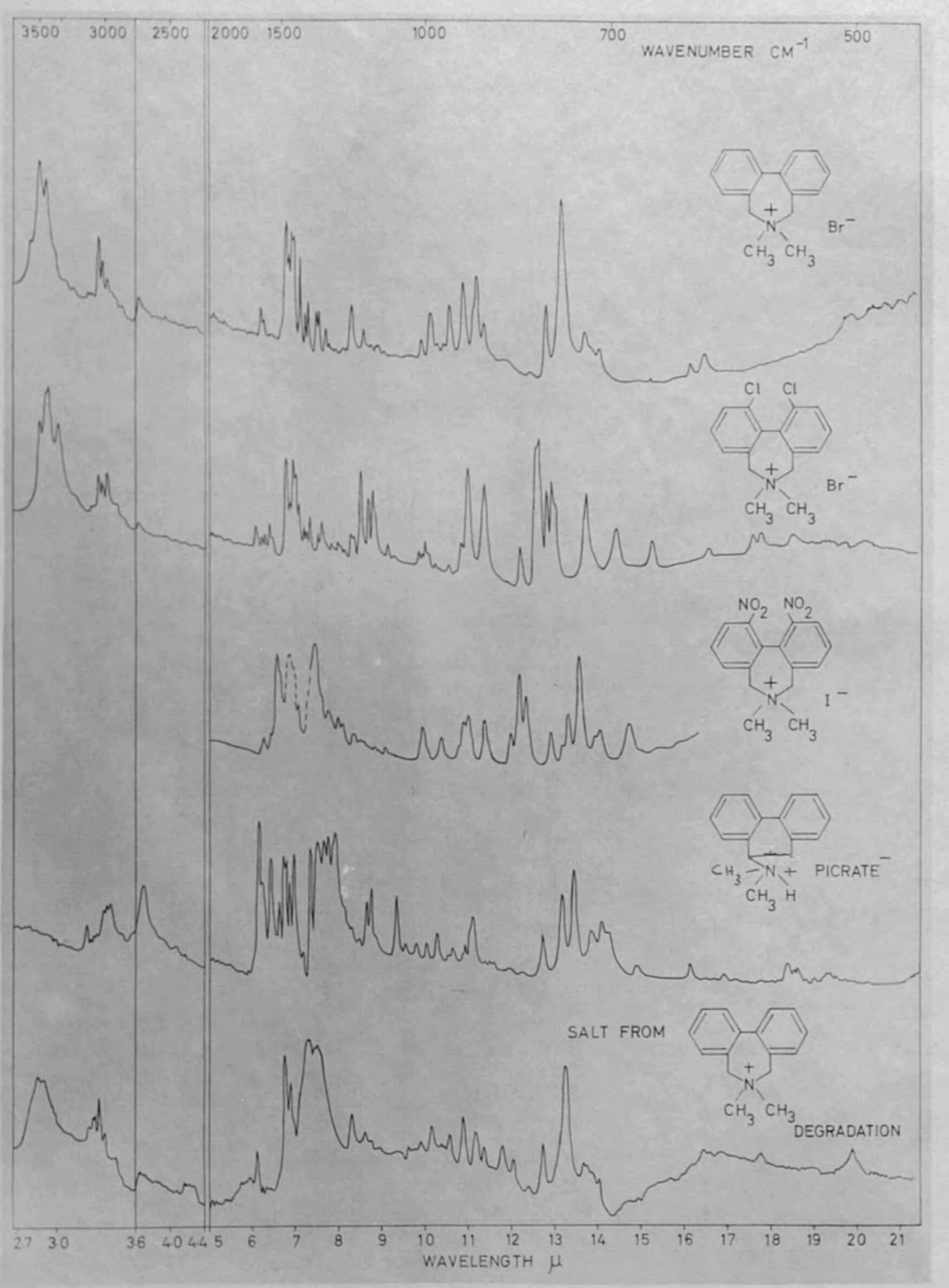

3000
2500
2000
1500
1000
700
WAVENUMBER CM.-1
500
Cl
Cl
N+
Br-
Br
Br
N+
Br-
I
I
N+
Br-
2.5
3.0
3.6
4.0
4.5
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
WAVELENGTH μ

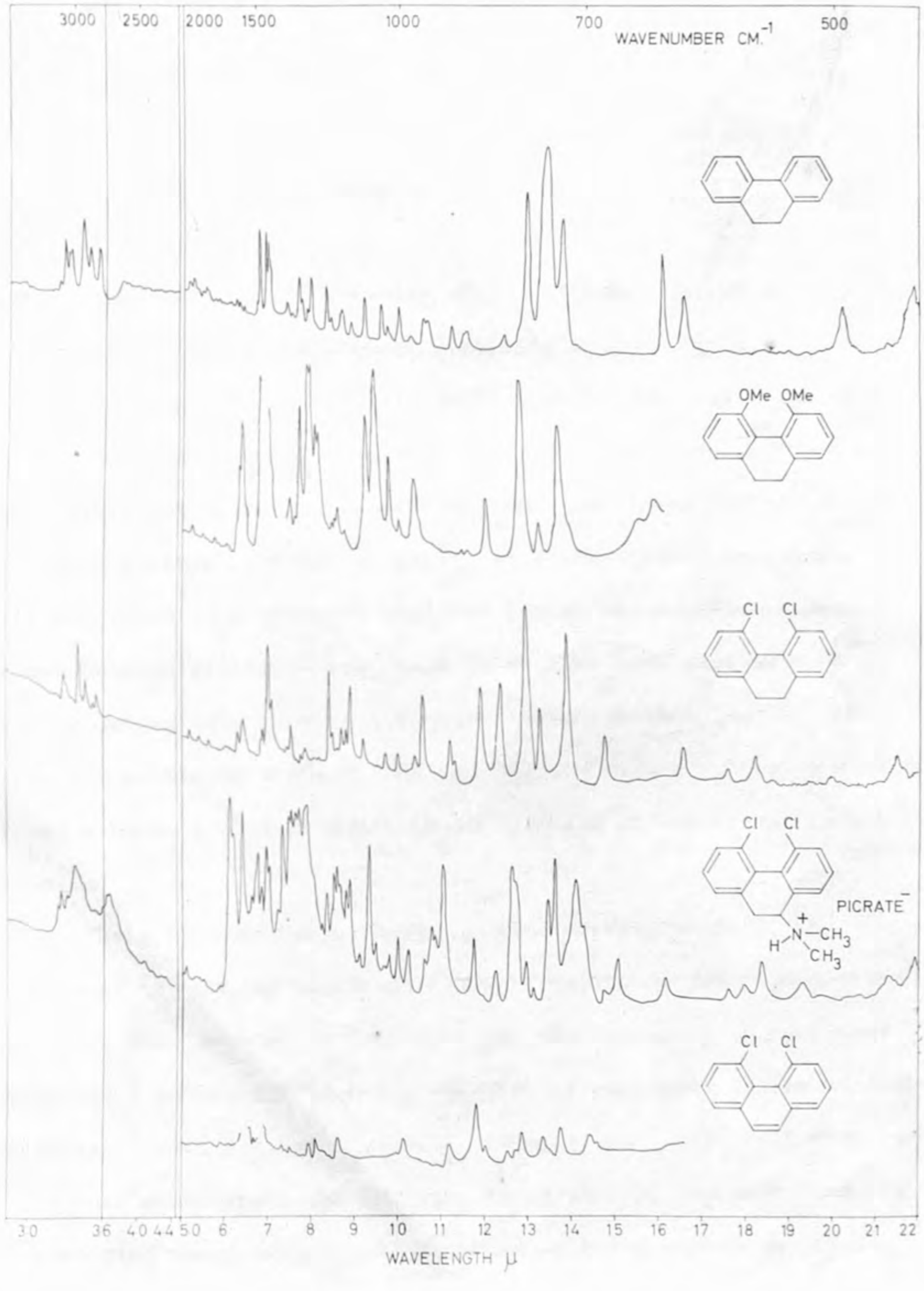

3000
2500
2000
1500
1000
700
WAVELENGTH CM.$^{-1}$
500
COOMe
I
Cl
Cl Cl
COOMe COOMe
Cl Cl
COOH COOH
(+)
Cl Cl
COOH COOH
Cl Cl
Cl Cl
COOH COOH
Cl Cl
Cl Cl
3.0 3.6 4.0 4.4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22
WAVELENGTH μ


3000
2500
2000
1500
1000
700
500
WAVENUMBER CM.$^{-1}$
Cl
Cl
CH$_2$
OH
CH$_2$
OH
(+)
Cl
Cl
CH$_2$
OH
CH$_2$
OH
Cl
Cl
CH$_2$
Br
CH$_2$
Br
(+)
Cl
Cl
CH$_2$
Br
CH$_2$
Br
CH$_2$
Br
CH$_2$
Br
2.7
3.0
3.6
4.0
4.4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
WAVELENGTH μ


3000
2500
2000
1500
1000
700
WAVENUMBER CM.⁻¹
500
Cl Cl
N⁺
Br⁻
CH₃ CH₃
Cl Cl
O
(−)
Cl Cl
O
Cl Cl
Cl Cl
O
Cl Cl
Cl Cl
COOH COOH
3.0
3.6
4.0
4.4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
WAVELENGTH μ


3000
2500
2000
1500
1000
700
500
WAVENUMBER CM.$^{-1}$
UNBRIDGED AMINE
PICRATE
Cl Cl
$\overset{+}{N}$
CH$_3$ CH$_3$
PICRATE
(-)
Br$^-$
YELLOW BROMIDE
SALT FROM
DEGRADATION
3.0
3.6
4.0
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
WAVELENGTH μ


3500 3000 2500 2000 1500 1000 700 500
WAVENUMBER CM^{-1}
Br$^-$
CH_3 CH_3
Cl Cl
Br$^-$
NO_2 NO_2
I$^-$
PICRATE$^-$
CH_3 H
SALT FROM
DEGRADATION
27 30 36 40 44 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21
WAVELENGTH μ


3000
2500
2000
1500
1000
700
WAVENUMBER CM.⁻¹
500
OMe OMe
Cl Cl
Cl Cl
PICRATE⁻
H N CH3 CH3
Cl Cl
3.0
3.6
4.0
4.4
5.0
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
WAVELENGTH μ

ULTRAVIOLET SPECTRA

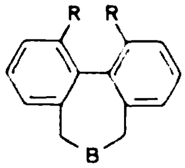
The spectra were measured on a Unicam S.P. 500 spectrophotometer using solutions made up in 96% EtOH.

a) Biphenyls

Truce and Emrick[92] consider that a correlation can be drawn between band position and optical stability in seven-membered ring bridged biphenyls when no significantly auxochromic groups are present. They consider that compounds with a band at longer wavelength than 2420 Å could not be very optically stable. Hall and Minhaj[18] believe that while a rough correlation exists in unsubstituted compounds, small variation in wavelength need not effect racemisation rates.. All the bridged dichloro- compounds which have been studied here have the conjugation band at a longer wavelength than 2420 Å. The oxepin and azepinium bromide, BB1 and BB2, are highly optically stable: BB1 has a half-life of 3½ hours at 160°, while BB2 is slightly more stable.

There is a definite change to shorter wavelength in the position of the conjugation band (except for the dihydrophenanthrene BB7, which does not change position) and the intensity is decreased considerably in going from the unsubstituted compounds to the dichloro-compounds. This indicates reduced conjugation. Since chlorine is only a weak auxochrome, the decrease in intensity, compared with the unsubstituted compounds, may be regarded as being steric in origin, although. after studying the tetrachloro-compounds, Hall and Minhaj[18] consider that there is little steric effect and that large groups are easily accommodated because of the size of the dihedral angle.

The oxepin BB1 and azepinium bromide BB2 have conjugation bands at the same position (2460 Å) and the lower intensity of the azepinium bromide (ε_{max} 9,400 cf. 10,700 of oxepin) may be a result of the slightly increased dihedral angle of the biphenyl. Data for the conjugation bands in these and related compounds are given in the table below:



	λ Å	ε_{max}	solvent	dihedral angle	ref
R=H					
B=O	2505	16,500	EtOH	43 or 44	18,23,25
$B=\overset{+}{N}(CH_3)_2$	2490	14,200	EtOH		24
$B=\overset{+}{N}(CH_2)_5$	2480	15,000	water	47	18,22
R=Me					
B=O	24~~2~~40	11,000	dioxan		26
$B=\overset{+}{N}(CH_3)_2$	2420	9,100	EtOH		26a.
R=Cl					
B=O	2460	10,700	96%EtOH		
$B=\overset{+}{N}(CH_3)_2$	2460	9,400	96%EtOH		
$B=\overset{+}{N}(CH_2)_5$	2470	10,000	96%EtOH		27

Both the unsubstituted and dichloro-spiro-piperidinium compounds have conjugation bands slightly more intense than the corresponding 1,1-dimethyl-azepinium compounds, although the small wavelength shifts are opposite in directions. However, the unsubstituted spiro-piperidinium compound is measured in a different solvent.

When the values for the dimethyl-oxepin and azepinium bromide are compared with the di-chloro- compounds, the intensities are seen to be about the same, but the position of the conjugation band is at slightly lower wavelength for the dimethyl-compounds. Unfortunately, the spectra of the dimethyl compounds were measured in different solvents, so a strict comparison cannot be made. Methyl and chlorine are considered to have about the same size, although Adam and Yuan's intermolecular distances give $Cl > CH_3$ and Williamson and Rodebush's order of interference, estimated from van der Waals' radii, also gives $Cl > CH_3$. Racemisation data of certain biphenyls give $CH_3 > Cl$, but other factors enter into consideration here. Generally, methyl and chlorine are considered to be of the same order of size and to have comparatively little electronic interaction with the conjugation system. The intensity of the conjugation bands are of the same order, but since the wavelengths of the conjugation bands are different, the groups must differ in size or in electronic interaction with the benzene ring, or perhaps in both.

Beaven and Johnson[88] have reported that chlorine, being only a weakly polar auxochrome, has a scarcely greater effect on the benzene spectrum than methyl does: the bathochromic shift is greater, but the intensities are little affected. This is in accordance with the observations on the spectra of the oxepin and azepinium compounds.

The azepinium bromide, BB2, and picrate, BB3, show bands at similar wavelength except in the case of the conjugation band, when that of the picrate is at a definitely lower wavelength. All the picrates show a displacement of the conjugation band to shorter wavelength. This displacement is probably due to the superimposition of the picrate absorption on that of the biphenyl system (cf. Hall and Poole[24]). This appears to have an even greater effect on the 9-dimethylamino- compound, BB5, which, being a compound with a 2-atom bridge, absorbs at a longer wavelength. The conjugation band in BB6 appears as a very broad shoulder and it is difficult to estimate the position accurately. This band would seem to be very weak, since there is little difference between this and the absorption of picric acid at the same wavelength, and the picrate ion may be expected to have a similar absorption to the acid at this wavelength.

Accordingly, the ultraviolet spectrum of the hydrochloride of the liberated base was measured, and this shows little absorption in this region. The spectrum of this compound will be mentioned separately later in this section.

The position of the azepinium picrate BB3 conjugation band is in the range of 2400–2440 Å which is given by Mislow[2~~3~~6] for three-atom bridged compounds substituted with chlorine or methyl. The rest of the seven-membered ring compounds have bands above this range. Mislow's ranges are based on a limited number of compounds, which only includes two compounds substituted with chlorine, one of which has a band at 2440 Å and the other at 2470 Å.

The dichloro-dimethylaminodihydrophenanthrene picrate is also outside the range given for biphenyls with a 2-atom bridge i.e. 2600–2640 Å. This band, at 2560 Å ε_{max} 17,700 is below, and the dichloro-dihydrophenanthrene at 2645 Å ε_{max} 11,100 very slightly above the given range.

On going from the three-atom bridge to the two-atom bridge, there is an increase in wavelength, but little increase in intensity. There must be considerable distortion of the molecule and this is borne out by the difficulty in preparing the compound from the dichlorobisbromomethylbiphenyl. A similar difficulty in ring closure is found with the dimethoxy- compound[~~18~~74], although methoxy is very much smaller. The yields from the reactions are about the same under the same conditions. However, other workers[75,76] have prepared the dimethyl dihydrophenanthrene in good yield.

The dichlorodihydrophenanthrene (BB7) conjugation band is close to the position of the unsubstituted compound, although reduced in intensity; extinction coefficients are ε_{max} 11,100 and ε_{max} 17,000 respectively. The reduction in intensity is thus to about the same extent as in the oxepins. The dimethyldihydrophenanthrene absorbs at a higher frequency and intensity[23] (2610 Å, ε_{max} 15,000) than the dichloro- compound. Since the effects in the dihydrophenanthrenes are considered[18] to be primarily steric, the differences in reduction of intensity suggest that chlorine is larger than methyl, or else that with methyl the strain can more easily be relieved by distortion of the methyl group than of the biphenyl skeleton. Again, there is a lesser blue shift with the dichloro- compound than with the methyl- compound from the conjugation band position in the unsubstituted compound: the difference is of the same order as was found for seven-membered ring compounds.

The compound BB6 appeared to have little biphenyl absorption in the conjugation band region and the hydrochloride shows no conjugation band in the region above 2400 Å. The spectrum strongly resembles that of an unbridged biphenyl, with a broad shoulder about 2200 Å (ε_{max} about 20,000) on the shortwavelength band, due to the residual conjugation of the biphenyl system. The short wavelength band is also at a considerably shorter wavelength (< 2020 Å) than that of the bridged compounds (2150-2200 Å), and the long wavelength features, although much weaker and at a shorter wavelength, are clearly defined.

The azepinium bromide BB2 is the only other compound to show three definite long wavelength features. The shortest wavelength of these being a distinct peak. Most of the long wavelength bands show only as inflections. The circular dichroism spectrum of the oxepin reveals the presence of a third, and optically active, band, which does not show up in the ultraviolet spectrum. The oxepin long wavelength bands are at shorter wavelength and have considerably lower intensity than those of the azepinium bromide.

The six-membered ring compounds show only one long wavelength inflection. Any low intensity bands at a shorter wavelength are likely to be hidden under the conjugation band.

b) 4,5-Dichlorophenanthrene

Murrell[35] reports that steric hindrance of the methyl groups in 4,5-dimethylphenanthrene is relieved both by displacement of the substituents and twisting of the 1,1'- bond, and this leads to a larger shift in the p band than is normally due to a methyl group. The dichlorophenanthrene also shows a considerable red shift compared to phenanthrene (250 Å for the longest wavelength peak). The shift is greater than that in the 4-fluoro- and 4-nitro- compounds (200 and 150 Å respectively) as would be expected from a steric effect. The α and β bands have also undergone a red shift; the two peaks shown in the α band are both at longer wavelengths than those of phenanthrene and 4-fluorophenanthrene. Murrell considers that steric distortion leads to changes in wavelength of the p band rather than changes in intensity; only when mesomerism between the substituent and the nucleus is hindered do large changes in intensity occur. There is no change in intensity between phenanthrene and 4,5-dimethylphenanthrene; but 4-fluoro- and 4-nitro- phenanthrene show a slight decrease in intensity and 4,5-dichlorophenanthrene a little more, suggesting that in these three compounds, there is a greater degree of electronic interaction than in the dimethyl- compound. Of the two longitudinally polarised transitions, a and β, the former shows an increase and the latter a small decrease in intensity.

ULTRAVIOLET ABSORPTION SPECTRA

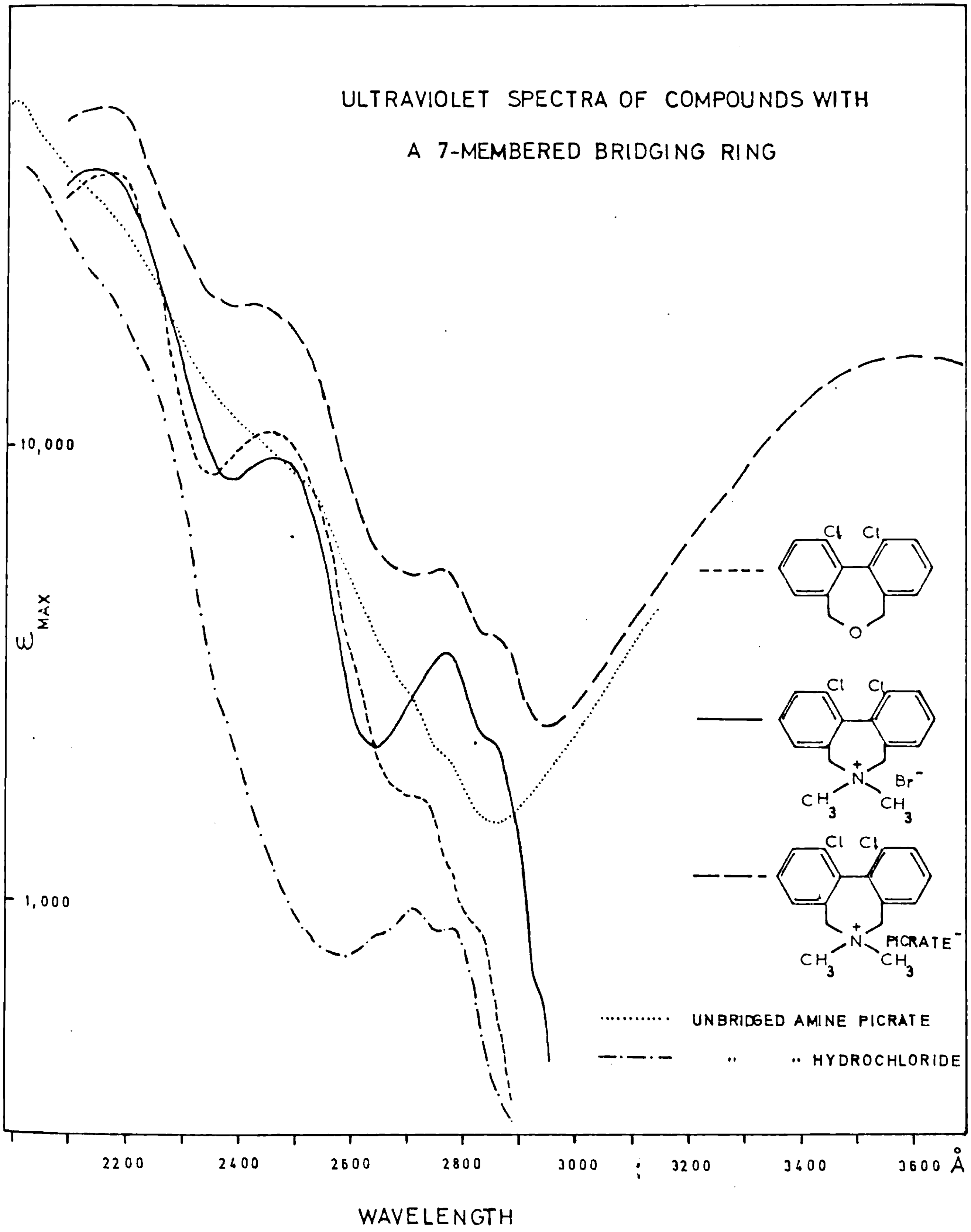
Compound	Shortwave band		Conjugation band		Longwave band	
	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
BB1 oxepin	2160	41,000	2460	10,700	(2730)	1,700
					(2830)	850
BB2 azepinium	2175	39,800	2460	9,400	2765	3,500
bromide					(2840)	2,250
					(2930)	500
BB3 azepinium	2170	55,600	2425	20,700	2760	5,350
picrate					(2850)	3,850
					3580	15,800
BB5 dimethyl-						
amino picrate	2145	50,500	2560	17,700	(2690)	15,300
	(2220)	43,500			(2970)	4,600
					3575	15,600
BB7 dihydro-	2155	29,400	2645	11,100	(2920)	2,150
phenanthrene						

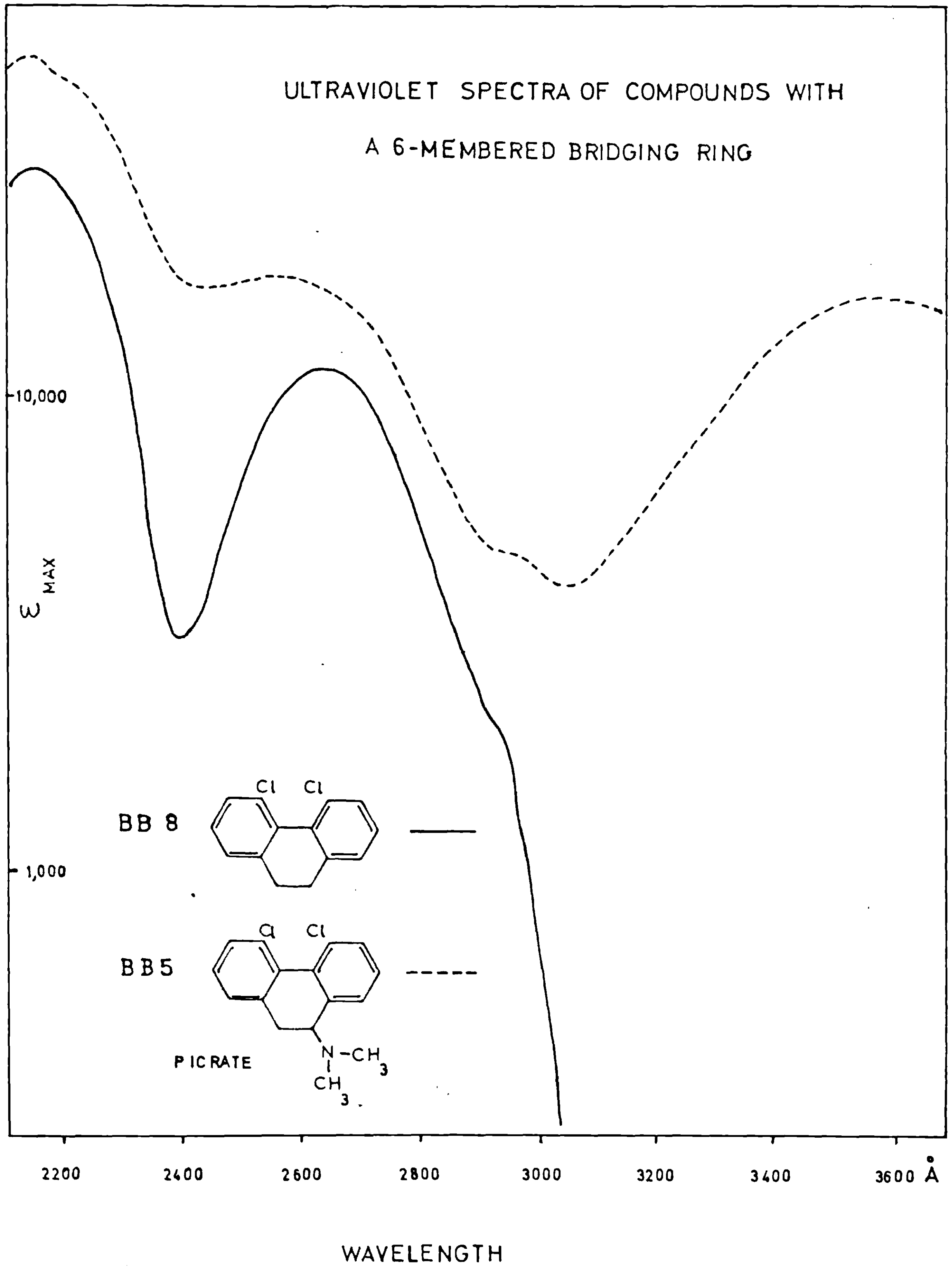
ULTRAVIOLET ABSORPTION SPECTRA

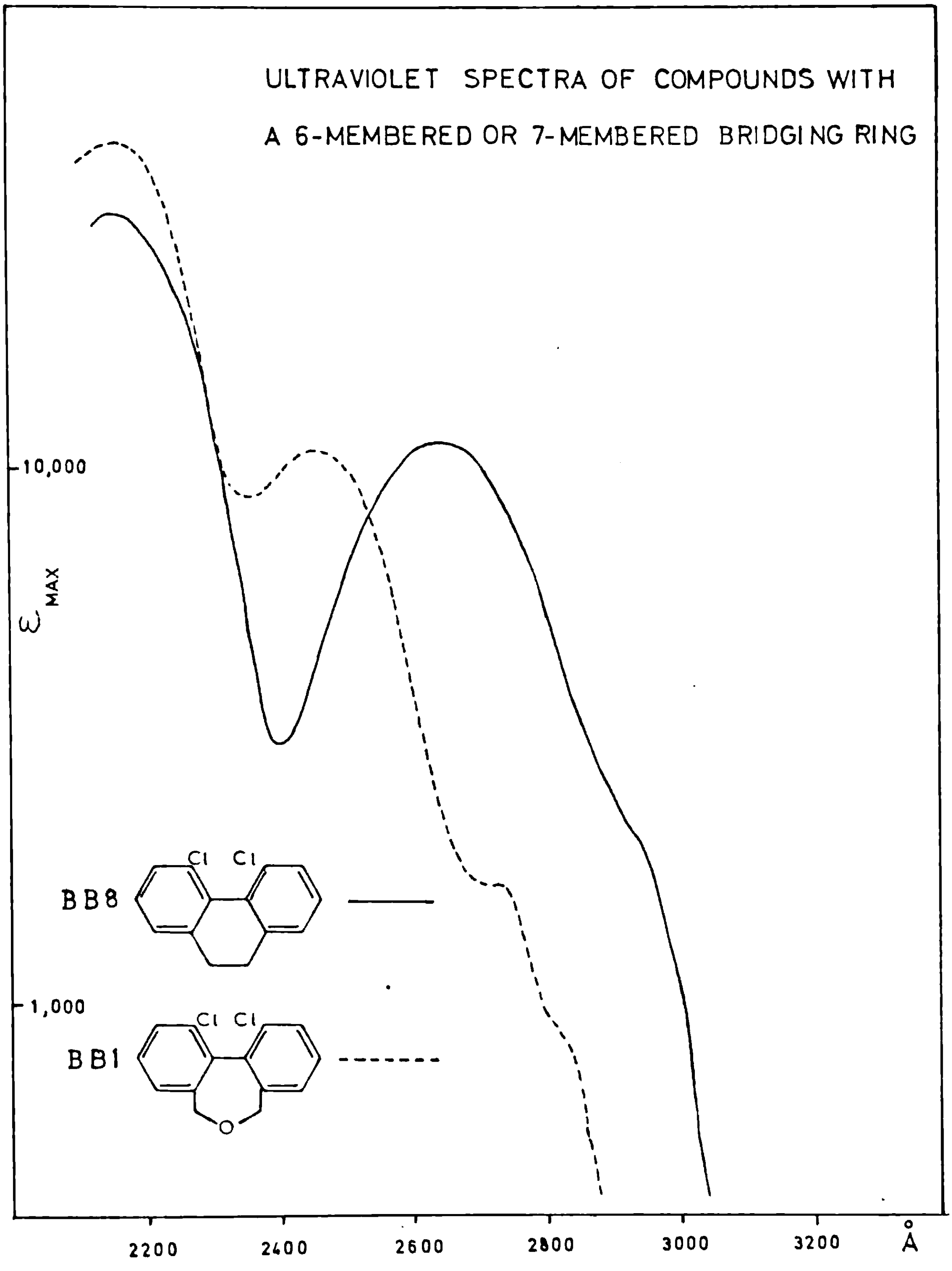
Compound	Shortwave band		Conjugation band		Longwave band	
	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
BB6 unbridged biphenyl						
picrate	<u>ca</u>.2010	<u>ca</u>.58,000	(2450)	10,300	(2700)	3,000
	(2150)	35,900			(2780)	2,050
hydrochloride	< 2020	>40,800	(2200)	20,000	(2640)	810
					2710	940
					2780	850

ULTRAVIOLET ABSORPTION SPECTRUM OF 4,5-DICHLOROPHENANTHRENE

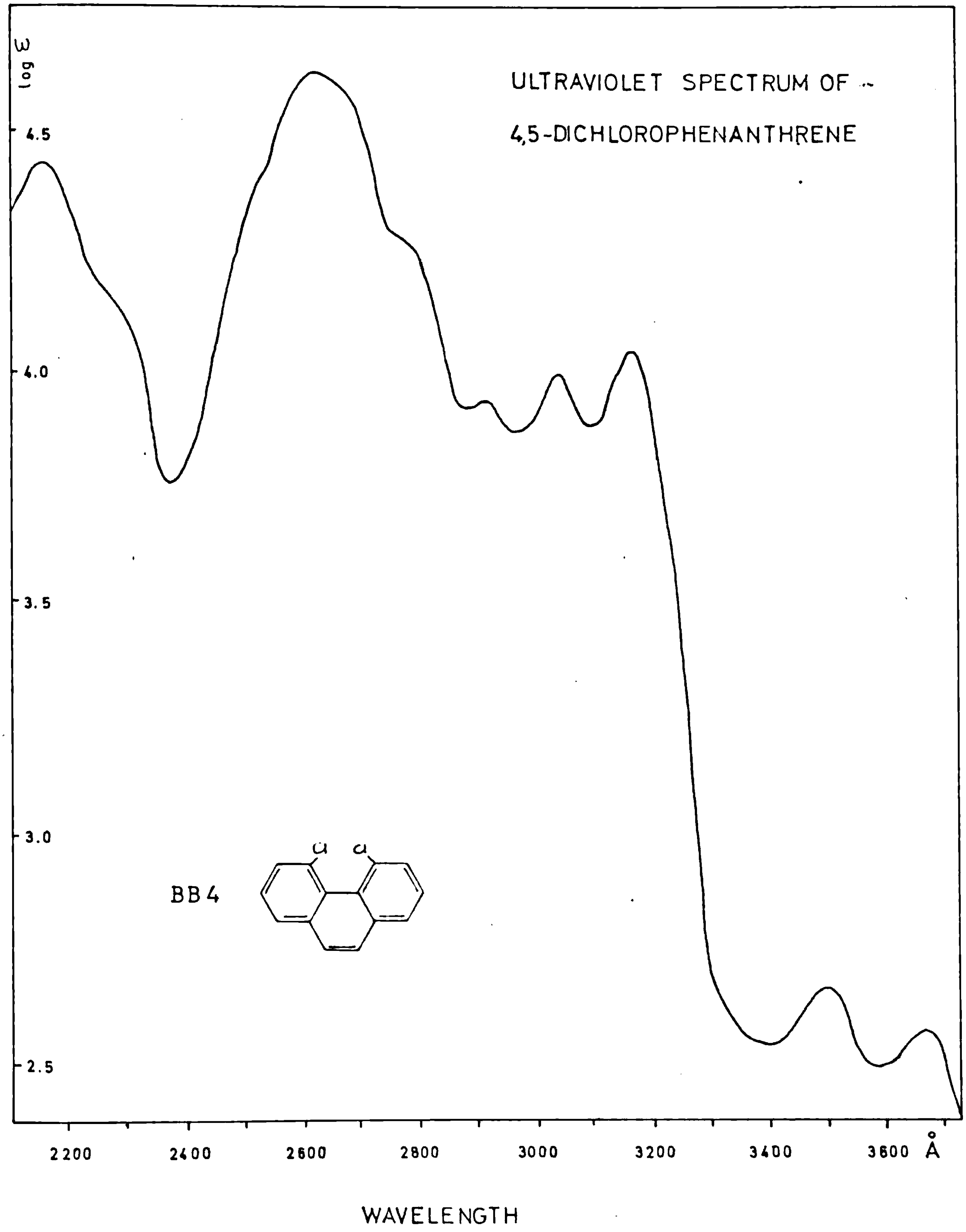
λ Å	ε_{max}	log ε	
3665	382	2.58	
3490	474	2.68	group I
3160	11,000	4.04	
3030	9,830	3.99	group II
2910	8,480	3.93	
(2770)	19,000	4.28	
2620	42,800	4.63	
(2500)	20,900	4.32	group III
(2270)	14,300	4.16	
2150	27,700	4.44	


ULTRAVIOLET SPECTRA OF COMPOUNDS WITH A 7-MEMBERED BRIDGING RING


ULTRAVIOLET SPECTRA OF COMPOUNDS WITH
A 6-MEMBERED BRIDGING RING
ε MAX
10,000
1,000
BB 8
Cl Cl
BB5
Cl Cl
PICRATE
N-CH3
CH3
2200
2400
2600
2800
3000
3200
3400
3600 Å
WAVELENGTH


ULTRAVIOLET SPECTRA OF COMPOUNDS WITH
A 6-MEMBERED OR 7-MEMBERED BRIDGING RING
10,000
1,000
ϵ_{MAX}
BB8
Cl Cl
BB1
Cl Cl
O
2200
2400
2600
2800
3000
3200
Å

WAVELENGTH


log ε
ULTRAVIOLET SPECTRUM OF –
4,5-DICHLOROPHENANTHRENE
4.5
4.0
3.5
3.0
2.5
BB4
Cl
Cl
2200
2400
2600
2800
3000
3200
3400
3600
Å
WAVELENGTH

CIRCULAR DICHROISM SPECTRA

The circular dichroism spectra were measured on a Roussel-Jouan dichrograph at West Ham College of Technology. The lower wavelength limit of the machine is about 2150 Å but the hydrogen lamp is a source of insufficient power to enable readings below 2250 Å to be made on the 2,2'-dichloro-6,6'-bishydroxymethylbiphenyl (+BP3). For compounds of this type which absorb strongly in this region, the solution being measured is, of necessity, dilute and the spectra show only small deflections. Measurements were made on the diol +BP3, the oxepin -BB1 and the azepinium bromide -BB2. The diol (+BP3) has a broad positive band centred about 2650 Å, but no lower wavelength band maxima before 2250 Å although the sign is shown to be negative. This means that either any remaining conjugation band or the high frequency band is associated with a negative Cotton Effect. The conjugation band Cotton Effect, if weak, which would be expected, would appear as a shoulder on that of the short-wavelength band if they were the same sign, or might becancelled out by the short-wavelength band if they are of different sign. A negative Cotton Effect corresponding to the conjugation band of a biphenyl with R configuration would mean a <u>trans</u> conformation of the biphenyl. The infrared spectrum in chloroform solution[82] shows the presence of OH....O hydrogen bonding and this indicates that in this solvent, the diol is in the <u>cis</u> conformation, and suggests that the conjugation band Cotton Effect has been cancelled out by the strong short-wave band.

Measurements on the diol at temperatures of 10° and 50° showed no noticeable differences in the C.D. curves. However, small differences would not be able to be discerned. Advances in instrumentation may, in the future, extend the wavelength range and improve the spectra and this may enable any temperature dependence of the C.D. Spectrum to be investigated, and help to explain the temperature dependence of the rotation of these compounds.

The C.D. curves of the oxepin and azepinium bromide show that all of the transitions which give rise to bands in the ultraviolet spectra are optically active. Like the ultraviolet spectra, the C.D. spectra of the two compounds are very similar. The C.D. spectrum of the oxepin reveals the presence of a third longwave absorption band which is not obvious in the ultraviolet spectrum. It is possible that it is at shorter wavelength than that in the ultraviolet spectrum of the azepinium bromide, since this is the case with the other two long-wavelength bands, and that it is very weak indeed; comparison with the azepinium bromide would suggest that it might be of the order of $\varepsilon_{\text{inf.}}$ 200. On inspection of the ultraviolet spectrum it appears that there may be a shoulder at λ 2880 Å, $\varepsilon_{\text{inf.}}$ ca. 430. It is not very noticeable because it is very weak and close to the 2830 Å band.

The short-wave band and conjugation band both have a positive Cotton Effect. The sign of the latter is confirmation of the absolute configuration, (R), of the biphenyl moiety[23]. The longest wavelength Cotton Effect is also positive, as expected from Mislow's rule for use with bridged biphenyls[26], i.e. with 6,6'-dichloro-substituents the longwave Cotton Effect is positive for the R configuration. The other two long-wavelength absorption bands show negative Cotton Effects.

The dimethyl oxepin C.D. spectrum is reported[93] to be an exception to that generally given by a seven-membered ring bridged biphenyl, since it does not exhibit the long-wave Cotton Effect. The dichloro-oxepin spectrum resembles that of the dimethyl compound with the homocyclic bridge rather than that of the dimethyl oxepin.

CIRCULAR DICHROISM SPECTRA

(-) DB1 oxepin		(-) DB2 azepinium bromide	
λ_{max}(Å)	sign	λ_{max}(Å)	sign
2880	+	2880	+
(2820)	-	(2820)	-
2720	-	2720	-
2420	+	(2420)	+
<u>ca</u>.2230	+	2250	+

Values in brackets are inflections

Diol +DB3 has a broad positive band centred about 2650 Å

Solvent: methanol

DATA FOR C.D. SPECTRA

Oxepin

Soln. 1 0.56 g./litre

Measured down to 2070 Å

5 mm. cell

Deflection x $^2/5$

Soln. 2 0.056 g./litre

Measured down to 2340 Å

5 mm. cell

Deflection x 4

Soln. 3 0.0056 g./litre

Measured down to 2200 Å

5 mm. cell

Deflection x 40

Azepinium Bromide

Soln. 1 0.4 g./litre

Measured down to 2760 Å

10 mm. cell

Deflection x ½

Soln. 1 measured down to 2500 Å

2 mm. cell

Deflection x $^5/2$

Soln. 2 0.08 g./litre

Measured down to 2200 Å

2 mm. cell

Deflection x $^{25}/2$

$$\varepsilon_L-\varepsilon_R = \pm\frac{1.5 \times 10^{-4} \times \text{molecular wt.} \times \text{no. mm. deflection}}{\text{g./litre} \times \text{path length}}$$

At 2420 Å, deflection = 16.6 mm.

$\varepsilon_L-\varepsilon_R=2.4$, $[\theta] = 3300 \times 2.4=7900$

At 2720 Å, deflection = 16.6 mm.

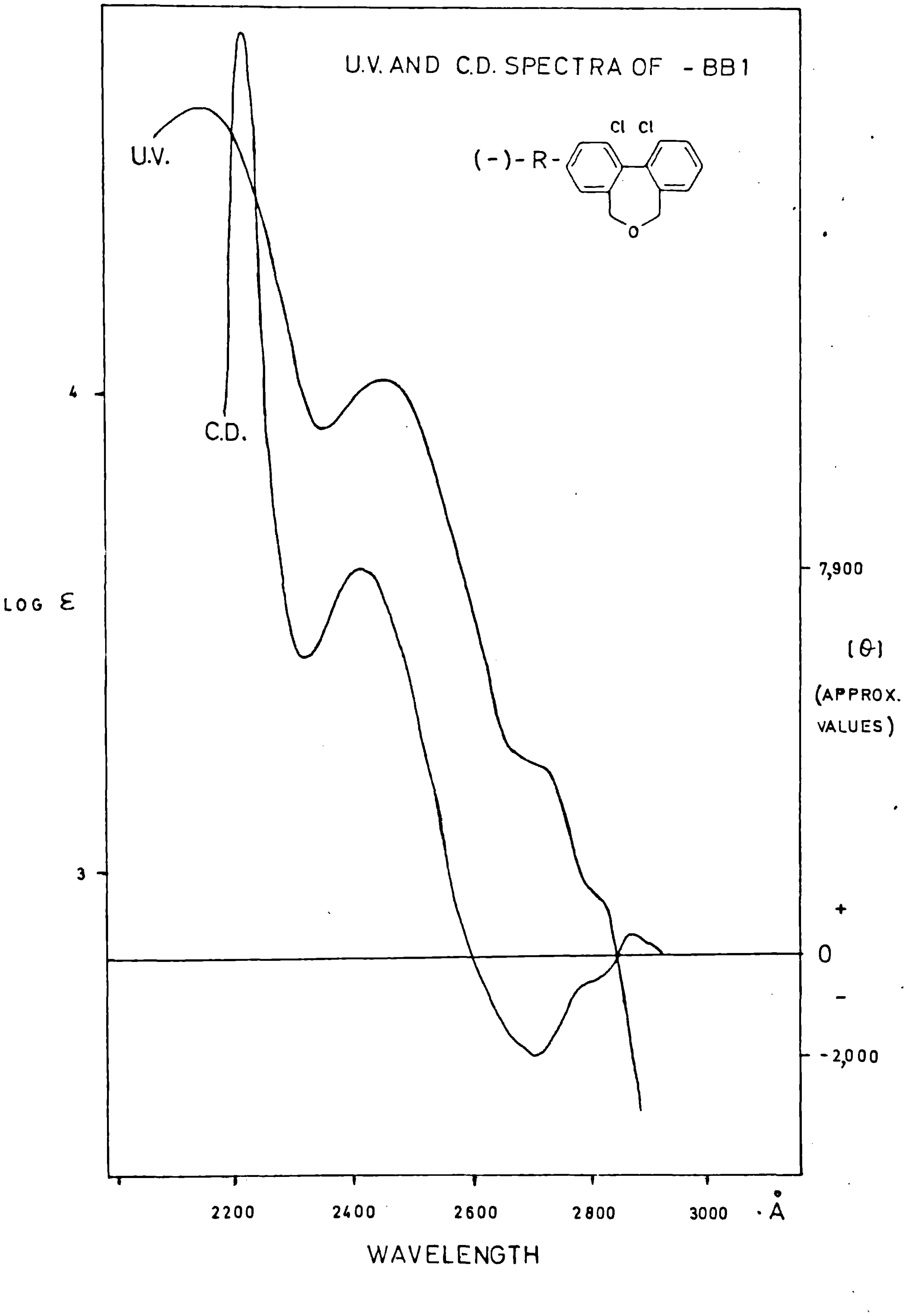
$\varepsilon_L-\varepsilon_R=-0.6$, $[\theta]=-3300 \times 0.6=2000$

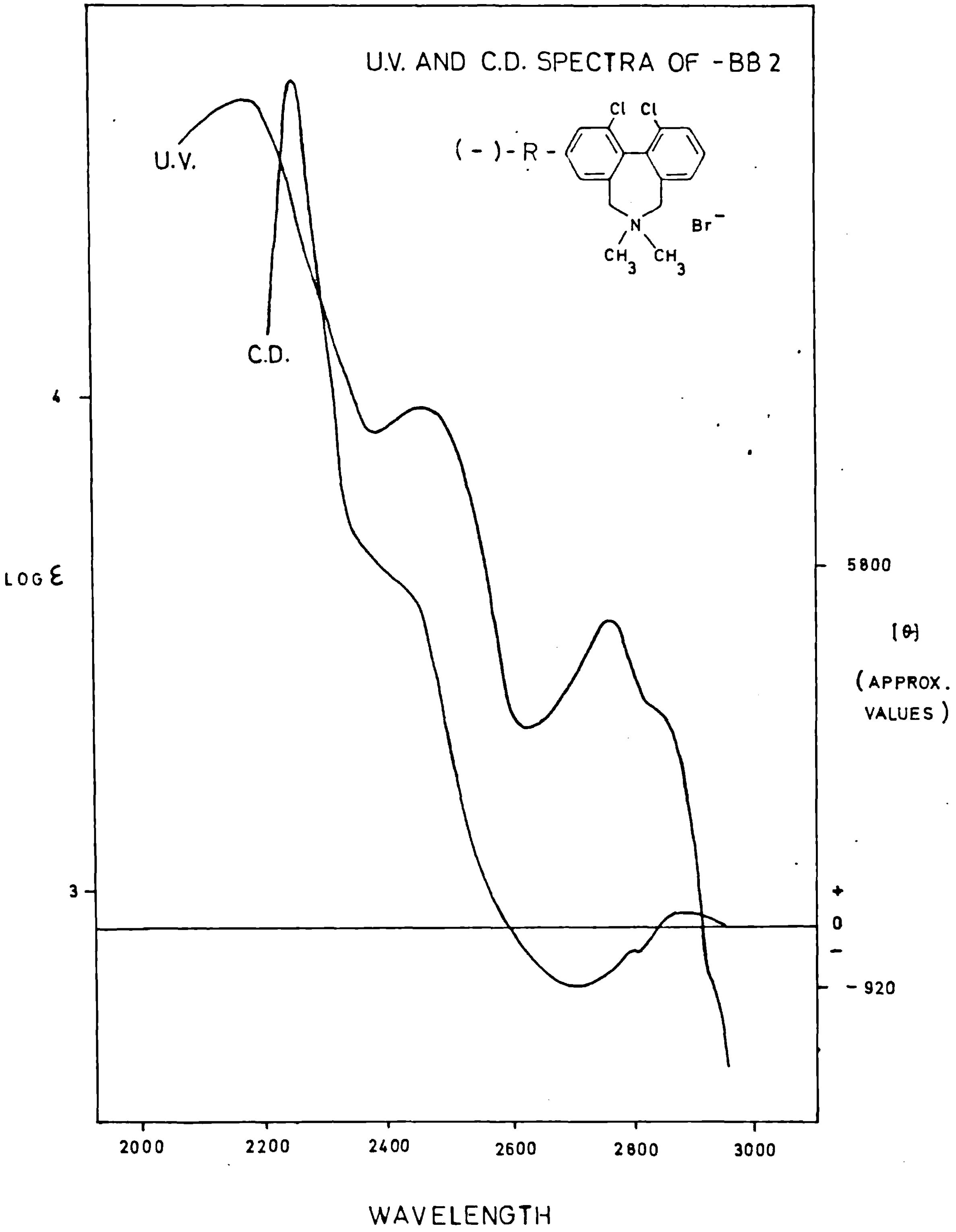
At 2420 Å, deflection = 5 mm.

$\varepsilon_L-\varepsilon_R=1.75$, $[\theta]=3300 \times 1.75=5800$

At 2720 Å, deflection = 4 mm.

$\varepsilon_L-\varepsilon_R=-0.28$, $[\theta]=-3300 \times 0.28=-920$


U.V. AND C.D. SPECTRA OF - BB1
(-)-R-
Cl Cl
O
U.V.
C.D.
LOG ε
4
3
7,900
[θ]
(APPROX. VALUES)
+
0
-
-2,000
2200
2400
2600
2800
3000
Å
WAVELENGTH


U.V. AND C.D. SPECTRA OF -BB 2
(-)-R-
Cl Cl
N
Br⁻
CH3 CH3
U.V.
C.D.
LOG ε
4
3
5800
[θ]
(APPROX. VALUES)
+
0
-
- 920
2000
2200
2400
2600
2800
3000
WAVELENGTH

EXPERIMENTAL

3-Chloro-2-iodotoluene 2-Amino-3-chlorotoluene (28g., 1 mol.) was diazotised in the usual manner using 6N hydrochloric acid (150 c.c.) and sodium nitrite (15g., 1.1 mol.) dissolved in water (28 c.c.). The diazo solution was slowly added to potassium iodide (15g.,1.5 mol) dissolved in water (80 c.c.) and contained in a 3 litre flask, with shaking. When the reaction was carried out with larger quantities, mechanical stirring was used.

If the addition of the diazo compound to potassium iodide solution was carried out at room temperature, bright orange-red crystals were formed, which decomposed, sometimes explosively if the solution was not shaken, with evolution of nitrogen to give an oil. It was found that if the potassium iodide solution was warmed to about 50° before the diazo solution was added, the reaction proceeded smoothly.

Sodium metabisulphite was added to remove the free iodine, and the iodo- compound was steam distilled. The distillate was cooled in the refrigerator and the crude product was filtered off, giving 39g. (78%) of 3-chloro-2-iodotoluene,m.p. 26°-27°. Fieser and Cason[62] give m,p. 27.3°-27.6°. Altogether, 565g. were prepared.

Attempted Preparation of 6,6'-Dichloro-2,2'-ditolyl by an Ullman Reaction

3-Chloro-2-iodotoluene (30 g., 1 mol.) was heated under reflux (air condenser), with mechanical stirring, in a metal bath, and copper bronze (30 g., 4 atoms) was added at intervals. The metal bath was maintained at a temperature of about 250° for two days, and although the temperature of the mixture could not be accurately recorded, it apparently never rose above that of the metal bath. After cooling to 150°, the solid was extracted with toluene, which was subsequently distilled off and the resulting liquid was distilled under reduced pressure giving fractions a) b.p.79°-84° /25.3 mm., b) b.p. 80°-90°/10 mm. and leaving c), which solidified. Samples of the fractions were examined and compared with toluene and the starting material by vapour phase chromatography, using 6 ft. columns of 25% silicone on celite at 220° and 215° and a flow rate of 2 litres per hour. This showed the fractions to be mixtures of between two and five components. Fractions a) and b) were combined and distilled under atmospheric pressure giving 5 g. of fraction 1), 0.9.g. of fraction 2), and 1.1 g. of fraction 3). These were also examined by vapour phase chromatography and found to be mixtures. The residue from this distillation was extracted with toluene and the solvent then removed. The resulting tar was crystallised twice from aqueous ethanol, and then from ethanol, giving 0.5 g. of a solid R m.p. 87°-80°. Tests on a thin layer alumina plate using light petroleum (b.p. 40°-60°) gave four spots which were shown up by fluorescence in ultraviolet light. A solution of R was put through an alumina column giving 0.18 g. of a 1st fraction, m.p. 90°-97°, and a small 2nd fraction, m.p. about 70°. The 1st fraction was retreated and the melting point was then 90°-107°.

Fraction c) from the first distillation was crystallised from ethanol and had m.p. 84°-94°. Using light petroleum (b.p. 40°-60°) and silica gel thin layer plates, four widely spaced spots were obtained, fluorescing in ultraviolet light. 0.7.G. of c) were put down a silica gel column and 45 fractions of solution were collected. Fractions 22-27 gave a trace of solid and fractions 41-45 gave a solid of m.p. 98°-108° (fraction 41) to m.p. 95°-105° (fraction 45).. 6,6'-Dichloro-2,2'-ditolyl[94] has m.p. 119°.

Attempted Preparation of 6,6'-Dichloro-2,2'-ditolyl by a Grignard Reaction

A. Using anhydrous cupric chloride

3-Chloro-2-iodotoluene (63 g., 1 mol.) was dissolved in sodium dried ether and part of it added to magnesium turnings (6.1 g., 1 atom) just covered with ether. After ½ hour, the reaction was initiated by scraping and stirring the magnesium turnings with a glass rod. When the reaction started, the rest of the 3-chloro-2-iodotoluene solution was added so that the ether was gently refluxing. The mixture was stirred for a further ½ hour, but still contained some unreacted magnesium. Anhydrous cupric chloride (45 g., 1.25 mol.) which had been dried by heating at less than 120° for two hours, was added down the condenser and washed through with ether. The mixture was heated, with stirring, on a water bath for 2½ hours, then left for 36 hours. Decomposition was effected by pouring it onto ice and adding concentrated hydrochloric acid, followed by ferric chloride (45 g., 1 mol.) dissolved in water, to oxidise the cuprous chloride formed. The ethereal layer was separated and the aqueous layer extracted four times with ether. The combined extracts were washed with dilute hydrochloric acid, water, sodium hydroxide, then water, and dried over anhydrous magnesium sulphate. The ether was removed and the residue distilled at atmospheric pressure. Decomposition started and so the material was all washed out with ether, washed three times with sodium hydroxide solution, then with water, and dried over anhydrous magnesium sulphate. After removing the ether, distillation was carried out under a pressure of 1 mm. giving 8.3 g. of b.p. up to 130°, 3,4 g. of b.p. 130°-198°, 5.8 g. of b.p. 198°-260° and 6 g. of b.p. 260°-280°; on further distillation, decomposition occurred. The fractions obtained were of increasing viscosity and the 4th set to a glass. Attempts to crystallise the 3rd and 4th fractions were unsuccessful. <u>m</u>-Chlorotoluene has a boiling point of 162° under atmospheric pressure, so the 1st and 2nd fractions were thought to have too low a boiling point to be the required product.

B. Using anhydrous cobalt chloride

A solution of 3-chloro-2-iodotoluene (25 g., 1 mol.) in sodium dried ether was added to magnesium turnings (2.4 g., 1 atom) covered with ether. The total volume of ether was 150 c.c. After reaction had taken place, anhydrous cobalt chloride (4 g., 0.3 mol), which had been dried by heating at 120° for 2 hours was added, then methyl iodide (6.5 mls., 1 mol) which acts as a radical scavenger. The suspension was heated under reflux, with stirring, for 2 hours, then decomposed by pouring onto hydrochloric acid and ice. The organic layer was separated, and dried over sodium sulphate. The ether was removed and the residue distilled under a pressure of 2 mm., giving fraction 1) b.p. 64°-78°, fraction 2) b.p. 78°-116°, (combined weight 7.75g.) and fraction 3), b.p. 176°-206°, which came over as a viscous yellow syrup. This showed no peak with vapour phase chromatography and gave a gum on attempted crystallisation from ethanol.

A sample of fraction 3) was dissolved in light petroleum (b.p. 40°-60°) and tested on a silica gel thin layer plate. After spraying with fluorescein and silver nitrate, six spots were obtained. Work on this fraction was abandoned.

Fractions 1) and 2) were combined and distilled at atmospheric pressure. Distillation started at 150° and decomposition occurred, iodine being produced. This was not investigated further.

3-Chloro-2-iodo-benzoic Acid

Potassium permanganate (20 g., 3.25 mol) was dissolved in water (700 c.c.) and added gradually, with stirring, to 3-chloro-2-iodotoluene (10 g., 1 mol) in a 2 litre flask, heating under reflux on a water bath. The mixture was heated until the potassium permanganate had been almost decolourised (33 hours) and the precipitate of manganese dioxide was dissolved by passing sulphur dioxide through the suspension. The acid solution was cooled and a white precipitate obtained. Any starting material was removed from the acid by adding sodium carbonate solution, filtering, and acidifying the filtrate with concentrated hydrochloric acid. 4.2 G. of starting material were recovered, and 2.6 g. (45%) of the acid m.p. 141.5°-142.5° were obtained. Christie, James and Kenner[61] (J. 1923, 83, 1948) give m.p. 137°-138°.

When the oxidation was carried out with double the quantities, 2.2g. (28%) of acid were obtained. In all, 28g. were prepared.

2-Acetamido-3-chlorotoluene

2-Amino-3-chlorotoluene (142g.,) was acetylated by refluxing with acetic anhydride (100 c.c.) and acetic acid (100 c.c.) for a half hour, and then pouring the resulting solution into 2 litres of water. The crude product was filtered off and recrystallised from acetic acid/water, giving 168 g. (92%) of 2-acetamido-3-chlorotoluene, m.p. 164.5°-165.5°. Bamberger[65,66] gives 165°. A total of 1280 g. were prepared.

2-Acetamido-3-chlorobenzoic Acid

Potassium permanganate (140 g. 2.25 mol) was dissolved in the minimum amount of water (about 2½ litres) and added to 2-acetamido-3-chlorotoluene (74 g., 1 mol) in a 4-litre flask and heated on a water bath with stirring until the permanganate had been almost decolourised (2 hours). The solution was cooled and sulphur dioxide was passed through until the solution was colourless and a white precipitate had been obtained. The solid was filtered off and the acid was separated from the starting material by taking it through the sodium salt. 10 g. of starting material were recovered and 60 g. (80%) of acid obtained. The crude acid had m.p. 204°-206°. A portion was crystallised from methanol giving m.p. 207°-208°. Bamberger[66] (*Annalen* 1925, **413**, 205) gives m.p. 206.5°-207. In all, 830 g. were prepared.

2-Amino-3-chlorobenzoic Acid

Hydrolysis of the corresponding acetamido- compound was carried out by heating the 2-acetamido-3-chlorobenzoic acid (20 g.,) with 35% sulphuric acid (30 c.c.) for half an hour. The resulting solution was cooled and caustic soda solution was added until the pH was 4. The precipitated acid was filtered off and crystallised from aqueous methanol, giving 13.7 g. (85%) of pale yellow needles, m.p. 193°-194°. Sadler and Warren[95] give m.p. 192°. A total of 497 g. were prepared.

3-Chloro-2-iodobenzoic Acid

2-Amino-3-chlorobenzoic acid was diazotised by the method used by Wittig and Petri[70] for 2-amino-3-methoxybenzoic acid. The 2-amino-3-chlorobenzoic acid (136g., 1 mol) and sodium nitrite (60g., 1.1 mol) were dissolved in N sodium hydroxide (800 c.c.). 10% Hydrochloric acid (1168 g., made by adding 320 c.c. concentrated acid to 1050 c.c. water), was added, keeping the temperature below 5° and using mechanical stirring. The diazo solution was filtered and added to a solution of potassium iodide (200 g., 1.6 mol.) in water (320 c.c.) kept at about 80°. At lower temperatures, the reaction was rather slow, and a brown solid was formed which did not readily give the yellow acid. After the diazo solution had been added, the temperature was kept between 80° and 100° until the reaction appeared to be complete. After cooling the mixture, sodium metabisulphite was added to remove the free iodine, and the crude acid was filtered off, washed with sodium metabisulphite solution and then with water. Crystallisation from aqueous ethanol (charcoal) gave 198g.(89%) of pale yellow plates, m.p. 141°-143°. Christie, James and Kenner[61] give m.p. 137°-138°. In all, 445g. were prepared.

Methyl 3-chloro-2-iodobenzoate

3-Chloro-2-iodobenzoic acid (200 g.,) was heated under reflux with methyl alcohol (1250 c.c.) and concentrated sulphuric acid (110 c.c.) for 9 hours. About half of the methyl alcohol was distilled off, and the remaining solution poured into an excess of water. The ester was extracted with ether, and the extract washed with sodium bicarbonate solution, then water and dried over anhydrous sodium sulphate. The ether was removed by distillation and the ester distilled under reduced pressure, giving 198 g. (94%) of the ester, b.p. 172°/17 m.m.. Christie, James and Kenner[61] give b.p. 182°/28 m.m. A portion from another preparation solidified on keeping. The ester was seeded with this, and with some difficulty, the whole was obtained solid, m.p. 35°-36°. The m.p. of this compound does not seem to have been previously reported.

Altogether, 404 g. were prepared.

Dimethyl-6,6'-dichloro-2,2'-diphenate

Christie, James and Kenner (J. 1923, 83, 1948)

The Ullmann reaction used by Christie, James and Kenner[61] was slightly modified. Methyl-3-chloro-2-iodobenzoate (99 g., 1 mol) was heated to about 150° in a metal bath. Copper bronze (about 32g. in all; 4.3 atom) was gradually added keeping the temperature of the reacting material about 5° above that of the metal bath which was maintained at 150°. The addition took between $^3/4$ hour and 1 hour and was continued until further addition of copper powder gave no rise in temperature. The temperature was then raised to 180° and maintained at that value for 10 minutes. The apparatus was then cooled to about 150°, and hot chlorobenzene added. After thorough stirring, the slurry was filtered on a Buchner and the residue repeatedly extracted with more hot chlorobenzene. The chlorobenzene solution was refiltered to remove completely the copper bronze and most of the chlorobenzene was distilled off. The remaining solution was left to cool and the crystals which formed were filtered off. The mother liquors were concentrated to give a second crop and a total of 46.5 g. (90%) of the dimethyl. 6,6'-dichloro-2,2'-diphenate, m.p. 157°-159°, was obtained. Altogether, 192 g. of ester were prepared.

Preparation of 6,6'-Dichloro-2,2'-diphenic Acid by Hydrolysis of Dimethyl 6,6'-dichloro-2,2'-diphenate

The di-ester (34 g.) was heated under reflux with 10% sodium hydroxide (500 c.c.) for 6 hours. The mixture was cooled, filtered and the filtrate acidified with dilute hydrochloric acid. The precipitated acid was crystallised from aqueous ethanol, giving 16.5 g. From the reaction mixture, 12 g. of unchanged di-ester were recovered. This results in a percentage yield of 82%.

Preparation of 6,6'-dichlorodiphenic acid from 3-chloroanthranilic acid by reduction of the diazo compound

I. Using the cuproammonium ion formed by reduction with sodium metabisulphite.

Experiment 1 3-Chloroanthranilic acid (9.5 g.,1 mol.) was diazotised in the usual way, with concentrated hydrochloric acid (42 c.c.), water (100 c.c.), and sodium nitrite (3.7g., 1 mol.) in water (70 c.c.). The diazo solution was filtered before use. The catalyst was prepared as described by Hall and Turner[74]. Sodium metabisulphite (55g.) and ammonia (*d*. 0.88; 55 c.c.) were added to a solution of cupriammonium sulphate formed by dissolving copper sulphate (24g.) in water (140 c.c.) and ammonia (*d*. 0.88; 23 c.c.). The reducing solution was cooled to below 20° and the diazo solution added with rapid stirring, and left to stand for a short time until the evolution of nitrogen had finished.

In order to oxidise any cuprous copper still present, a solution of anhydrous ferric chloride (36g.) in water (55 c.c.) was added. Concentrated hydrochloric acid (180 c.c.) was added at room temperature and the precipitate obtained was filtered off and dissolved in sodium bicarbonate solution. Non-acidic material was removed and the dichlorodiphenic acid was reprecipitated with concentrated hydrochloric acid. The pale yellow precipitate (3.5 g., 44%) had m.p. 250-290° with previous softening. It was crystallised from aqueous ethanol, giving small plates, m.p. 287°-290° (2g., 22%). Christie, James and Kenner[61] obtained needles m.p. 288°, from ethanol. A small second crop, mostly melting at *ca*. 140°, was obtained.

Experiment 2

The quantities used in Experiment 1 were slightly modified as follows:- 17 g. (1 mol.) of 3-chloroanthranilic acid were diazotised using 75 c.c. of 6N hydrochloric acid, 7.5g.(1.1 mol.) sodium nitrite in 14 c.c. of water, and twice the amount of catalyst used in Experiment 1. The crude acid after precipitation from the sodium salt, had m.p. 286°-287.5°, softening at 140°. Crystallisation from aqueous acetic acid gave 4 g. (29%) m.p. 288°-290°.

Experiment 3.

Diazotisation was carried out by the method used by Wittig and Petri[70] for 2-amino-3-methoxybenzoic acid. 3-Chloroanthranilic acid (5.7 g., 1 mol.) and sodium nitrite (2.3 g., 1 mol.) were dissolved in N. sodium hydroxide (33 c.c.) with the addition of water (50 c.c.); 10% hydrochloric acid (49 g.) was added, keeping the temperature below 0°. The reducing solution was prepared as before, by adding sodium metabisulphite (18 g.) and ammonia (d. 0.88, 18 c.c.) to a solution of copper sulphate (8.1 g.) in water (46 c.c.) and ammonia (d. 0.88, 9.c.c.) just before use.

After addition of the diazo solution to the reducing agent at 10°, the solution was left for 1-2 hours and then anhydrous ferric chloride (12 g.) in water (18 c.c.) and concentrated hydrochloric acid were added. The acid was separated from other material via the sodium salt and crystallised from aqueous alcohol (charcoal), giving 2.1 g. (44%), m.p. 289°-291°.

II Using the cuproammonium ion formed by reduction with hydroxylamine.

Experiment 4

The method of Atkinson, Lawler, Heath, Kimball and Read[71] for diphenic acid was adopted.

3-Chloroanthranilic acid (6.2 g., 1 mol.) was diazotised in the normal manner, using concentrated hydrochloric acid (9.2 c.c.), water (15 c.c.) and a solution of sodium nitrite (2.6 g., 1 mol.) in water (35 c.c.). The catalytic solution was prepared by dissolving copper sulphate (12.6 g.,1.4 mol.) in water (50 c.c.) and ammonium hydroxide (d. 0.88, 21 c.c.) and adding to this just before use a solution of hydroxylamine hydrochloride (3.55 g., 1.4 mol.) in 6N sodium hydroxide (8.5 c.c.) and water (12 c.c.). The diazo solution was added to the reducing solution, keeping the temperature at about 20°. The solution was then heated to boiling point and was treated with anhydrous ferric chloride (15 g.) in water (22 c.c.) and concentrated hydrochloric acid (75 c.c.). The required product was separated from non-acidic material via the sodium salt, and was crystallised from aqueous ethanol (charcoal) giving 2.95 g. (57%) of the 6,6'-dichlorodiphenic acid m.p. 291°-292°.

A subsequent preparation on 18.6 g., in which the reaction mixture was left over the weekend before acidification, resulted in a dark brown mixture after addition of the acidic ferric chloride, and a blue and an orange impurity were separated. The yield of acid was 12.0 g. (77%) with m.p. 290-296°. A second, similar, preparation gave only 9 g. (58%) of the acid.

III Using cuprous salts formed by reduction with hydroxylamine.

Experiment 5

The alternative method described by Atkinson et.al.[71] was used. 3-Chloroanthranilic acid (6.2 g.) was diazotised as in Experiment 4, except that an extra 85 c.c. of water were present. The reducing solution was prepared by adding a solution of hydroxylamine hydrochloride (16.7 g., 6.7 mol.) in N. sodium hydroxide (40 c.c.) and water (40 c.c.) to a solution of copper sulphate (13.7 g., 1.5 mol.) in water (50 c.c.). The diazo solution was added to the reducing solution, keeping the temperature at about 20°. The resulting solution was acidified at the boiling point with anhydrous ferric chloride (15.g.) dissolved in water (22 c.c.) and concentrated hydrochloric acid (75 c.c.) as in Experiment 6. The diphenic acid was taken through the sodium salt and crystallised from aqueous methanol (charcoal) giving 3.5 g., m.p. 140°-275°.

Two sets of crystals were clearly distinguishable. Crystallisation from various solvents did not give pure dichlorodiphenic acid. The mixture was treated with a small volume of hot benzene, filtered hot, and cooled. The resulting crystals were filtered off and had m.p. 162°-165°. This process was repeated, to give a reasonably pure sample of the by-product which now had m.p. 165.5°-166.5°.

It seemed likely that the by-product was 2,3-dichlorobenzoic acid, the product of a Sandmeyer reaction of the diazonium salt. 2,3-Dichlorobenzoic acid has m.p. 164° (Crauw[96]) and m-chlorobenzoic acid has m.p. 158°. The by-product had an unsatisfactory analysis and was therefore converted into the Benzylamine salt by the method of Cheeseman and Poller[97]. The acid (0.1 g.,) was dissolved in the minimum volume of hot benzene and 10% solution (1 c.c.) of benzylamine in benzene was added. The salt was rapidly precipitated; it was crystallised from ethanol/ethyl acetate, and had m.p. 150°-152°. (Found: C,56.5; H,4.4; Cl,23.7. $C_{14}H_{13}Cl_2NO_2$ requires C,56.4; H,4.4; Cl,23.8%).

Preparation of Dimethyl 6,6'-dichloro-2,2'-diphenate from 6,6'-Dichloro-2,2'-diphenic Acid

6,6'-Dichloro-2,2'-diphenic acid (3.5 g.) was heated under reflux with methyl alcohol (22 c.c.) and concentrated sulphuric acid (2 c.c.) for 2½ hours. A solid had precipitated and the mixture was poured into water and the solid was filtered off and dried. The crude product weighed 3.5 g. (92%) and had m.p. 151-152°. After crystallisation from benzene, the m.p. was 145-151°. Christie, James and Kenner[61] give m.p. 156°. The reaction thus appeared to be incomplete. The reaction was repeated on 4.2 g. of acid using the same weight of sulphuric acid (4.2 g.=2.5 c.c.) with ten parts of methanol instead of five (42 g.= 52.5 c.c.). Solid started to separate after heating for 5½ hours, and the reaction mixture was heated for a total of 6 hours. After cooling, the solid which had precipitated was filtered off and washed with sodium bicarbonate solution and water.

3.4 G. (74%) of ester with m.p. 155-156° were obtained.

6,6'-Dichloro-2,2'-bishydroxymethylbiphenyl

Dimethyl 6,6'-dichloro-2,2'-diphenate (17 g., 1 mol.) was suspended in sodium-dried ether (300 c.c.) and added to a solution of lithium aluminium hydride (47 g., 3.5 mol.) in sodium-dried ether (100 c.c.) at such a rate that the ether was refluxing gently. The mixture was heated on a water-bath for 15 minutes, and then allowed to cool. The excess lithium aluminium hydride and the alkoxides formed were decomposed by cautiously adding first wet ether, and then water. 2N Sulphuric acid was added until there were two clear solutions. The ethereal layer was separated and dried over anhydrous sodium sulphate for a short time. Most of the ether was removed by distillation, and the remainder was left overnight in a covered beaker, in order to allow the rest of the solvent to evaporate. The resulting sticky plates were crystallised from benzene, giving 13.6 g. (95%) of white needles m.p. 119°-120°. Mislow and Siegel[72] give the same melting point. In all, 69 g. were prepared.

6,6'-Dichloro-2,2'-bisbromomethylbiphenyl

6,6'-Dichloro-2,2'-bishydroxymethylbiphenyl (13 g.) was heated under reflux with 48% hydrobromic acid (650 c.c.) for two hours. The resulting mixture was poured into a beaker, while the dibromo-compound was still an oil, and stirred while cooling, until the oil went solid. It was filtered off, washed with water and dried in a vacuum des~~s~~cicator over solid sodium hydroxide. Crystallisation from light petroleum (b.p. 60°-80°)(charcoal) gave 14.1 g. (75%), m.p. 99.5°-100° and 3.2 g., m.p. 95.5-97°, a total of 17.2 g. (92%) (Found: C, 41.1; H, 2.5; Br, 39.05; Cl, 17.15%. Calc. for $C_{14}H_{10}Br_2Cl_2$: C, 41.5; H, 2.5; Br. 39.1; Cl, 17.3 %)

A total of 44 g. were prepared.

4',1"-Dichloro-2,7-dihydro-1,1-dimethyl-3,4:5,6-dibenzazepinium Bromide

(a) 6,6'-Dichloro-2,2'-bisbromomethyl biphenyl (5 g., 1 mol) was dissolved in the minimum amount of sodium-dried ether at room temperature and cooled in ice. An excess of dimethylamine (4 c.c., d. 0.68=2.75g., 5 mol.) previously cooled in an ice/salt mixture was added. A precipitate formed after a few minutes and the reactants were allowed to warm up to room temperature and left overnight. The precipitate was filtered, washed with dry ether and then with dry benzene and dried *in vacuo*, giving 5.8 g. of a mixture of the quaternary salt (theoretical yield 4.6 g.) and dimethylammonium bromide. The m.p. of the product was 165°-170° with softening at 156°. After attempts to obtain pure azepinium bromide by crystallisation from acetone, the residues were all combined and crystallised from water, giving 3.8 g. with m.p. 130°-160°. A portion was treated with potassium hydroxide solution to decompose the dimethylammonium bromide. Azepinium bromide with m.p. 168°-174° was obtained. (Found: C,47.85; H,4.7; Br. 20.4 (gravimetrically); Cl, 18.9; $C_{16}H_{16}BrCl_2N$ requires C,51.5; H,4.3; Br, 21.4; Cl, 19.0 $C_{16}H_{16}BrCl_2N.H_2O$ requires C,49.1; H,4.6; Br,20.4; Cl,18.1 $C_{16}H_{16}BrCl_2N.2H_2O$ requires C,47.0; H,4.9; Br,19.5; Cl,17.3). The unsatisfactory analysis may be due to variable solvation.

(b) 6,6'-Dichlorobisbromomethylbiphenyl (20 g.,1 mol) and dimethylamine (11.6 c.c., d. 0.68=7.9 g., 4.4 mol.) were used and left to react for three days. The precipitate which formed was dissolved in water and the ether layer was removed. Saturated potassium hydroxide solution was added to the aqueous layer to decompose the dimethylammonium bromide and precipitate the azepinium bromide. This was filtered and washed with a small amount of water to give the theoretical yield of crude bromide. Crystallisation from water gave 12 g. (66%) with a melting point over a range (160°-190°) and with decomposition.

(Found: C,49.1; H,4.6; Br,20.3; Cl,17.95; N,3.7; O,4.0; $C_{16}H_{16}BrCl_2N.H_2O$ requires C,49.1; H,4.7; Br,20.4; Cl,18.1; N,3.6; O,4.0). A subsequent preparation on 12 g. of the dibromo- compound yielded 8.5 g. (72%). In this preparation, the ether residue was taken down to dryness and a small residual gum obtained. The infrared spectrum showed that this was neither starting material, but the substance was not identified.

A total weight of 21.5 g. of the azepinium bromide was prepared.

4',1"-Dichloro-2,7-dihydro-1,1-dimethyl-3,4:5,6-dibenzazepinium Picrate

The above azepinium bromide (0.5 g., 1 mol) and sodium picrate (0.5 g., 1.5 mol) were separately dissolved in water and the two solutions mixed. The precipitated picrate was filtered off and crystallised from ethanol until it had a constant m.p. of 222°-223°. (Found: C,50.6; H,3.8; N,10.7; Cl,13.5; O,21.35; $C_{22}H_{18}Cl_2N_4O_7$ requires C,50.7; H,3.5; N,10.75; Cl,13.6; O,21.5.)

4',1"-Dichloro-2,7-dihydro-3,4:5,6-dibenzazepinium-1-spiro-1"-piperidinium Bromide

D.D. Fitts, M. Siegel and K. Mislow, *J. Amer. Chem. Soc.* 1958,*80*,480

S. R. Ahmed and D. M. Hall *J.* 1960,4165.

Piperidine (1c.c; 2 mol.) was added to a solution of 6,6'-dichloro-2,2'-bisbromomethylbiphenyl (2 g. 1 mol) in benzene at a temperature of about 40°. A gum separated, and the temperature was maintained for 20 minutes. The solution was decanted from the gum, which was washed with warm benzene. Trituration with cold water caused a large portion of the gum to dissolve. The water was removed by evaporation on a water-bath. The gum was then placed in a vacuum desiccator in order to remove any solvent which may have been present. The gum formed a glass, which was crystallised from absolute alcohol and dry ethyl acetate, giving crystals of m.p. 190°-270°. D. D. Fitts, M. Siegel and K. Mislow[55] give m.p. 297°-298.5° and a m.p. on S. R. Ahmed and D. M. Hall's compound[27] gave a value of 300°-302°. The infrared spectrum showed that this was piperidinium hydrobromide (m.p. 235°). The mother liquors were therefore collected together and the solvent removed on a water-bath giving a white solid which was crystallised three times from alcohol-ethyl acetate giving the required bromide m.p. 302°-303.5°.

2,2'-Bisbromomethylbiphenyl

D. M. Hall, M. S. Lesslie and E. E. Turner, *J.* 1950,711.

2,2'-Bishydroxymethylbiphenyl (14 g.) was gradually added to 48% hydrobromic acid (700 c.c.) at 90°. The mixture was heated to boiling and maintained at this temperature for 20 minutes. After cooling, the solid obtained was filtered, washed with water and dried under reduced pressure over sodium hydroxide. Crystallisation from light petroleum (b.p. 60°-80°), with charcoal added just before filtering gave 16 g. (72%) m.p. 89°-91°. The melting point reported[99] is 91-93°.

2,7-Dihydro-1,1-dimethyl-3,4:5,6-dibenzazepinium Bromide

K. Hori, Y. Abe, Y. Yamakawa and H. Fujimura *Gifu Yakka Daigaku Kiyô* 1958,*8*,65 *Chem. Abs.* 1959,*53*,10148)

Dimethylamine (11.2 c.c., 4 mols) cooled in an ice-salt mixture was added to 2,2'-bisbromomethylbiphenyl (16 g., 1 mol) dissolved in the minimum amount of sodium dried ether and cooled to room temperature. There was a vigorous reaction, and a milky precipitate was obtained. The mixture was allowed to warm up to room temperature and left for about 24 hours. The precipitated bromides were filtered off, dissolved in the minimum amount of water and concentrated potassium hydroxide solution added to decompose the dimethylammonium bromide and precipitate the azepinium bromide. The precipitate was filtered, washed with a little water, and dried in air. On crystallisation from methanol-ethyl acetate, 14.3 g. (78%) of 2,7,-dihydro-1,1-dimethyl-3,4:5,6-dibenzazepinium bromide m.p. 284°-288° were obtained. 'K. Hori, Y. Abe, Y. Yamakawa and H. Fujimura[98] give m.p. above 250°; D. M. Hall and T. M. Poole[24] J. 1963,268 give m.p. 285°-287°.

(Found: Br 25.0% gravimetrically

Calc. for $C_{16}H_{18}NBr$: Br 26.3; $C_{16}H_{18}NBr.H_2O$: Br 24.8;

$C_{16}H_{18}NBr.2H_2O$: 23.5)

Action of Heat on 2,7-dihydro-1,1-dimethyl-3,4:5,6-dibenzazepinium Hydroxide (D. M. Hall and T. M. Poole J. 1963, 268)

An aqueous solution of the azepinium bromide (5 g.,1 mol) was shaken for one hour with an excess of silver oxide freshly prepared from 5.6 g. of silver nitrate and 1.3 g. of sodium hydroxide. The water was freshly boiled to remove carbon dioxide. The silver bromide and residual silver oxide were quickly filtered off and washed with water, and the filtrate distilled under reduced pressure under an atmosphere of nitrogen from a water bath at 70°-100° until the water had distilled over. The residue was heated on an oil bath at 130°-135° for 15 minutes. Ether and water were added to the residue and ether to the distillate. The aqueous portions were extracted three times with ether and the ethereal layers combined. The aqueous distillate layer was discarded after a test portion left no residue on evaporation. The ethereal solution was treated with dilute hydrochloric acid in order to remove the bases from any neutral components. The aqueous layer was separated, the bases liberated by the addition of 10% sodium hydroxide and extracted with ether. After drying over A.R. anhydrous potassium carbonate, removal of the ether gave 1.726 g. of liquid bases. Treatment with picric acid yielded 3.011 g. of picrate m.p. 165°-174°. Crystallisation from methanol gave 2.16 g. (72% of picrate) of 9.10-dihydro-9-dimethylamino-phenanthrene picrate m.p. 175°-176° and crops of mixed picrates which did not yield pure specimens of any other component on further crystallisations. There was an indication of a higher melting component since two different crystal forms of m.p. 178-180° and 173-174° gave a depressed mixed m.p. of 158-160°. The neutral ethereal layer gave 0.814 g. (22%) of phenanthrene m.p. 95°-98°. The experiment was repeated using the same quantities. After the distillation, a smell similar to that of dimethylamine was noticed when the apparatus was dismantled in order to work up the products.

The aqueous residue layer gave 1.063 g. of solid. A solution of this gave precipitates with calcium chloride and silver nitrate, both of which were soluble in acid. No precipitate was obtained with magnesium sulphate solution in the cold, but on boiling, a white precipitate formed, showing presence of bicarbonate. From the neutral ethereal layer, 1.141 g. of phenanthrene were isolated. This gives a yield of 39% on the total amount of azepinium bromide used and 50% calculated on the amount of material which has reacted. The basic fraction gave 1.657 g. of a liquid from which 3.03 g. of picrate were obtained. Crystallisation from methanol gave 2.19 g. (72% of the picrate) of 9,10-dihydro-9-dimethylaminophenanthrene picrate m.p. 175°-176° and crops of mixed picrates from which pure material could not be separated.

Action of Heat on 4',1"-dichloro-2,7-dihydro-1,1-dimethyl-3,4:5,6-dibenzazepinium Hydroxide

Experiment I

Using freshly boiled water, an aqueous solution of the azepinium bromide (5,006 g.) was shaken for 3/4 hour with excess silver oxide which had just been prepared from 4.6 g. of silver nitrate and 1.1 g. of sodium hydroxide. The filtered solution was distilled under a pressure of 23 mm. in an atmosphere of nitrogen, from a water bath until almost all the water was removed, then from an oil bath at

130-135° for 15 minutes. Ether and water were added to the residue and ether to the distillate. The aqueous portions were extracted three times with ether and the combined extracts separated into a basic and a neutral fraction by treatment with dilute hydrochloric acid. The bases were liberated by 10% sodium hydroxide solution and extracted with ether. Both the basic and neutral ethereal solutions were dried over anhydrous potassium carbonate, most of the ether distilled off, poured into tared dishes and the rest of the ether removed.

The neutral portion gave 0.13 g. (5.4%) of a solid of m.p. 118-125°. which, on crystallisation from light petroleum (b.p. 60-80°) had m.p. 125-127°.
(Found: C, 69.4; H,3.4; Cl,27,1; $C_{14}H_8Cl_2$ requires C,68.0; H,3.3; Cl,28.7) The basic portion gave 2.74 g (95%) of an oil which deposited crystals after the addition of ethanol. Instead of making the picrate, the alcoholic solution was concentrated and four crops of crystals were obtained with melting points from 100-102° to 102-104° and totalling 1.15 g. Further crystallisation gave m.p. 103-110°. 0.42 G. of picrate were prepared by adding a concentrated solution of picric acid in ethanol to 0.26 g. of the solid amine dissolved in ethanol. After one crystallisation from methanol, the melting point was still 211.5-212.5°. The ultraviolet spectrum showed this to be the six-membered ring compound.

Picrates were made of the basic oil which remained and 0.15 g. of picrate m.p. 227.5-228.5°, 0.04 g. with m.p. 212-213°, a small crop with m.p. 232-240° and crops of mixed picrates, including one of m.p. 146-185°, were separated from 2.03 g. of picrate after crystallisation from methanol, ethanol and 2-methoxy-ethanol. These four picrates were shown to have different infrared spectra, The amines have been separated into 44% of the aminophenanthrene and 7% of the unbridged amine .

Evaporation of water from the aqueous layer gave 1.33 g. of an oily solid melting between 200° and 290°. Thus, decomposition of the azepinium hydroxide was incomplete. The picrate of this was made with a concentrated aqueous solution of sodium picrate and had m.p. 222-225°. After two crystallisations from ethanol the m.p. was 223.5-224.5°.

The reaction and working up procedure for the following experiments were the same as described for Experiment I, but with the noted modifications.

Experiment II

1) 4.724 G. of azepinium bromide were used.

2) The distillation was carried out under a pressure of 21 mm.

3) The oil bath was raised to a temperature of 140-145° and kept at this for one hour.

The aqueous portion gave 0.829 g. of residue. The infrared spectrum was run (see p. 141) but the compound was not identified. It is expected that it will be the azepinium bicarbonate or a mixture of this and the hydroxide.

The neutral ethereal extracts gave 0.20 g. (7.8%) of oily needles which were put through an alumina column and eluted with light petroleum (b.p. 40-60°), then with increasing proportion of ether until 100% ether. 0.069 g. (2.7%) of a white crystalline solid m.p. 127-128° was obtained, together with 9 mg. of an oil which had a different infrared spectrum from the first fraction, the starting material and the subsequently prepared oxepin.

2.81 G. of bases were obtained and partly solidified. The solid was separated and crystallised from light petroleum (b.p. 60-80°) and had m.p. 98-100°. Further crystallisation yielded a pure specimen of one of the amines m.p. 101°-102° but not enough for analysis; the other perhaps melts near 118°. Picrates were made from the remaining basic gum. Crystallisation gave 0.18 g. of the higher melting picrate (m.p. 228°-229°) and 0.16 g. of the lower melting picrate (m.p. 212 -213°), together with a very small amount with m.p. 156°-158° and crops of mixed picrates, from the 1.64 g. of picrates made. From the total basic product, 52% of the aminophenanthrene was separated as picrate and impure base.

The ultraviolet spectra of the amine picrates (p.154) show a six-membered ring (2-atom bridge) for the picrate with m.p. 212-213°, and the analysis is: found C,50.5; H, 3.8; N,10.6; Cl,13.7; $C_{22}H_{18}N_4O_7Cl_2$ requires C,50.7; H,3.5; N,10.75; Cl,13.6.

The ultraviolet spectrum for the picrate with m.p. 228-229° (p.153) showed less absorption in the 2500 Å region than expected for a compound with a 3-atom bridge, and since this region is complicated by picrate absorption, the free base was liberated by shaking with sodium hydroxide solution and then ether extraction. The ethereal solution was dried over anhydrous sodium sulphate and the ether removed, giving a glass. An ultraviolet spectrum of the ethanolic solution of this, containing a few drops of dilute hydrochloric acid to make the hydrochloride showed no conjugation band in the 2300-2600 Å region.

Experiment III

a) 1) The weight of azepinium bromide was 5.421 g.

2) The distillation was carried out under a pressure of 13 mm.

3) The bath temperature was kept at 130-135° for one hour.

The filtering of the silver oxide and silver bromide was slow and it seems that carbon dioxide may have dissolved in the solution, for 4.16 g. of aqueous residue were recovered. From 0.21 g. of bases, 0.6 g. of picrates were made, and 0.12 g. of the lower melting picrate was separated. The neutral ethereal portion gave 0.02 g. solid.

The aqueous residue was treated with 48% hydrobromic acid in order to recover the bromide. Effervescence occurred and the mixture was warmed on a hot plate at low heat. However, the mixture turned yellow and a smell similar to that of bromine was noticed. The yellow solid was not soluble in water to any great extent and was filtered, washed, dried, and the weight found to be 4.1 g. It was also insoluble in light petroleum (b.p. 60–80°), cyclohexane and ether, slightly soluble in benzene and chloroform and more so in ethyl acetate and ethanol. It could be crystallised from ethanol but if the solution was boiled for some time, the yellow colour disappeared and crystals with a similar infrared spectrum (p.141) and wide range melting point to the azepinium bromide were obtained. After storing for some time, the yellow colour was more rapidly lost in solution. However, an attempt was made to estimate the bromine content gravimetrically, and although a little may have been lost during the process of solution, the ratio of bromine to azepinium ion was shown to be slightly greater than 1½/1. (Found: Br,31.6; $C_{16}H_{16}NBrCl_2$ requires Br,21.4; $C_{16}H_{16}NBr_2Cl_2$ requires Br,35.3; and $C_{16}H_{16}NBr_{1\frac{1}{2}}Cl_2$ requires Br,29.0). It thus seems likely that bromine or hydrogen bromide is occluded in the azepinium bromide and may be taking the place of water of crystallisation in the molecule. A sample of the yellow compound was retained and 2.025 g. of the azepinium bromide were recovered and retreated.

b) 1) 2.025 g. of azepinium bromide were used.

2) The distillation was carried out under a pressure of 15 mm. until the water was removed, and the pressure then lowered to 13 mm.

3) The temperature was maintained at 140-145° for one hour.

The aqueous residue weighed 0.52 g.

0.038 g. of neutral material were recovered and 0.91 g. of bases which gave 1.85 g. of picrates. On treatment with ethanol and acetone, only crops of mixed picrates were obtained.

4',1"-Dichloro-2,7-dihydro-3,4:5,6-dibenzoxepin

6,6'-Dichloro-2,2'-bishydroxymethylbiphenyl (0.5 g.) was warmed in a beaker with 50% sulphuric acid (20 cc.) until the melted diol had reacted to form a thick gum. This solidified on cooling and was filtered off and crystallised from ethanol giving 0.2 g. of needles, m.p. 159.5°-161°, and 0.05 g. of a second crop with m.p. 159°-161° (total yield 53%). After combining these and crystallising two more times from ethanol, the m.p. was 161°-162°. (Found: C,63.3; H,3.6; Cl,26.65; O,6.2. $C_{14}H_{10}Cl_2O$ requires C,63.4; H,3.8; Cl,26.75; O,6.0.)

Resolution of 6,6'-Dichloro-2,2'-diphenic Acid through the Brucine Salt.

G. H. Christie, C. W. James and J. Kenner[61] (J. 1923, 83, 1948)

The polarimeter used gives readings directly to 0.01° and the results were usually reproduceable to 0.02°. The solution was filtered through a fast-filtering filter paper into the polarimeter tube, and ten individual readings were taken and averaged to give each reported rotation.

Hot alcoholic solutions of 6,6'-dichloro-2,2'-diphenic acid (2.00 g., 1 mol.) and brucine (6.01 g., 2 mol.) were filtered into a conical flask and left to crystallise. Fractional crystallisation of the deposited crystals and crops obtained by concentrating the mother liquors gave 2.98 g. with $[\alpha]^{20.0}_{5461}$ +8.5° and 0.5 g. with $[\alpha]^{19.8}_{5461}$ -89° to $[\alpha]^{23.3}_{5461}$ -79° together with intermediate crops. The rotations of the br~~om~~ucine salts were all measured in chloroform. The dextrorotatory acid was generated by washing a chloroform solution of the brucine salt three times with 10% sodium hydroxide solution and carefully acidifying the alkaline solution with dilute hydrochloric acid. The precipitated acid was filtered and dried and 0.65 g. were obtained. After crystallisation from aqueous methanol, the needles formed had m.p. 262°-269° (turning opaque at 190°). The acid had $[\alpha]^{20.0}_{5461}$ +26.7°, $[\alpha]^{23.8}_{5461}$ +22.8° (0.1N NaOH, c 0.776). A jacketed tube was used for further readings at different temperatures and the rotation of the solution was shown to be markedly temperature dependent (see table 13, graph 1.).

Remaining crops of the brucine salt were included in a second resolution using 10.00 g. of acid and 30.06 g. of brucine, which gave 15.49 g. of salt with rotation $[\alpha]^{24.6}_{5461}$ +9.0° and 2.69 g. with $[\alpha]^{19.4}_{5461}$ -82°, together with 7.64 g. with $[\alpha]^{19.2}_{5461}$ -80°, 9.17 g. with $[\alpha]^{20.5}_{5461}$ -78° and 3.8 g. with $[\alpha]^{21.4}_{5461}$ -76.6°, and other intermediate crops. The 3.8 g. with $[\alpha]^{21.4}_{5461}$ -76.6° was made into the acid as previously described and gave 0.81 g. with rotation $[\alpha]^{21.5}_{5461}$ -18.8°, which, after crystallisation from aqueous ethanol gave 0.52 g. with $[\alpha]^{21.3}_{5461}$ -20.0°.

From the positively rotating salt, 3.69 g. of acid were obtained, which, on crystallisation yielded 3.23 g. with $[\alpha]_{5461}^{17.3}$ +31.3°.

The remaining crops were included in a third resolution using 36 g. of acid and 108 g. of brucine, which gave 50 g. of salt with rotation $[\alpha]_{5461}^{19.5}+9.0°$, 11.3 g. with $[\alpha]_{5461}^{24.8}+9.7°$ and 2.78 g. with $[\alpha]_{5461}^{24.4}+10.2°$, (a total of 64g.) and 8g. with rotation $[\alpha]_{5461}^{22.4}-89°$, 14.5 g. with $[\alpha]_{5461}^{25.4}-85°$, 19.4 g. with $[\alpha]_{5461}^{25.6}-83°$ and 24 g. with $[\alpha]_{5461}^{24.6}-80°$ (a total of 66 g.), together with other crops of less optically pure material.

The dextrorotatory salt was converted into the acid, yielding 15.4 g. (43%) recovery on total acid used, and this was crystallised, giving 14 g. with a rotation of $[\alpha]_{5461}^{23.8}+18.0°$.

(+)-R-6,6'-Dichloro-2,2'-bishydroxymethylbiphenyl

The procedure was as for the inactive compound described on page 179, using 1 g. of (+)-R-6,6'-dichloro-2,2'-diphenic acid (1 mol) and 0.3 g. of lithium aluminium hydride (2.5 mol.). A gum was obtained, which would not solidify and it was retreated with 0.5 g. lithium aluminium hydride to ensure complete reaction. A gum was left again, but after trituration with a variety of solvents, cooling and scratching, a white solid separated. On crystallisation from benzene, the compound (0.4 g., 44%) had m.p. 104.5°-106°. M. Siegel and K. Mislow[72] (*J.Amer.Chem.Soc.*1958,*80*, 473) give m.p. 106°-107°.

It had $[\alpha]^{20.2}_{5461}$+175°, $[\alpha]^{20.2}_{5791}$+153° and $[\alpha]^{20.7}_{D}$+149° (c 0.540 in benzene). K. Mislow and M. Seigel give $[\alpha]^{30}_{D}$+141° (c 0.91 in benzene).

Readings at different temperatures showed that the rotation was temperature dependent, see table 14, graph 2.

A second preparation gave 1.84 g. (92%) of the active diol. Crystallisation of this from benzene/cyclohexane gave 0.77 g. with $[\alpha]^{19.3}_{5461}$+174° and two crops with lower rotation. These, on recrystallisation yielded 0.5 g. with $[\alpha]^{20.8}_{5461}$+176°.

A third preparation gave 11.7 g. (92%) of the active diol, which, on crystallisation from benzene, yielded 4.4 g. with $[\alpha]^{21.2}_{5461}$+176° and 2.7 g. with $[\alpha]^{21.6}_{5461}$+174°.

(−)-R-4',1"-Dichloro-2,7-dihydro-3,4:5,6-dibenzoxepin

0.2 g. of (+)-R-6,6'-dichloro-2,2'-bishydroxymethylbiphenyl were warmed with 10 c.c. of 50% sulphuric acid on a water bath until the mixture thickened. The gum obtained solidified on scratching, and weighed 0.02 g. (11%). The specific rotation was $[\alpha]^{17.2}_{5461}$−374° (c 0.820 in benzene).

A second preparation, using 1.50 g. of (+) diol and 70 cc. of 50% sulphuric acid gave a theoretical yield of solid product, which was crystallised from ethanol, giving 0.79 g. (53%) m.p. 143°-144°, $[\alpha]^{16.2}_{5461}$−391° and 0.42 g. with a slightly lower rotation (total yield 73%). Measurements were made at different temperatures to see if the rotation was temperature dependent (see table 15, graph 3).

The change was slight and could be accounted for by change in volume due to expansion of the solution.

Found: C,63.3; H, 3.8; Cl,26.7; O, 6.2; $C_{14}H_{10}Cl_2O$ requires C,63.4; H,3.8; Cl,26.75; O,6.0;.

Racemisation of the oxepin in 2-phenylethanol was studied in the temperature range 154°-185°. The solution was heated under nitrogen in sealed tubes which were placed in a thermostat controlled oil bath. The tubes were removed at suitable intervals for polarimetric examination, (table 18, graph 6).

One sample was left until the rotation was, within experimental error, zero, and the infrared spectrum of the residue shown to be identical to that obtained from the optically inactive oxepin.

The energy of activation (E), the Arrhenius parameter (A) and the entropy of activation ($\Delta S^{\dagger}$)were determined from the experimental plots (table 19 , graph 7) using the least squares method.

(+)-R-6,6'-Dichloro-2,2'-bisbromomethylbiphenyl

F. A. McGinn, A. K. Lazarus, M. Siegel, J. E. Ricci and K. Mislow[73]
J. Amer. Chem. Soc. 1958, 80, 476.

The compound was prepared as described on page179 and by the above workers, using 7.0 g. of (+)-R-6,6'-dichloro-2,2'-bishydroxymethylbiphenyl and 320 c.c. of 48% hydrobromic acid, and heating on a water bath for 2 hours. The reaction was apparently not complete, for a gum was obtained which would not solidify, even when triturated with a variety of solvents. The gum was heated for another 2 hours with more 48% hydrobromic acid (300 c.c.) and this time a solid was obtained when the reaction mixture was cooled. The solid was filtered off and dried in a vacuum des~~s~~iccator over sodium hydroxide. The yield was 9.5 g. (94%). After crystallisation from methanol, 3.4 g. of the compound with m.p. 70-71° and with specific rotation $[\alpha]_{5461}^{20.0}$+93° and $[\alpha]_{D}^{23.8}$+80° (c. 0.99 in benzene) and 2 g. with $[\alpha]_{5461}^{26.6}$ +92° were obtained (54%). Literature m.p. 70-71° and specific rotation is $[\alpha]_{D}^{289}$+77° (c 0.93 in benzene). Readings at different temperatures showed that the rotation was, to a small extent, temperature dependent.

(-)-R-4;1",-Dichloro-2,7-dihydro-1,1-dimethyl-3,4:5,6-dibenzazepinium Bromide

The compound was prepared by the method (b) used for the inactive compound described on page 181 using 0.8 g. of 6,6'-dichloro-2,2'-bisbromomethylbiphenyl and 0.6 ml. dimethylamine. The white azepinium bromide was obtained in theoretical yield and was crystallised from methanol-ethyl acetate mixture, giving 0.35 g. with specific rotation $[\alpha]_{5461}^{22.2}$-159° (c 0.97 in chloroform). Readings were taken at different temperatures and the rotation was found to be temperature dependent. The rotation in 2-phenylethanol was $[\alpha]_{5461}^{18.5}$-300°.

A second preparation on 3 g. of bisbromomethyl compound yielded on crystallisation, 1.38 g. of needle-shaped crystals with specific rotation $[\alpha]^{21.0}_{5461}$ -299° (*c* 1.03 in 2-phenylethyl alcohol).

Racemisation of the azepinium bromide was studied in the temperature range 188–230°, in the same way as for the oxepin, and the activation energy E, the Arrhenius parameter A and the entropy of activation $\Delta S^{\dagger}$ were determined from the experimental plots (table 21 , graph 9) using the least squares method. (See also table 20, graph 8.)

4,5-Dichloro-~~2,7~~9,10-dihydrophenanthrene

Lithium (0.47 g.; 2.1 atoms + 0.1 g. to allow for the amount remaining in the press) was weighed under dry toluene and pressed out as a wire through a 1 mm. die. The wire was cut up into small pieces as it emerged from the press and allowed to drop into 50 ml. of sodium dried ether in a flask previously flushed out with nitrogen. (The reaction mixture was kept under nitrogen until the phenyl lithium had been destroyed). A little freshly distilled bromobenzene was added and the solution was warmed. Then the rest of the bromobenzene (a total of 3.8 g.; 1 mol. was added), was gradually run in and the reaction mixture warmed on a water-bath for ½ hour, during which time the lithium gradually reacted. The dibromide (8.g.; 1 mol. which had previously been left in a vacuum dessicator) was dissolved in sodium dried ether and added to the phenyl lithium. At first the solution went yellow, then a cloudy precipitate appeared and the yellow colour became less. The mixture was heated under reflux for 1 hour. After filtering the solution through glass wool, water and dilute hydrochloric acid were added to form two clear solutions. The ethereal layer was separated, washed with water and dried over anhydrous sodium sulphate. After removing the ether, a gum and some solid were left. By treatment with ether and ethanol a solid was obtained, which was crystallised from petroleum ether (b.p.40-60°) giving 0.6 g. (12%) of a product with m.p. 105-107°. Crystallisation from ethanol raised the m.p. to 106.5-107.5°. (Found: C,67.65; H,4.2; Cl,28.35; $C_{14}H_{10}Cl_2$ requires C,67.5; H,4.05; Cl,28.5).

A subsequent preparation using 0.66 g. (3.3 mol.) of lithium and 5.7 g. (1.5 mol.) of bromobenzene and heating the reaction mixture for four hours gave a yield of 1.1 g. (22%) with m.p. 105-106°.

An attempted preparation of the active dichlorodihydrophenanthrene was unsuccessful. There was an indication, however, that besides the dextrorotatory dibromide, there was also some material with a negative rotation. Work on this is still in progress.

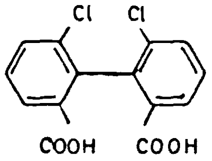
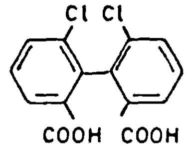
TEMPERATURE DEPENDENCE OF ROTATION OF (+)-R-  IN 0.IN NaOH

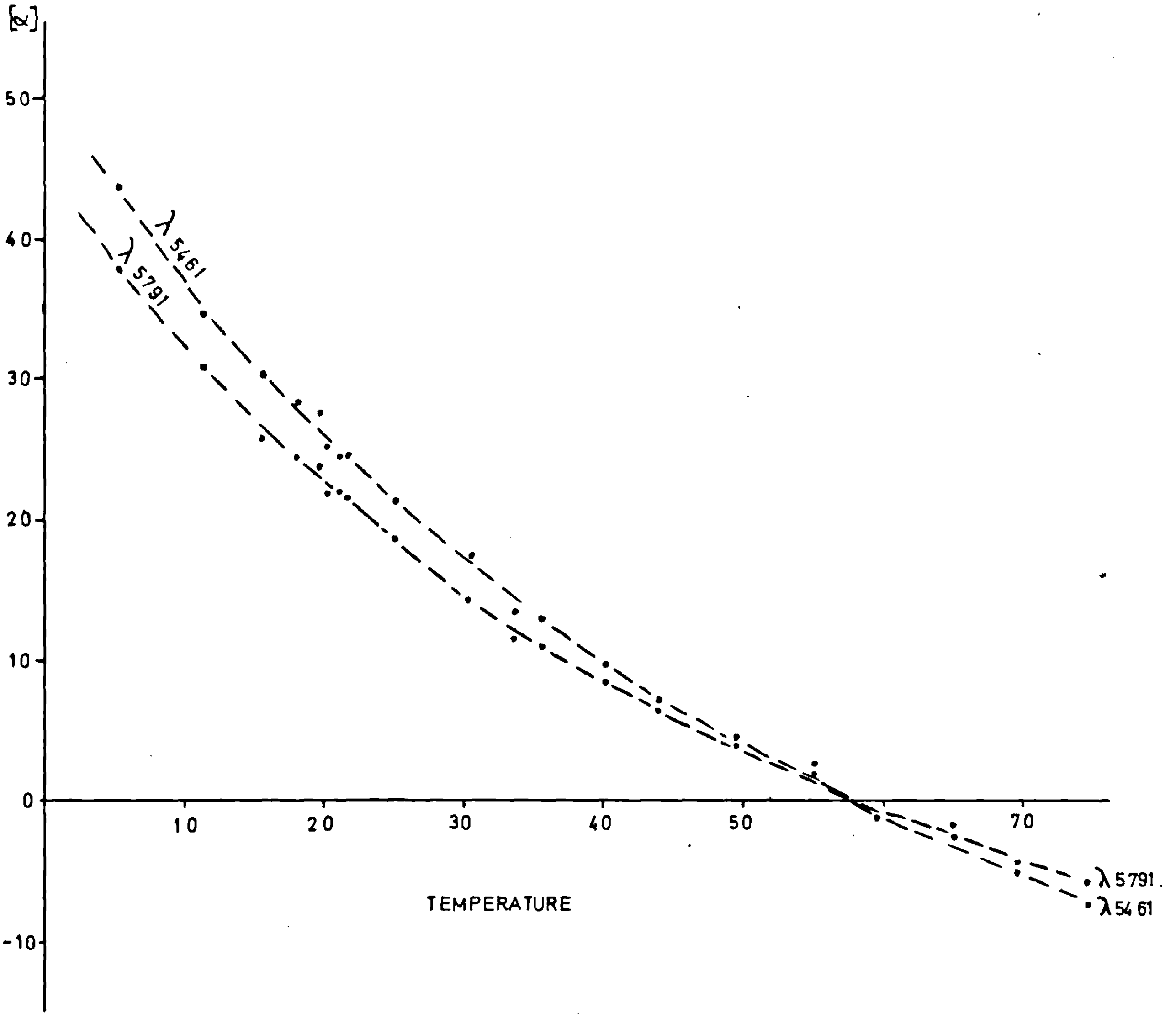
Table 13

1 = 2 c = 0.776

TEMPERATURE	λ 5791 zero 179.99			λ 5461 zero 179.98		
	reading	α	[α]	reading	α	[α]
5.2°	180.58°	+0.59°	+38.0°	180.66°	+0.68°	+43.8°
11.2°	180.47°	+0.48°	+30.9°	180.52°	+0.54°	+34.8°
15.5°	180.39°	+0.40°	+25.8°	180.45°	+0.47°	+30.3°
18.0°	180.38°	+0.38°	+24.5°	180.42°	+0.44°	+28.4°
20.1°	180.33°	+0.34°	+21.9°	180.37°	+0.39°	+25.1°
21.6°	180.32°	+0.33°	+21.6°	180.36°	+0.38°	+24.5°
25.0°	180.28°	+0.29°	+18.7°	180.31°	+0.33°	+21.3°
30.4°	180.21°	+0.22°	+14.2°	180.25°	+0.27°	+17.4°
33.5°	180.17°	+0.18°	+11.6°	180.19°	+0.21°	+13.5°
35.4°	180.16°	+0.17°	+11.0°	180.18°	+0.20°	+12.9°
4o.0°	180.12°	+0.13°	+8.4°	180.13°	+0.15°	+9.7°
43.8°	180.09°	+0.10°	+6.4°	180.09°	+0.11°	+7.1°
49.5°	180.05°	+0.06°	+3.9°	180.05°	+0.07°	+4.5°
55.0°	180.02°	+0.03°	+1.9°	180.02°	+0.04°	+2.6°
59.5°	179.97°	-0.02°	-1.3°	179.96°	-0.02°	-1.3°
65.0°	179.96°	-0.03°	-1.9°	179.94°	-0.04°	-2.6°
69.5°	179.93°	-0.07°	-4.5°	179.90°	-0.08°	-5.2°
74.5°	179.90°	-0.09°	-5.8°	179.86°	-0.12°	-7.7°
19.6°	180.36°	+0.37°	+23.8°	180.41°	+0.43°	+27.7°

Graph 1

[α] OF R -  IN 0.1 N NaOH VS. TEMPERATURE



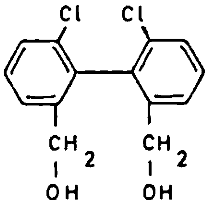
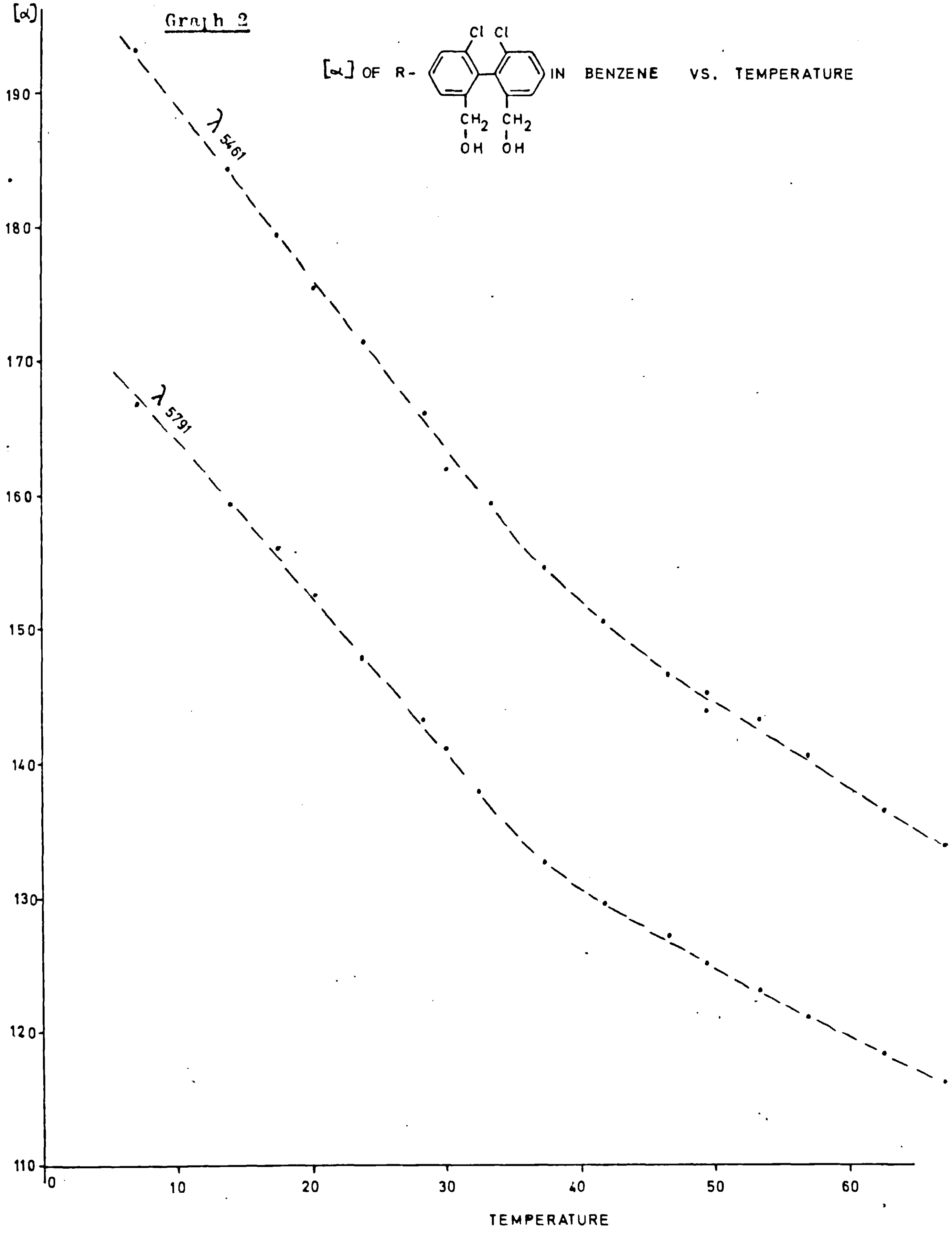
TEMPERATURE DEPENDENCE OF ROTATION OF (+)-R-  IN BENZENE

Table 14

l = 2 c = 0.7400

TEMPERATURE	λ 5791 zero 179.98			λ 5461 zero 179.99		
	reading	α	[α]	reading	α	[α]
7.0	182.46	+2.47	+167	182.84	+2.86	+193
13.8	182.35	+2.36	+159	182.71	+2.73	+185
17.4	182.30	+2.31	+156	182.64	+2.66	+180
20.3	182.25	+2.26	+153	182.58	+2.60	+176
23.8	182.18	+2.19	+148	182.52	+2.54	+172
28.4	182.11	+2.12	+143	182.44	+2.46	+166
30.0	182.08	+2.09	+141	182.38	+2.40	+162
33.4	182.03	+2.04	+138	182.34	+2.36	+159
37.4	181.97	+1.98	+134	182.27	+2.29	+155
41.8	181.91	+1.92	+130	182.21	+2.23	+151
46.6	181.87	+1.88	+127	182.15	+2.17	+147
49.4	181.83	+1.84	+124	182.11	+2.13	+144
change of thermometer						
49.4	181.84	+1.85	+125	182.13	+2.15	+145
53.4	181.81	+1.82	+123	182.10	+2.12	+143
57.0	181.78	+1.79	+121	182.06	+2.08	+141
62.7	181.74	+1.75	+118	182.00	+2.02	+137
67.2	181.71	+1.72	+116	181.96	+1.98	+134
24.2	182.25	+2.26	+153	182.61	+2.63	+178

Graph 2


[α] OF R- IN BENZENE VS. TEMPERATURE
Cl Cl
CH2 CH2
OH OH
[α]
190
180
170
160
150
140
130
120
110
0
10
20
30
40
50
60
TEMPERATURE
λ 5461
λ 5791

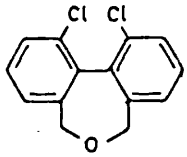
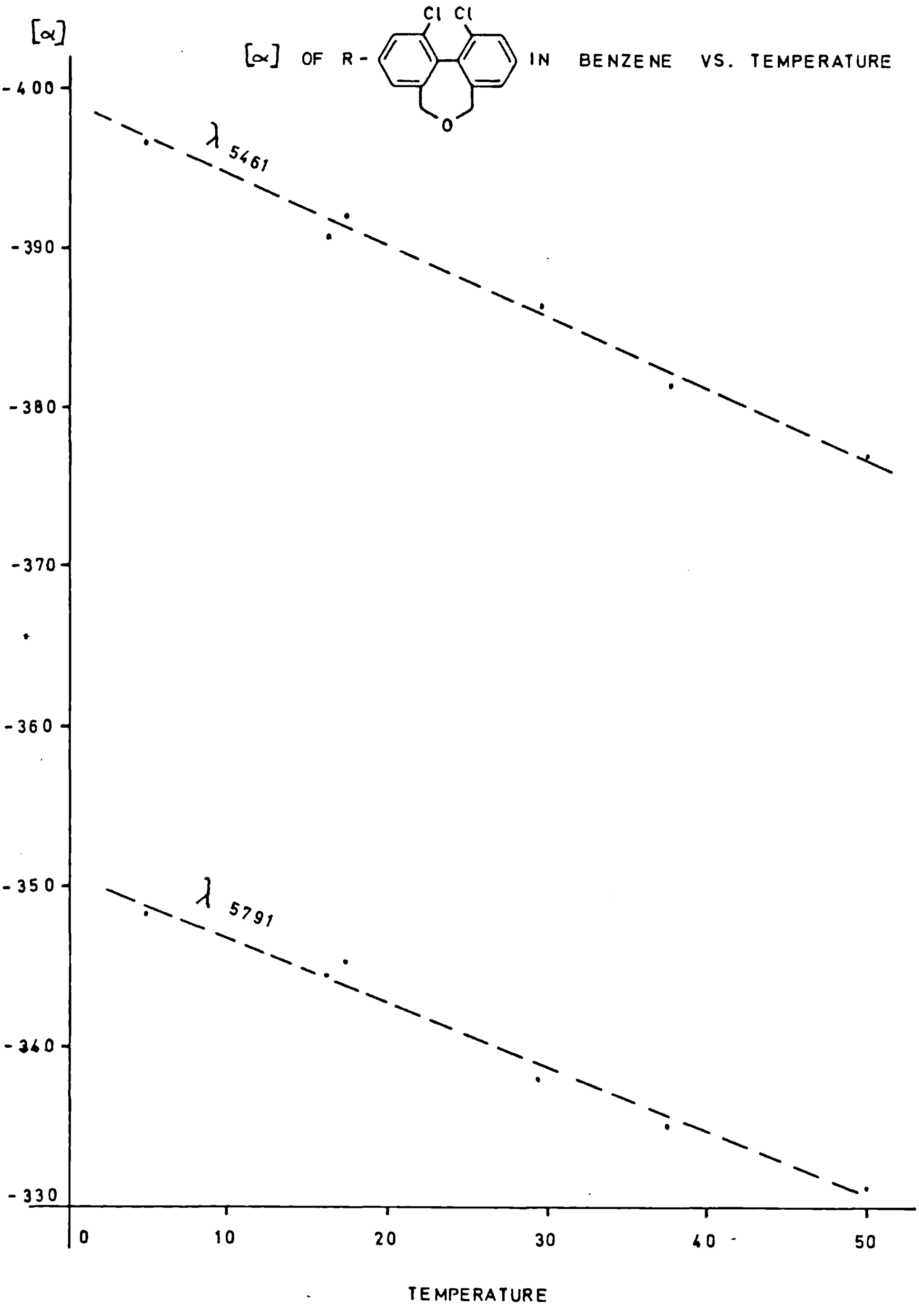
ROTATION OF (-)-R-  IN BENZENE AT DIFFERENT TEMPERATURES

Table 15

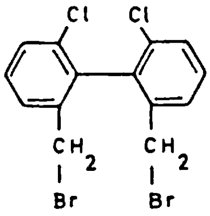
l = 2 c = 0.770

TEMPERATURE	λ 5791 zero 179.965°			λ 5461 zero 179.98°		
	reading	α	[α]	reading	α	[α]
4.8°	173.600°	-5.365°	-348°	173.870°	-6.110°	-397°
16.3°	174.660°	-5,305	-345°	173.960°	-6.020°	-391°
29.6°	174.750°	-5,215°	-338°	174.035°	-5,945°	-386°
38.6°	174.805°	-5.160°	-335°	174.105°	-5,875°	-381°
50.0°	174.865°	-5.100°	-331°	174.175°	-5,805°	-377°
17.2°	174.645°	-5,320°	-345°	173.980°	-6,040°	-392°

Graph 3


[α] OF R- IN BENZENE VS. TEMPERATURE
Cl Cl
O
[α]
-400
-390
-380
-370
-360
-350
-340
-330
λ 5461
λ 5791
0
10
20
30
40
50
TEMPERATURE

ROTATION OF (+)-R-



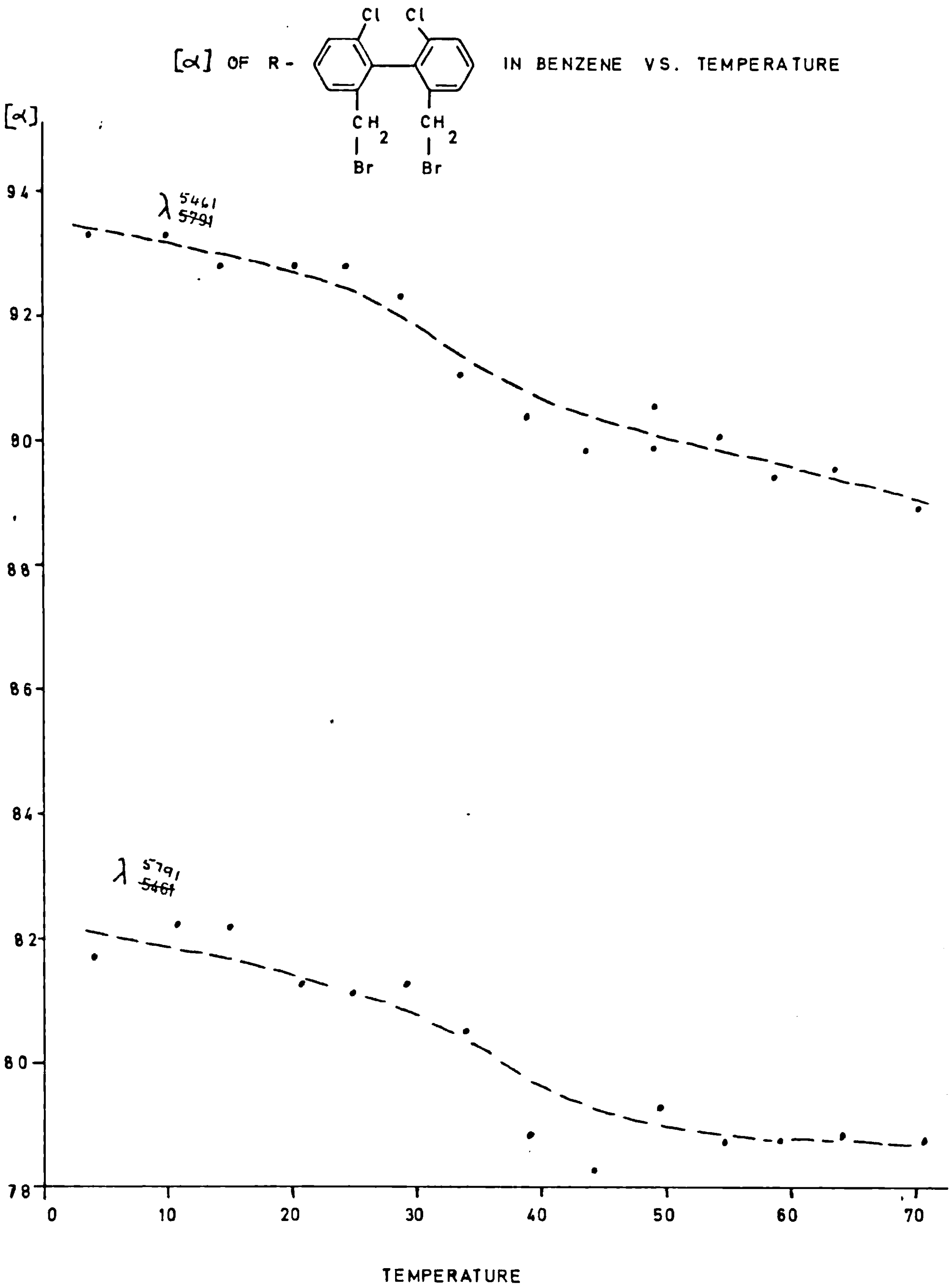
IN BENZENE AT DIFFERENT TEMPERATURES

Table 16

1 =2 c = 0.9960

TEMPERATURE	λ 5461 zero 180.040			λ 5791 zero 180.040		
	reading	α	[α]	reading	α	[α]
4.2°	180.900°	+1.86°	+93.4°	181.670°	+1.63°	+81.3°
10.8°	181.900	+1.86°	+93.4°	181.680°	+1.64°	+82.3°
14.8°	181.890°	+1.850°	+92.9°	181.680°	+1.64°	+82.3°
20.8°	181.890°	+1.85°	+92.9°	181.660°	+1.62°	+81.1°
24.8°	181.890°	+1.85°	+92.9°	181.655°	+1.615°	+81.1°
29.2°	181.880°	+1.84°	92.4°	181.660°	+1.62°	81.3°
34.0°	181.855°	+1.815°	+91.1°	181.645°	+1.605°	80.6°
39.2°	181.840°	+1.800°	+90.4°	181.610°	+1.57°	78.8°
44.0°	181.830°	+1.79°	+89.9°	181.600°	+1.56°	+78.3°
49.5°	181.830°	+1.79°	+89.9°	181.620°	+1.58°	+79.3°
change of thermometer						
49.4°	181.845°	+1.805°	+90.6°	181.620°	+1.58°	+79.3°
54.7°	181.835°	+1.795°	+90.1°	181.610°	+1.57°	+78.8°
59.0°	181.820°	+1.78°	+89.4°	181.610°	+1.57°	+78.8°
64.0°	181.825°	+1.785°	+89.6°	181.610°	+1.57°	+78.8°
70.4°	181.810°	+1.77°	+88.9°	181.610°	+1.57°	+78.8°

Graph 4


[α] OF R-
Cl
Cl
CH2
CH2
Br
Br
IN BENZENE VS. TEMPERATURE
[α]
94
92
90
88
86
84
82
80
78
λ 5461 ~~5791~~
λ 5791 ~~5461~~
0
10
20
30
40
50
60
70
TEMPERATURE

ROTATION OF (-)-R- IN CHLOROFORM AT DIFFERENT TEMPERATURES

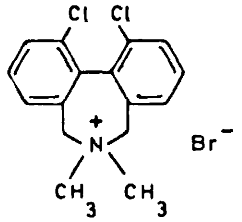
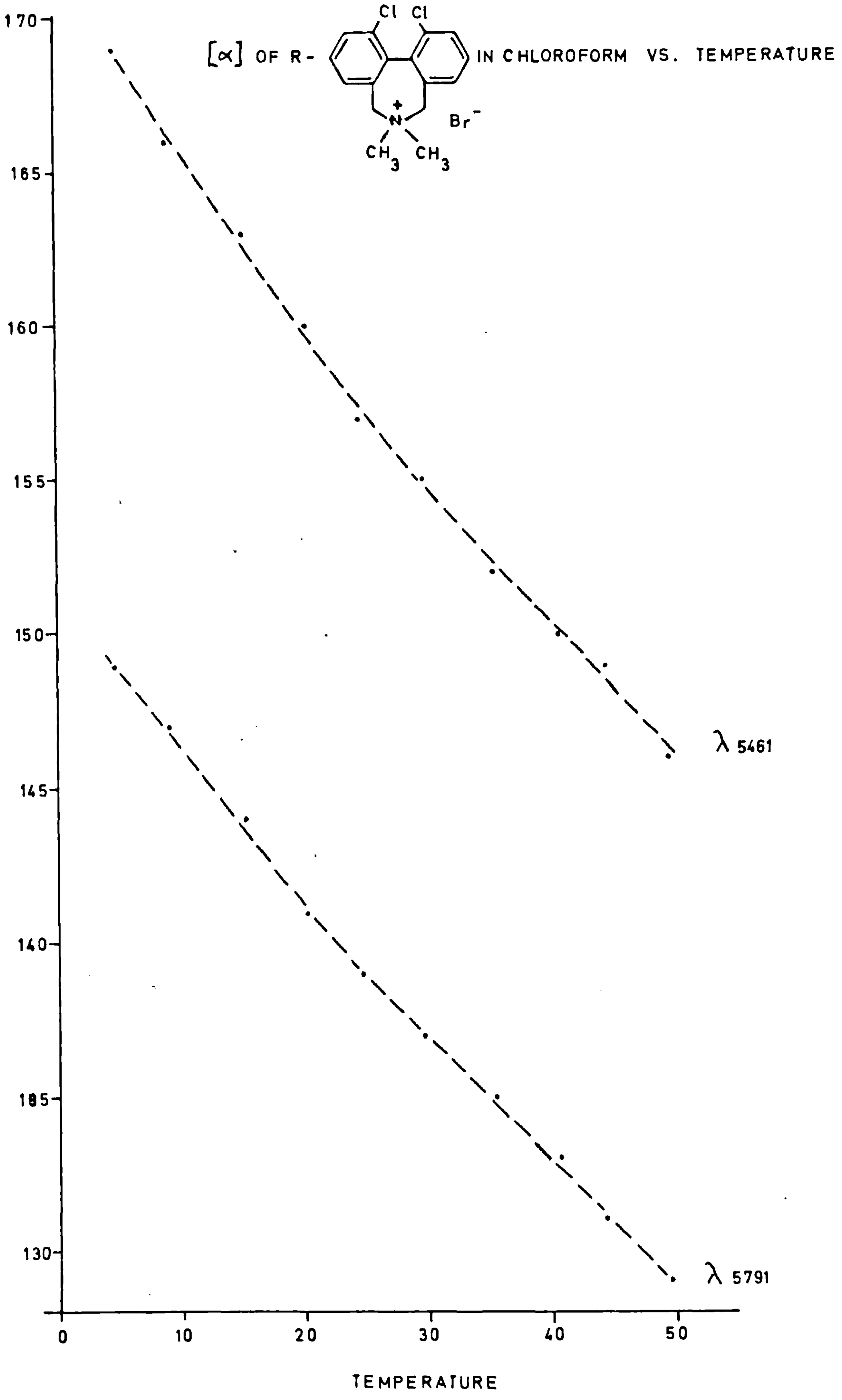


Table 17

l = 2 c = 0.972

TEMPERATURE	λ 5791 zero 360.005°			λ 5461 zero 360.01°		
	reading	α	[α]	reading	α	[α]
4.8°	357.110°	-2.885°	-148°	356.730°	-3.280°	-169°
9.0°	357.150°	-2.855°	-147°	356.780°	-3.230°	-166°
15.2°	357.205°	-2.800°	-144°	356.845°	-3.165°	-163°
20.2°	357.260°	-2.735°	-141°	356.900°	-3.110°	-160°
24.8°	357.300°	-2.705°	-139°	356.950°	-3.060°	-157°
29.8°	357.340°	-2,665°	-137°	357.000°	-3.010°	-155°
35.6°	357.390°	-2.615°	-135°	357.050°	-2,960°	-152°
40.8°	357.420°	-2.585°	-133°	357.090°	-2.920°	-150°
44.6°	357.455°	-2.550°	-131°	357.125°	-2.885°	-149°
49.8°	357.490°	-2.515°	-129°	357.175°	-2.835°	-146°

Graph 5


[α]
[α] OF R-
Cl
Cl
N
+
Br⁻
CH3
CH3
IN CHLOROFORM VS. TEMPERATURE
170
165
160
155
150
145
140
135
130
0
10
20
30
40
50
TEMPERATURE
λ 5461
λ 5791

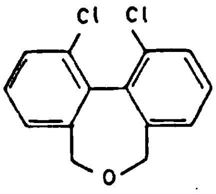
RACEMISATION OF (-)-R-  IN 2-PHENYLETHANOL

Table 18 (a)

t = 154.4° l = 1 c = 0.1198 g./20 cc.

T = 427.6°K

λ = 5461 Å Zero at 357.370°

Time (mins.)	Polarimetric reading	α observed
0	355.150	-2.220
30	355.320	-2.050
70	355.475	-1.895
120	355.630	-1.740
180	355.800	-1.570
240	356.000	-1.370
340	356.210	-1.160
420	356.365	-1.005
500	356.500	-0.870
600	356.655	-0.715
720	356.790	-0.580

$k = 3.112 \times 10^{-5}$ sec.$^{-1}$ $t_{\frac{1}{2}}$ = 371.4 mins.

log. k = -4.5070 $10^3/T$ = 2.339

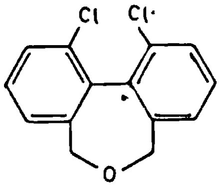
RACEMISATION OF (-)-R-  IN 2-PHENYLETHANOL

Table 18 (b)

t = 159.8° l = 1 c = 0.1202 g./20 c.c.

T = 433.0°K

λ = 5461 Å Zero at 357.330°

Time (mins.)	Polarimetric reading	$\alpha_{observed}$
0	355.150	-2.180
30	355.315	-2.015
60	355.530	-1.800
90	355.695	-1.635
135	355.890	-1.440
180	356.090	-1.240
225	356.250	-1.080
270	356.400	-0.930
330	356.580	-0.750
405	356.730	-0.600
495	356.885	-0.455
600	357.000	-0.330
720	357.090	-0.240

$k = 5.381 \times 10^{-5}$ sec.$^{-1}$ $t_{\frac{1}{2}}$ = 214.7 mins.

log. k = -4.2691 $10^3/T$ = 2.309

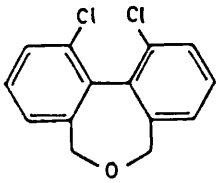
RACEMISATION OF (−)-R-  IN 2-PHENYLETHANOL

Table 18 (c)

t = 170.0°　　1 = 1　　c = 0.1210 g./20 c.c.

T = 443.2°K

λ = 5461 Å　　Zero at 357.350°

Time (mins.)	Polarimetric reading	$\alpha_{observed}$
0	355.150	−2.100
30	355.720	−1.630
60	356.075	−1.275
90	356.215	−1.035
140	356.675	−0.675
185	356.870	−0.480
235	357.040	−0.310
280	357.150	−0.200
330	357.210	−0.140
375	357.250	−0.100
455	357.330	−0.020
840	357.340	−0.010

k = 1.355×10^{-4} sec.$^{-1}$　　$t_{\frac{1}{2}}$ = 86.3 mins.

log. k = −3.8681　　$10^3/T$ = 2.256

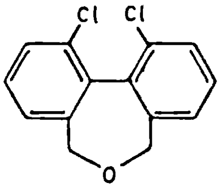
RACEMISATION OF (-)-R-  IN 2-PHENYLETHANOL

Table 18 (d)

t = 179.8° l = 1 c = 0.1208 g./20 c.c.

T = 453.0°K

λ = 5461 Å

Zero at 357.350°

Time (mins.)	Polarimetric reading	$\alpha_{observed}$
0	355.335	-2.015
6	355.615	-1.735
15	355.865	-1.485
24	356.070	-1.280
36	356.320	-1.030
48	356.540	-0.810
60	356.715	-0.635
75	356.865	-0.485
96	357.020	-0.330
132	357.230	-0.120
186	357.280	-0.070
246	357.330	-0.020

$k = 3.106 \times 10^{-4}$ sec.$^{-1}$ $t_{\frac{1}{2}}$ = 37.2 mins.

log. k = -3.5078 $10^3/_T$ = 2.208

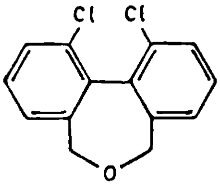
RACEMISATION OF (-)-R-  IN 2-PHENYLETHANOL

Table 18 (e)

t = 185.2°   l = 1   c = 0.1198 g./20 c.c.

T = 458.4°K

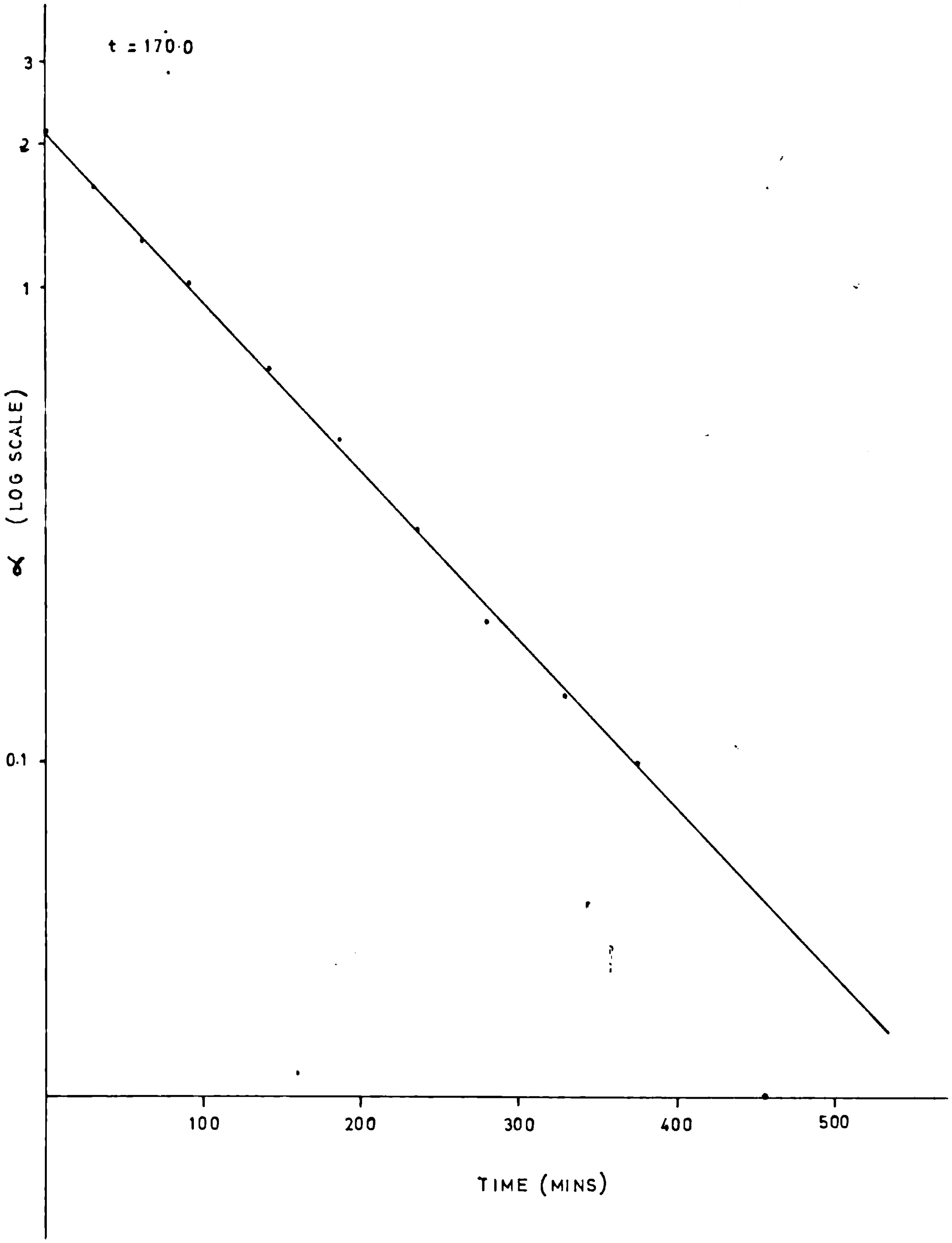
λ = 5461 Å   Zero at 357.330°

Time (mins.)	Polarimetric reading	$\alpha_{observed}$
0	355.360	-1.970
3	355.545	-1.785
6	355.670	-1.660
10	355.850	-1.480
14	356.000	-1.330
18	356.150	-1.180
22	356.280	-1.050
27	356.440	-0.890
32	356.560	-0.770
39	356.700	-0.630
45	356.820	-0.510
52	356.920	-0.410
60	356.995	-0.335

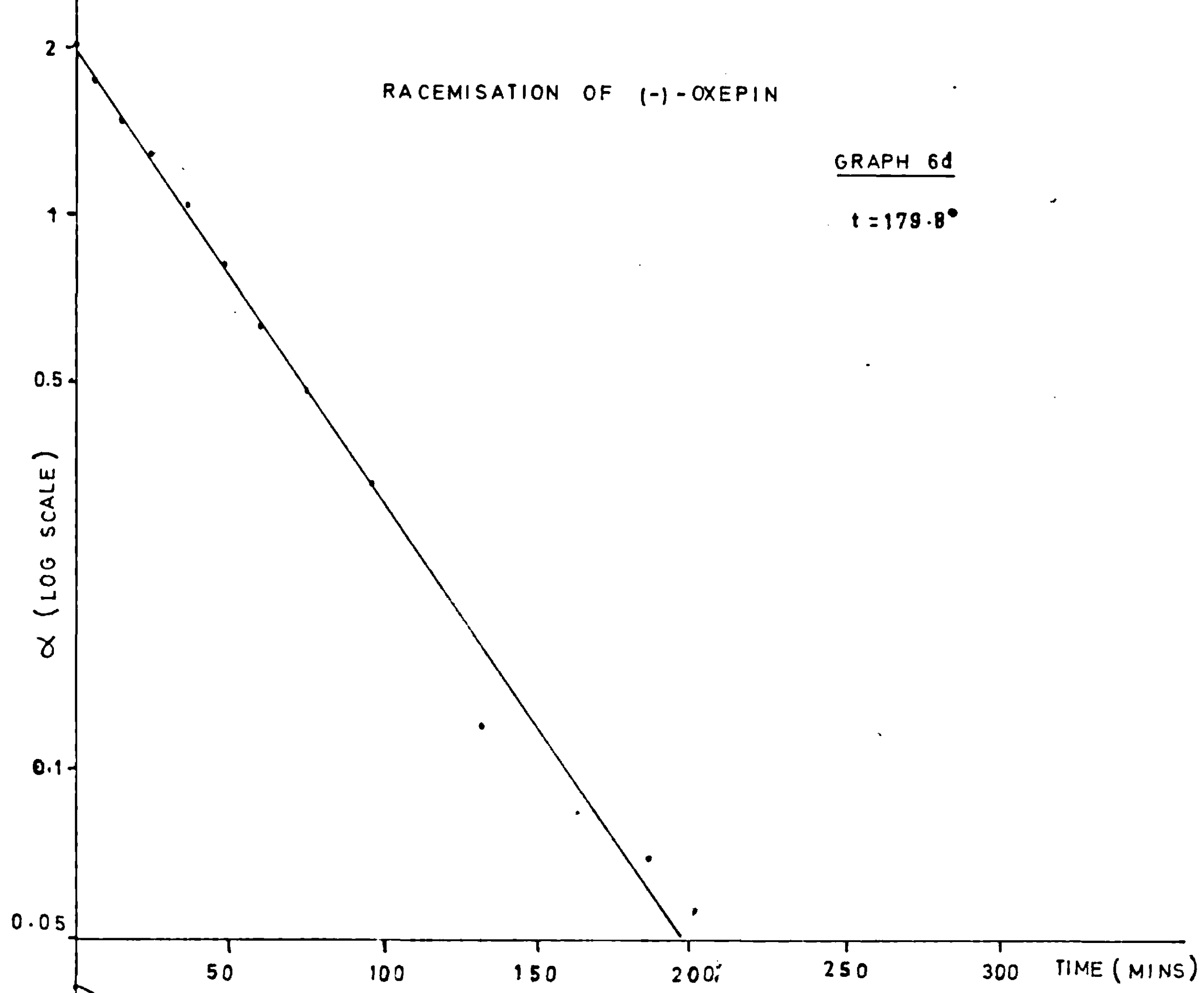
$k = 5.008 \times 10^{-4}$ sec.$^{-1}$ $t_{\frac{1}{2}}$ = 23.1 mins.

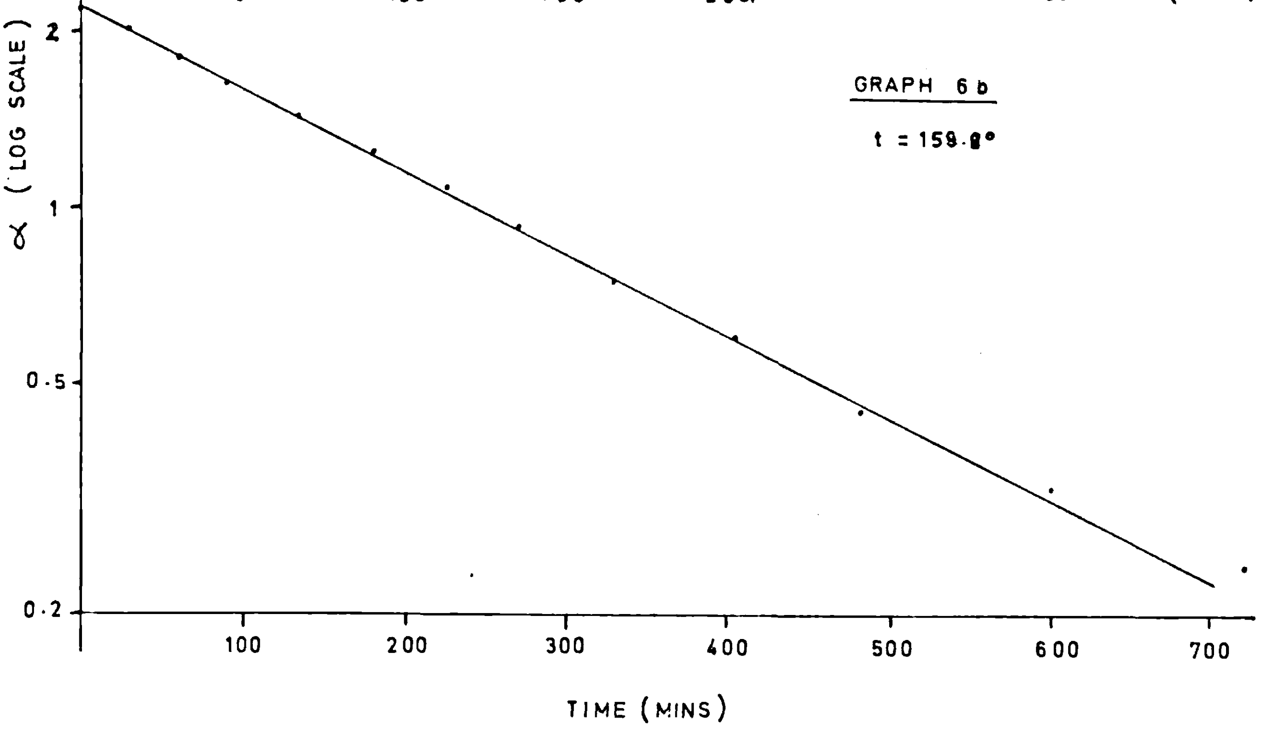
log. k = 3.3003 $10^3/_T$ = 2.181

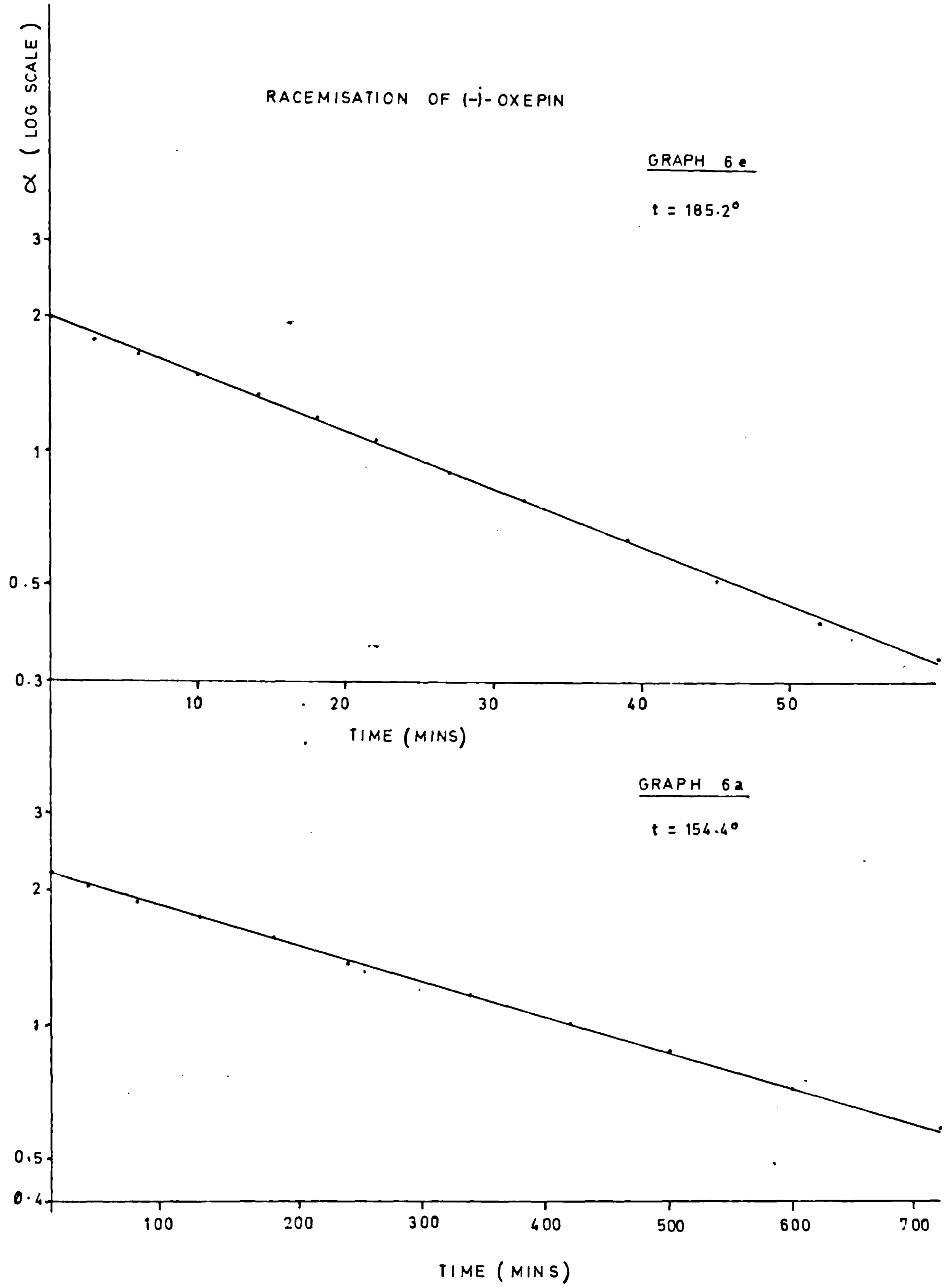
GRAPH 6c RACEMISATION OF (-)-OXEPIN



RACEMISATION OF (-)-OXEPIN







RACEMISATION OF (-)-OXEPIN

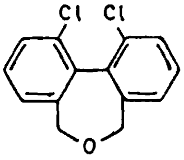
RACEMISATION OF (-)-R-  IN 2-PHENYLETHANOL

Table 19 graph 7

$\log_{10}k \;/\; 10^3/T$

T (K°)	$10^3/T$	k sec^{-1}	log k	log A (sec^{-1})	$\Delta S^{\ddagger}$ e.u.
427.6	2.339	3.112×10^{-5}	-4.5070	13.29	-0.5
433.0	2.309	5.381×10^{-5}	-4.2691	13.30	-0.4
443.2	2.256	1.355×10^{-4}	-3.8681	13.30	-0.4
453.0	2.208	3.106×10^{-4}	-3.5078	13.29	-0.5
458.4	2.181	5.008×10^{-4}	-3.3003	13.29	-0.5
MEAN VALUES				13.3	-0.5

The straight line plot of $\log_{10}k$ against $10^3/T$ is shown in graph 7 . Using the method of least squares, the value of E was calculated to be 34.8± 0.1 Kcal./mole. From this the value of A was found to be $10^{+13.3}$ and that of $\Delta S^{\ddagger}$ -0.5 e.u.

Values of A were calculated from the equation

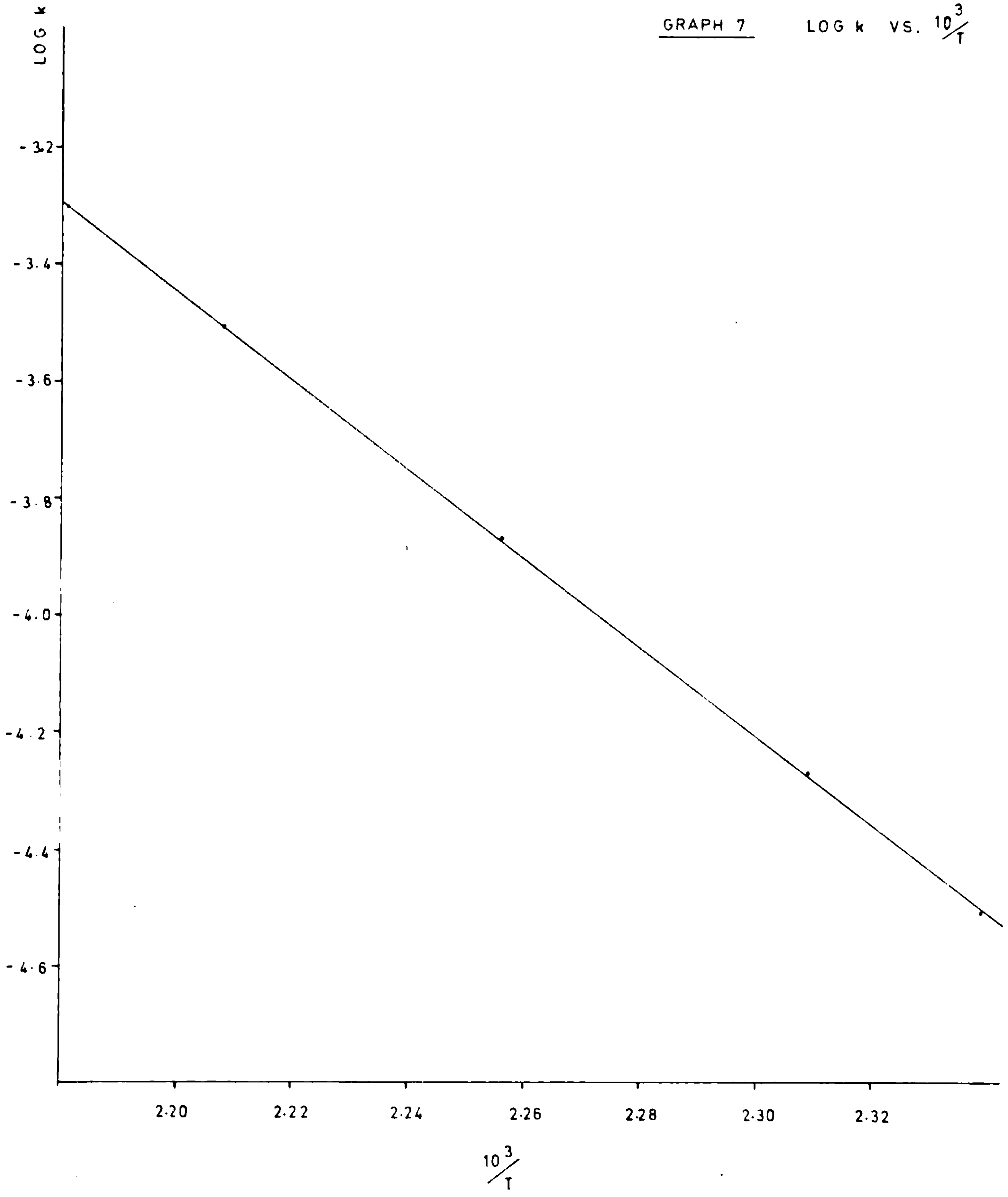
$$\log_{10}A = \log_{10}k + E/4.576 \cdot 1/T$$

and values of $\Delta S^{\ddagger}$ from

$$\Delta S^{\ddagger} = 4.576 \log_{10}k_{rac}/T + E/T - 49.20$$

Graphically, E is found to be 34.8 Kcal./mole

RACEMISATION OF (-)-OXEPIN



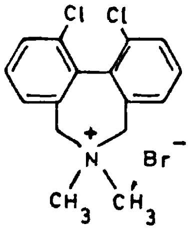
RACEMISATION OF (-)-R-  IN 2-PHENYLETHANOL

Table 20 (a)

t = 188.8° 1 = 1 dm.

T = 462.0°

λ = 5461 Å Zero at 359.00°

Time (mins.)	Polarimetric reading	$\alpha_{observed}$
0	358.120	-1.880
15	358.195	-1.805
30	358.190	-1.810
50	358.295	-1.705
72	358.340	-1.660
100	358.385	-1.615
140	358.475	-1.525
200	358.570	-1.430
280	358.810	-1.190
380	358.975	-1.025
480	359.140	-0.860
580	359.260	-0.740
770	359.460	-0.540
972	359.580	-0.420
1212	359.745	-0.255

$k = 2.690 \times 10^{-5}$ $t_{\frac{1}{2}} = 429$ mins.

$\log k = -4.5702$ $10^3/T = 2.165$

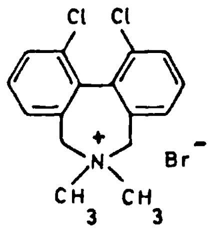
RACEMISATION OF (-)-R-  IN 2-PHENYLETHANOL

Table 20 (b)

t = 199.9°   l = 1 dm.

T = 473.1° λ = 5461 Å   Zero at 360.00

Time (mins.)	Polarimetric reading	$\alpha_{observed}$
0	358.230	-1.770
8	358.325	-1.675
18	358.420	-1.590
30	358.470	-1.530
45	358.555	-1.445
60	358.655	-1.345
80	358.780	-1.220
100	358.975	-1.025
132	358.970	-1.030
160	359.125	-0.875
202	359.300	-0.700
253	359.395	-0.605
313	359.570	-0.430
408	359.700	-0.300
520	359.800	-0.200

$k = 7.000 \times 10^{-5}$ $t_{\frac{1}{2}}$ = 165 mins.

log. k = -4.1543 $10^3/_T = 2.114$

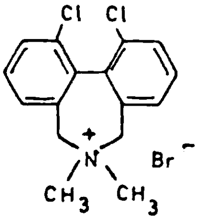
RACEMISATION OF (-)-R-  IN 2-PHENYLETHANOL

Table 20 (c)

$t = 211.3°$ $l = 1$ dm.

$T = 484.5°$ $\lambda = 5461$ Å Zero at 360.080

Time (mins.)	Polarimetric reading	α_{observed}
0	358.050	-2.030
2	358.165	-1.915
5	358.200	-1.880
10	358.330	-1.750
15	358.450	-1.630
20	358.520	-1.560
25	358.635	-1.445
31	358.755	-1.325
40	358.920	-1.160
50	359.020	-1.060
61	359.155	-0.925
75	359.740	-0.775
90	359.465	-0.615
110	359.550	-0.530
140	359.760	-0.320

$k = 1.916 \times 10^{-4}$ $t_{\frac{1}{2}} = 60.3$ mins.

$\log. k = -3.7175$ $10^3/_T = 2.064$

RACEMISATION OF (-)-R- IN 2-PHENYLETHANOL

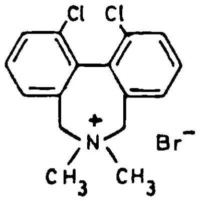


Table 20 (d)

t = 220.7°

T = 493.9°

l = 1 dm.

λ = 5461 Å

zero at 360.035

Time (mins)	Polarimetric reading	$\alpha_{observed}$
0	358.200	-1.835
2	358.290	-1.745
4	358.325	-1.710
7	358.480	-1.555
10	358.530	-1.505
15	358.645	-1.390
21	358.890	-1.145
25	359.015	-1.020
30	359,125	-0.910
40	359.255	-0.780
50	359.470	-0.565
61	359.590	-0.445
75	359.700	-0.335
90	359.820	-0.215
110	359.050	-0.130

$k = 3.925 \times 10^{-4}$

$t_{\frac{1}{2}}$ = 29.4 mins.

log. k = -3.4061

$10^3/_T = 2.024$

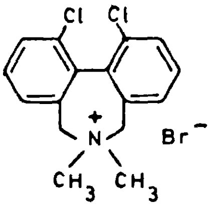
RACEMISATION OF (-)-R-  IN 2-PHENYLETHANOL

Table 20 (e)

$t = 229.1°$ $l = 1$ dm.

$T = 502.3°$ $\lambda = 5461$ Å Zero at 360.050

Time (mins.)	Polarimetric reading	$\alpha_{observed}$
0	358.250	-1.800
1	358.370	-1.680
2	358.450	-1.600
4	358.600	-1.450
6	358.730	-1.320
8	358.845	-1.205
11	359.000	-1.050
14	359.130	-0.920
18	359.290	-0.760
22	359.405	-0.645
28	359.570	-0.480
35	359.710	-0.340
42	359.785	-0.265
50	359.880	-0.170
60	359.935	-0.115

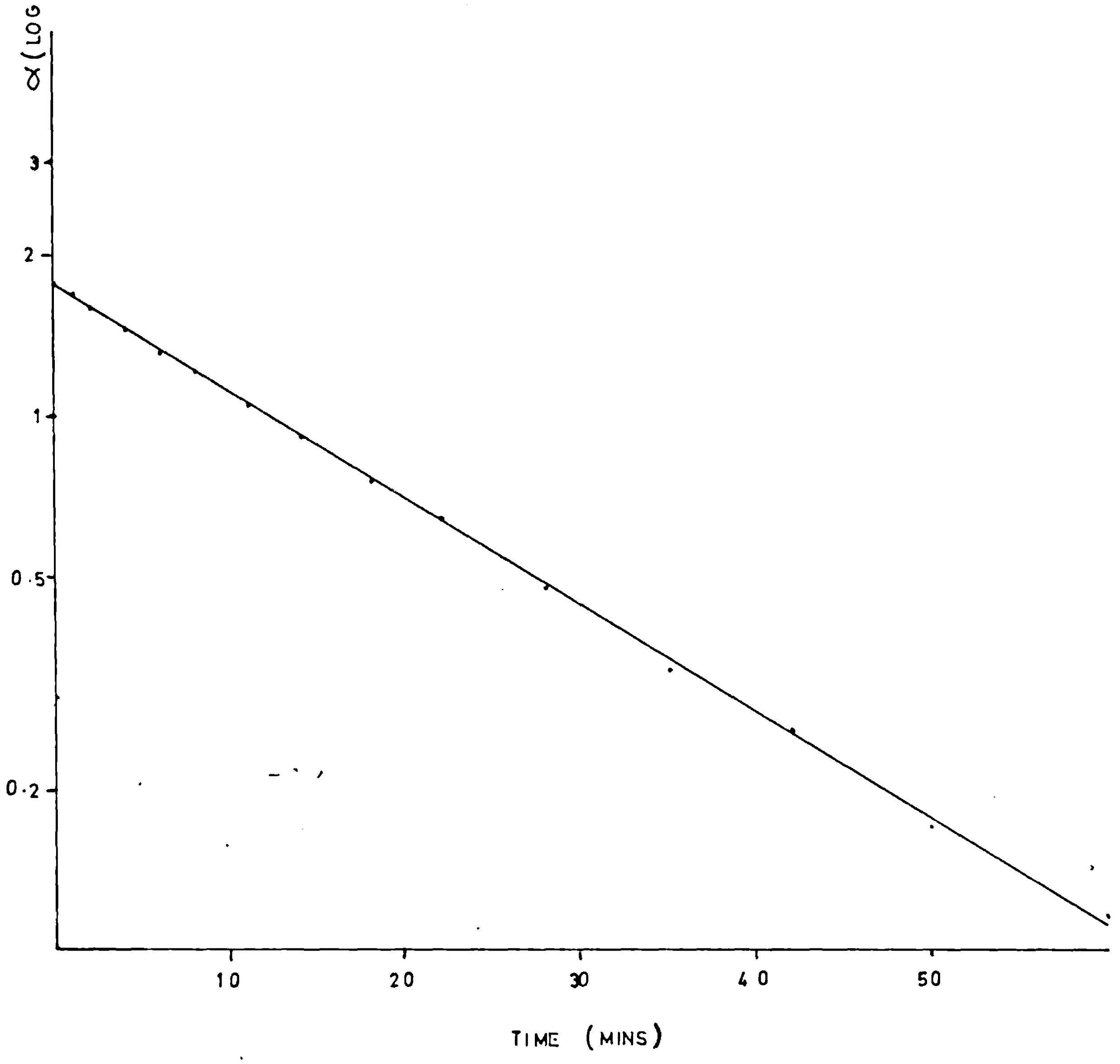
$k = 7.711 \times 10^{-4}$ $t_{\frac{1}{2}} = 15.0$ mins.

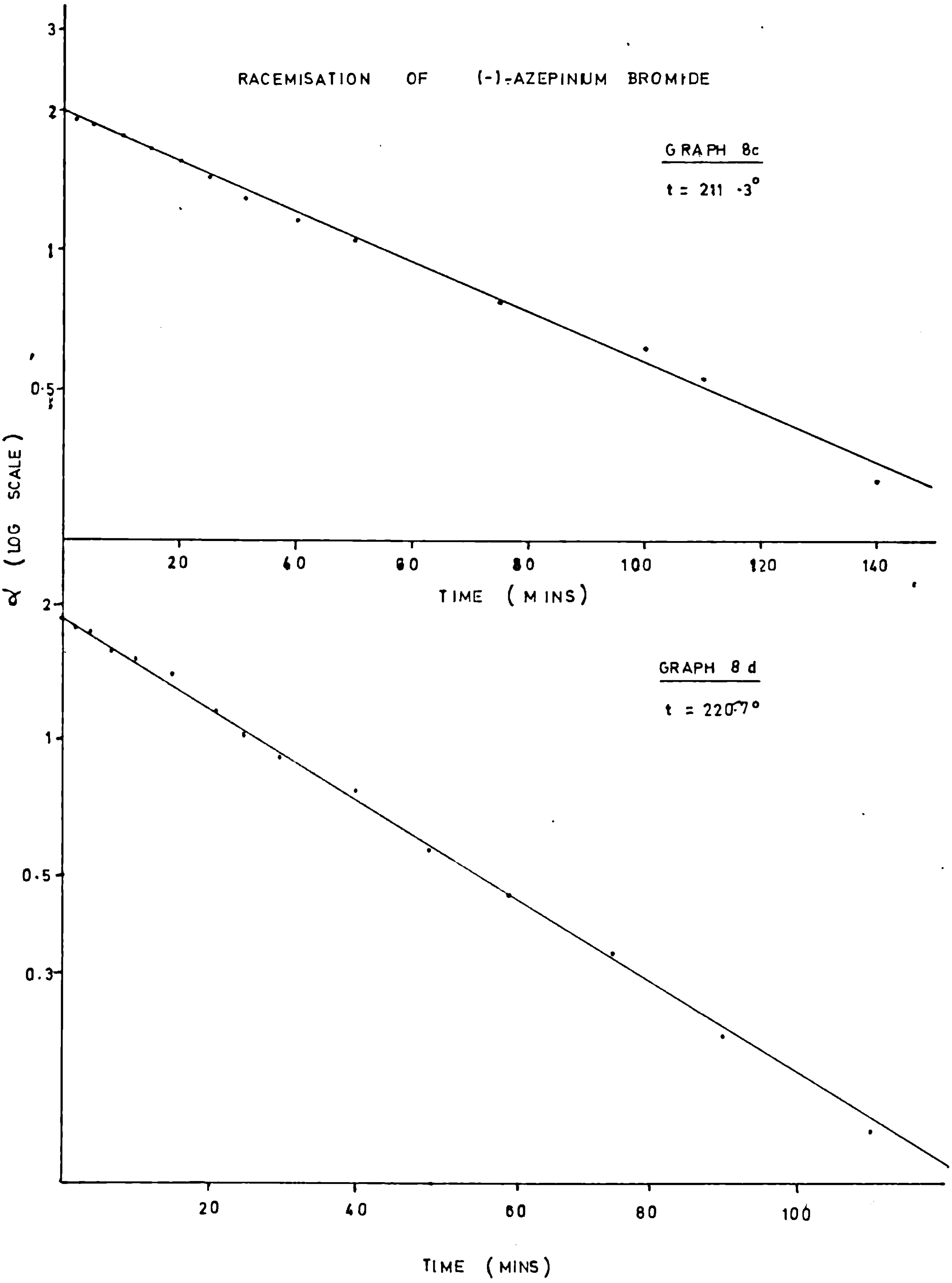
log. $k = -3.1129$ $10^3/_T = 1.991$

RACEMISATION OF (-)-AZEPINIUM BROMIDE

GRAPH 8e

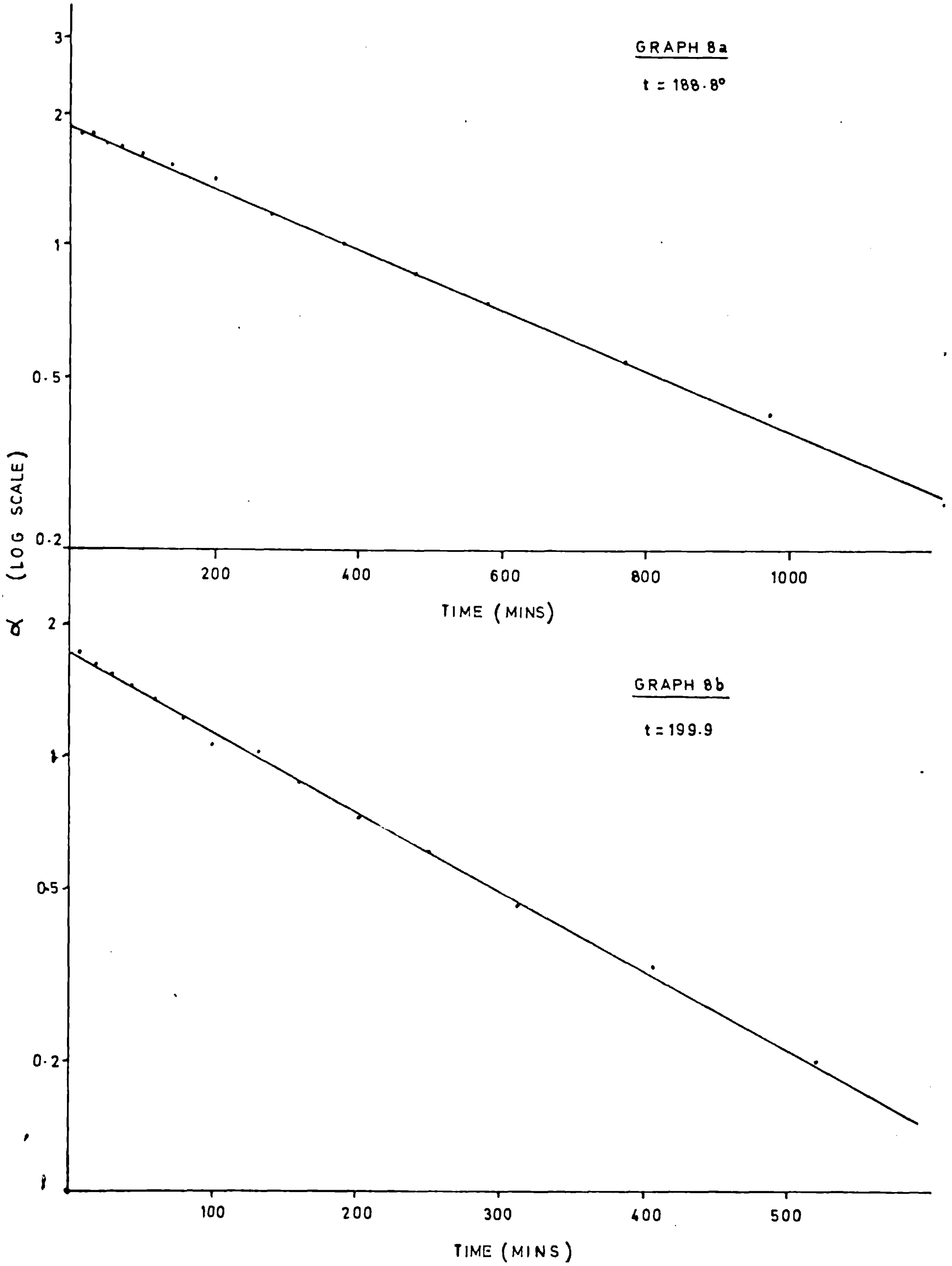
t = 229.1°



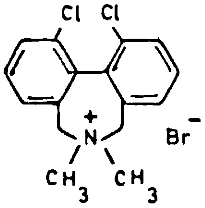


RACEMISATION OF (-)-AZEPINIUM BROMIDE

RACEMISATION OF (-)-AZEPINIUM BROMIDE



RACEMISATION OF (-)-R-



IN 2-PHENYLETHANOL

Table 21 graph 9

$\log_{10}k$ vs. $10^3/T$

T (K°)	$10^3/T$	k $sec.^{-1}$	log k	log A ($sec.^{-1}$)	$\Delta S^\dagger$ e.u.
462.0	2.165	2.690×10^{-5}	-4.5702	13.53	+0.37
473.1	2.114	7.009×10^{-5}	-4.1543	13.52	+0.33
484.5	2.064	1.915×10^{-4}	-3.7175	13.54	+0.47
4 939	2.024	3.925×10^{-4}	-3.4061	13.54	+0.43
502.3	1.991	7.711×10^{-4}	-3.1129	13.53	+0.53
MEAN VALUES				13.5	+0.4

The straight line plot of $\log_{10}k$ against $10^3/T$ is shown in graph 9 . Using the method of least mean squares, the value of E was calculated to be 38.3 ± 0.2 Kcal./mole. From this, the value of A was found to be $10^{13.5}$ and that of S + 0.4 e.u.

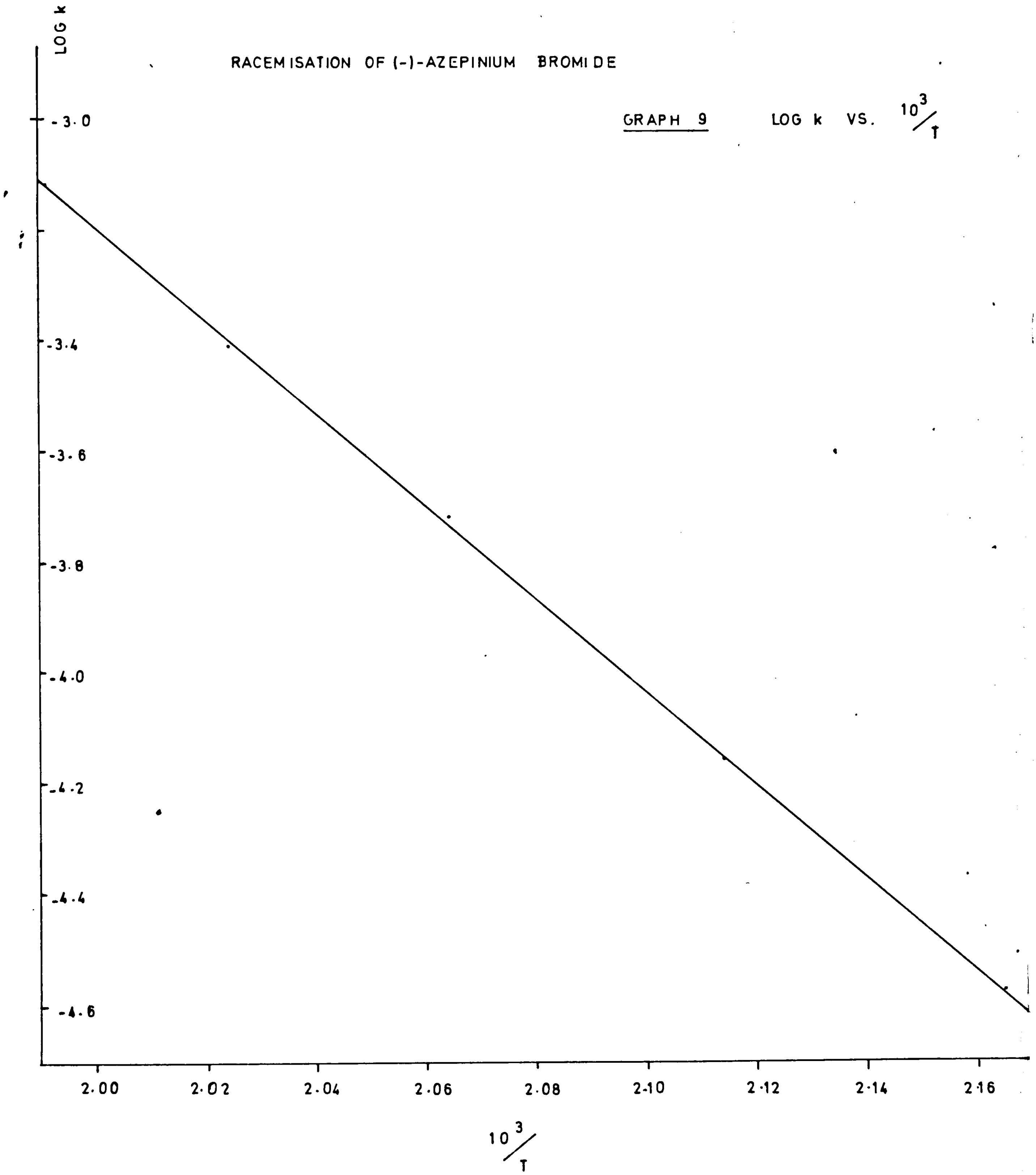
Values of A were calculated from the equation

$$\log_{10}A = \log_{10}k + E/4.576.\ 1/T$$

and values of $\Delta S^\dagger$ from

$$\Delta S^\dagger = 4.576 \log._{10}k_{rac}/T + E/T - 49.20$$

Graphically, E is found to be 38.3 Kcal./mol.



RACEMISATION OF (-)-AZEPINIUM BROMIDE

GRAPH 9 LOG k VS. $10^3/T$

REFERENCES

1. J. Dhar, *Indian H. Physics*, 1932, *7*, 43
2. J. Trotter, *Acta Cryst.*, 1961, *14*, 1135
3. G. B. Robertson, *Nature*, 1961, *191*, 593
4. A. Hargreaves & J. H. Rizvi, *Acta Cryst*, 1962, *15*, 365
5. I. L. Karle & L. O. Brockway, *J.Amer.Chem.Soc.*, 1944, *66*, 1974
6. O. Bastiensen, *Acta. Chem. Scand.*, 1949, *3*, 408
7. E. Merkel & C. Wiegand, *Z. Naturforsch*, 1948 *3b* 93;*Chem.Abs.43*,942e
8. K. E. Howlett, *J.*, 1960, 1055
9. E. A. Braude & E. S. Waight, "Progress in Stereochemistry", Ed. W. Klyne, 1954, chapt. 4, p. 139
10. G. Forrest Woods, A. Lee van Artsdale & F. T. Reed, *J. Amer. Chem. Soc.*, 1950, *72*, 3221
11. G. H. Beaven & D. M. Hall, *J.*, 1956, 4637
12. R. S. Mulliken, *J. Chem. Phys.*, 1939, *7*, 364
13. P. M. Everitt, D. M. Hall & E. E. Turner, *J.*, 1956, 2286
14. W. Pickett, G. F. Walter & H. France, *J. Amer. Chem. Soc.*, 1936, *58*, 2296
15. J. Dale, *Acta. Chem. Scand.*, 1957, *11*, 650
16. B. Williamson & W. H. Rodebush, *J. Amer. Chem. Soc.*, 1941, *63*, 3018
17. R. B. Sandin, R. Melby, A. S. Hay, R. N. Jones, E. C. Miller, & J. A. Miller, *J. Amer. Chem. Soc.*, 1952, *74*, 5073
18. D. M. Hall & F. Minhaj, *J.*, 1957, 4584

19. G. H. Beaven & E. A. Johnson, "Proc. of the Conference on Molecular Spectroscopy", Ed. E. Thornton & H. W. Thompson Pergamon Press, London, 1959, p780

20. E. A. Braude, F. Sondheimer & W. F. Forbes, *Nature*, 1954, *173*, 117

21. M. T. O'Shaughnessy & W. H. Rodebush, *J. Amer. Chem. Soc.* 1940, *62*. 2906

22. G. H. Beaven, D. M. Hall, M. S. Lesslie & E. E. Turner, *J.*,1952,854

23. K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon & G. H. Wahl Jr., *J. Amer. Chem. Soc.*, 1964, *86*, 1710

24. D. M. Hall & T. M. Poole, *J.*, 1963, 268

25. G. H. Beaven, & E. A. Johnson, *J.*, 1957, 651

26. K. Mislow, M. A. W. Glass, R. E. O'Brien, P. Rutkin, D. H. Steinberg, J. Weiss & C. Djerassi, *J.Amer.Chem.Soc.*, 1962, *84*, 1455

26a. G. Wittig & H. Zimmermann, *Chem*, *Ber.* 1953,*86*, 629

27. S. R. Ahmed & D. M. Hall, *J.*, 1960, 4165

28. G. H. Beaven, G. R. Bird, D. M. Hall, E. A. Johnson, J. E. Ladbury, M. S. Lesslie & E. E. Turner, *J.*, 1955, 2708

28a. A. C. Cope & R. D. Smith, *J. Amer. Chem. Soc.*, 1956, *78*, 1012

29. G. M. Badger & B. J. Christie, *J.*, 1956, 3438

30. E. Clar, "Aromatische Kohlenwasserstoffe", Julius Springer, Berlin, 1953, 2nd edition

31. J. R. Platt, *J. Chem. Phys.*, 1949, *17*, 484

32. M. S. Newman & A. S. Hussey, *J. Amer. Chem. Soc.*,1947, *69*, 3023

33. M. E. Heilbronner, H. U. Däniker, & P. A. Plattman, *Helv. Chim. Acta.*, 1949, *32*, 1724

34. P. M. G. Bavin & M. J. S. Dewar, *J.*, 1955, 4486

35. J. N. Murrell, "The Electronic Spectra of Organic Molecules" Methuen & Co., Ltd., London 1963, p.240

36. R. S. Cahn, C. K. Ingold & V. Prelog, *Experientia*, 1956, *12*, 81

37. M. Oki, H. Iwamura & N. Hayakawa, *Bull. Chem. Soc. Japan.*, 1964, *37*, 1865

38. D. M. Hall & M. M. Harris, *J.*, 1960, 490

39. M. M. Harris in "Progress in Stereochemistry" Vol. *II* , Ed. W. Klyne & P. B. D. de la Mare, Academic Press, Inc. New York, 1958, p. 174 calc.from published data by W.L.F. Armarego E. E. Turner, *J.*, 1956, 1665

40. D. M. Hall & T. M. Poole, *J.*, (B) 1966, 1034

41. R. Adams & H. C. Yuan, *Chem. Revs.*, 1933, *12*, 261

42. E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill,1962

43. J. W. Brooks, M. M. Harris & K. Howlett, *J.*, 1957, 1934

44. H. Eyring, *J. Chem. Phys.*, 1935, 3, 107; *Chem. Rev.*,1935, *17*, 65

45. S. Glasstone, K. J. Laidler & H. Eyring, "The Theory of Rate Processes", McGraw-Hill, New York, 1946

46. M. M. Harris & A. Mellor, *Chem. & Ind.*, 1959, 949

47. S. Ahmed & D. M. Hall, *J.*, 1958, 3043

48. L. V. Dvorken, R. B. Smyth & K. Mislow, *J. Amer. Chem. Soc.*, 1958, *80*, 486

49. S. M. Hall & J. M. Insole, *J.*, 1964, 2326

50. R. Kuhn & O. Albrecht, *Annalen*, 1927, *455*, 272

51. D. M. Hall & E. E. Turner, *J.*, 1955, 1242

52. D. M. Hall, *J.*, 1956, 3674

53. K. Mislow & M. A. W. Glass, *J. Amer. Chem. Soc.*, 1961, *83*, 2780

54. R. J. Kurland, M. B. Rubin & W. B. Wise, *J. Chem. Phys.* 1964, *40*, 2426

55. K. Mislow, D. D. Fitts & M. Siegel, *J. Amer. Chem. Soc.* 1958, *80*, 480

56. A. C. Cope, & E. R. Trumball "Organic Reactions", Ed. A. C. Cope,
J. Wiley, New York, 1960, Vol. XI, p.317

57. A. W. Hofmann, *Annalen* 1851, *78*, 253; *79*, 11

58. W. Hanhart & C. K. Ingold, *J.*, 1927, 997

59. T. S. Stevens, *J.*, 1930, 2107

60. T. M. Poole, Ph.D. Thesis

61. G. H. Christie, C. W. James & J. Kenner, *J.*, 1923, *83*, 1948

62. L. F. Fieser & J. Cason, *J. Amer. Chem. Soc.* 1939, *61*, 1740

63. H. J. Long & F. B. Dains, *Kansas Univ. Science Bull*, 1930, *9*, 208
Chem. Abs. 1932, *26*, 427

64. P. E. Fanta, *Chem. Revs* 1946, *38*, 139

65. E. Bamberger *Annalen*, 1921, *424*, ~~300~~ 291

66. E. Bamberger *Annalen*, 1925, *443*, ~~205~~ 192

67. B. R. Baker, R. E. Schaub, J. P. Joseph, F. J. McEvoy & J. H. Williams,
J. Org. Chem. 1952, *17*, 141

68. H. Hüber & G. Weiss, *Ber.* 1873, *6*, 175

69. N. S. Dokunikhin, Org. Poluprod i Krasiteli,, Nauch-Issledovatel Inst. Org. Poluprod i Krasitelei im K. E. Voroshilova, Sbornik Stateĭ 1959, 1, 148. Chem. Abs. 1961,55,21,140

70. G. Wittig & H. Petri, Annalen, 1933, 505, 17

71. E. R. Atkinson, H. J. Lawler, J. C. Heath, E. H. Kimball & E. R. Read, J. Amer. Chem. Soc., 1941, 63, 730

72. K. Mislow & M. Siegel, J. Amer. Chem. Soc., 1958, 80, 473

73. K. Mislow, F. A. McGinn, A. K. Lazarus, M. Siegel & J. E. Ricci, J. Amer. Chem. Soc., 1958, 80, 476

74. D. M. Hall & E. E. Turner, J., 1951, 3072

75. K. Mislow & H. B. Hopps. J. Amer. Chem. Soc. 1962, 84, 3018

76. E. D. Bergmann & Z. Pelchowicz, J. Amer. Chem. Soc. 1953,75, 2663

77. K. Mislow & H. Joshua, J. Amer. Chem. Soc., 1965, 89, 666

78. J. J. Fox & A. E. Martin, Proc. Roy. Soc, 1940, A175, 208, 234

79. H. A. Friedman, Spectrochim.Acta 1966, 22, 1465

80. H. M. Randall, R. G. Fowler, N. Fuson, J. R. Dangl "Infrared Determination of Organic Structures", von Nostrand, New York, 1949

81. M. St. C. Flett, J., 1951, 962

82. W. F. Baiker, P. von R. Schleyer & K. Mislow, J. Amer. Chem. Soc. 1965, 87, 3168

83. G. B. B. M. Sutherland, Disc. Farad.Soc. 1950, 9, 274

84. G. V. ~~Yuktineveck~~, Russian Chem.Revs., 1963, 619
Yukhnevich

85. D. E. C. Corbridge, & E. J. Lowe, *J.*, 1954, 493

86. D. M. Hall & B. Irakobsantisukh, *J.*, 1965, 6311

87. F. S. Mortimer, R. B. Blodgett & F. Daniels, *J. Amer. Chem. Soc.* 1947, *69*, 822

88. G. H. Beaven & E. A. Johnson, *Spectrochim. Acta*, 1959, *14*, 67

89. K. R. Buck & C. E. B. Connor, *Spectrochim. Acta*, 1964, *20*, 102

90. K. R. Buck & C. E. B. Connor, *Spectrochim. Acta*, 1959, *14*, 67

91. D. M. Hall, M. S. Lesslie & E. E. Turner, *J.*, 1950, 711

92. W. E. Truce & D. D. Emrick, *J. Amer. Chem. Soc.* 1956, *78*, 6130

93. E. Bunnenberg, C. Djerassi, K. Mislow & A. Moscowitz, *J. Amer. Chem. Soc.*, 1962, *84*, 2823
P. Crabbé, "O.R.D. & C.D. in Organic Chemistry", Holden-Day, San Fransisco, 1965, p.183 & 184

94. A. Angeletti, *Atti Accad. Sci. Torino, Classe Sci. fis. mat. nat.*, 1937, *72*, I, 373
Chem. Abs. 1940, *34*, 406

95. P. W. Sadler & R. L. Warren, *J. Amer. Chem. Soc.* 1956, *78*, 1251

96. T. Crauw, *Rec. Trav. Chim.* 1931, *50*, ~~777~~ 753

97. G. H. W. Cheeseman & R. C. Poller, *Analyst*, 1961, *86*, 256

98. K. Hori, Y. Abe, Y. Yamakawa & H. Fujimura, *Gifu Yakka Daigakŭ Kiyô*, 1958, *8*, 65. *Chem. Abs.* 1959, *53*, 10, 148