The Circular Dichroism of (−)-*S*-*trans*-1,2-di-4-pyridyloxiran

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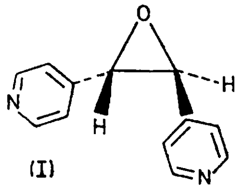
The absorption and c.d. spectra of (−)-*S*-*trans*-1,2-di-4-pyridyloxiran has been analysed by means of the coupled oscillator model. If the directions of pyridine electric dipole transition moments given by MO theory are used, satisfactory agreement is found between calculated and experimental dipole and rotatory strengths.

In previous work,[1] exciton analysis of the circular dichroism and absorption spectra of (+)-*trans*-stilbene oxide (II) gave the correct answer for the absolute configuration, which was already known to be *R* from chemical evidence.[2] The circular dichroism was shown to derive principally from coupling by coulombic interactions between the excitation moments of the two alkylphenyl chromophores.

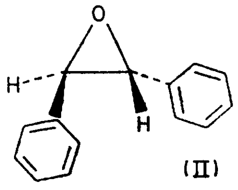
The agreement between the absolute configuration obtained from the chemical and the exciton treatment, and the satisfactory interpretation of the spectra, further confirmed the validity of the method and the direction of benzene electric dipole transition moments, already extensively studied theoretically and experimentally.

If the absolute configuration and the conformation of a simple system containing coupled chromophores are known, information about the directions of the transition moments of the chromophores is gained by an exciton analysis of the c.d. and u.v. spectra. This specific example is only a particular case of the general scheme recently given by Wagniere and Hug for chromophores having C_2 symmetry.[3]

In connection with an investigation on the optical activity of the pyridine chromophore,[4] we decided to apply this method to (—)-*S*-*trans*-1,2-di-4-pyridyloxiran (I) in order to obtain experimental information about the directions of pyridine transition moments which have only been deduced theoretically.[5]



(I)



(II)

trans-1,2-Di-4-pyridyloxiran (I) was synthesised following the general method of ref. 6. Resolution into enantiomers was performed by crystallisation of the mono-(—)-dibenzoyl tartrate from acetone. The absolute configuration of the (—)-isomer was shown to be *S* by correlation with (+)-*R*-*trans*-stilbene oxide by means of the quasi-racemate method (see Experimental section).

The absorption and c.d. spectra of (—)-*S*-(I) in cyclohexane and 10% aqueous sulphuric acid are shown in Figure 1.

The spectrum of pyridine both in the vapour phase and in solution has been extensively investigated[5] and the following singlet transitions have been identified

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[1] G. Gottarelli, S. F. Mason, and G. Torre, *J. Chem. Soc.* (*B*), 1970, 2349.

[2] G. Berti, F. Bottari, and B. Macchia, *Farmaco* (*Pavia*) *Ed. Sci.*, 1960, **15**, 377.

[3] G. Wagniere and W. Hug, *Tetrahedron Letters*, 1970, 4765.

[4] G. Gottarelli and B. Samorì', (*a*) *Tetrahedron Letters*, 1970, 2055; (*b*) unpublished results.

[5] K. K. Innes, J. P. Byrne, and I. G. Ross, *J. Mol. Spectroscopy*, 1967, **22**, 125.

[6] V. Mark, (*a*) *J. Amer. Chem. Soc.*, 1963, **85**, 1884; (*b*) *Org. Synth.*, 1966, **46**, 32.

in the region between 55,000 and 36,000 cm^{-1}; $\pi b' \leftarrow n$ $({}^1B_1 \leftarrow {}^1A_1)$ at 34,770 cm^{-1}; $\pi b' \leftarrow \pi a$ $({}^1B_2 \leftarrow {}^1A_1)$ at *ca.* 38,350 cm^{-1}; $\pi a' \leftarrow \pi a$ $({}^1A_1 \leftarrow {}^1A_1)$ at *ca.* 49,750 cm^{-1}; $\pi a' \leftarrow \pi b$, $\pi b' \leftarrow \pi b$ $({}^1B_2 \leftarrow {}^1A_1, {}^1A_1 \leftarrow {}^1A_1)$ at *ca.* 55,000 cm^{-1} (Figure 2).

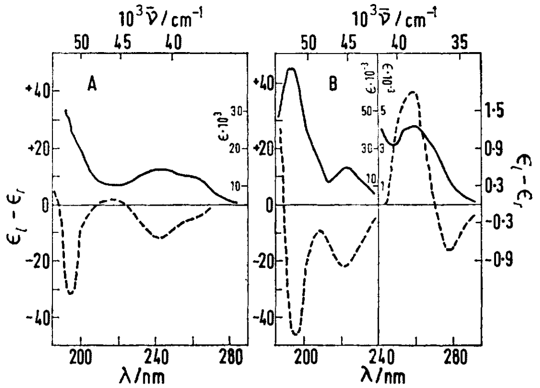

FIGURE 1 Absorption (——) and c.d. (– – – –) spectra of (I) in A, 10% sulphuric acid; B, cyclohexane

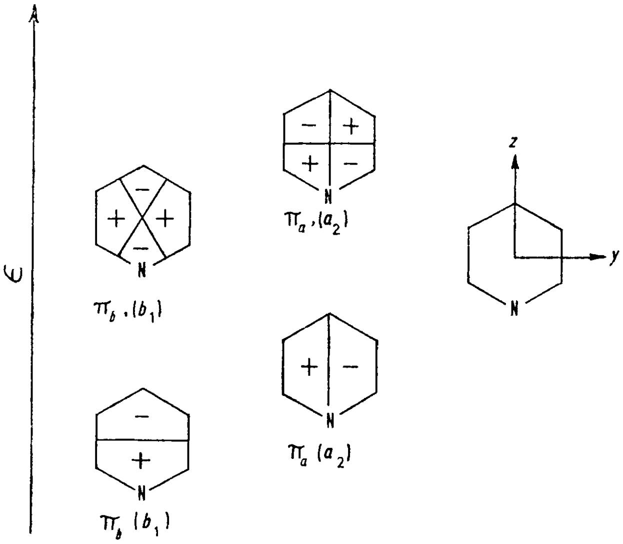

FIGURE 2 Notation for π molecular orbitals of pyridine

The isotropic absorption spectrum of compound (I) closely resembles that expected for two alkylpyridine chromophores, although the epoxide ring seems to exert a small conjugative effect, enhanced in acid solution as for 4-cyclopropylpyridines.[7] It consists of two moderate and one high intensity band at 38,500, 44,800, and 51,800 cm^{-1}, respectively. These bands are reasonably related to the first four singlet transitions of pyridine and in particular the absorption at *ca.* 38,500 is likely to correspond to both the $\pi b' \leftarrow n$ and $\pi b' \leftarrow \pi a$ transitions; the absorptions at 44,800 and 51,800 cm^{-1} may be ascribed to the $\pi a' \leftarrow \pi a$ and $\pi b' \leftarrow \pi b$ transitions respectively.

By assuming that the absorption of compound (I) between 55,500 and 49,800 cm^{-1} is caused only by a long-axis polarised transition, calculated rotational and oscillator strengths are obtained in reasonably good agreement with the experimental ones.

On the other hand the degenerate components of the benzene β transition should lie at different frequencies in pyridine and even more so in alkylpyridines and the $\pi b' \leftarrow \pi b$ transition is calculated to be at lower energy.[5] In *trans*-1,2-di-4-pyridyloxiran the *z*-axes of the individual pyridine chromophores have a fixed mutual stereochemistry whereas the *y*- and *x*-axes are not in a fixed position owing to the rotation of each pyridine group about the exocyclic carbon–carbon bond.

Consequently we expected the c.d. spectra corresponding to the long-axis polarised transitions to show the characteristic exciton pattern, whereas the transitions polarised along the *x*- and *y*-directions should give Cotton effects analogous to the one observed for simpler asymmetric pyridines.[4a,b] These expectations were met; we observed in fact (i) a negative and a positive low intensity band at 36,100 and 38,900 cm^{-1} respectively. These bands occurred in the absorption region of the $\pi b' \leftarrow n$ and $\pi b' \leftarrow \pi a$ transitions. They were weak and were dramatically modified in acid solution where the $\pi b' \leftarrow n$ transition disappears. Protonation of the nitrogen also increased the overall dipole strength at *ca.* 36,000 cm^{-1}. Consequently, if the two bands were caused by exciton coupling, a couplet should still be observed. Instead, these bands can be explained as being caused by the mixing of $\pi b' \leftarrow n$ and $\pi b' \leftarrow \pi a$ pyridine transitions under the static potential of the rest of the molecule.[4] (ii) A strong negative band was observed at *ca.* 44,800 cm^{-1} which corresponded to the $\pi a' \leftarrow \pi a$ pyridine transition. The positive high energy part of the couplet was undetectable as it is completely cancelled under the very intense negative band at higher frequency.

This view is supported by the changes in the spectra observed in acid solution (Figure 1A). Here the $\pi a' \leftarrow \pi a$ transition is shifted to the red by *ca.* 20 nm, while the $\pi b' \leftarrow \pi b$ is not. The overlap is less severe and the positive part of the couplet becomes detectable. The spectrum in Figure 1A is very similar (mirror image) to the one of (+)-*trans*-stilbene oxide (II),[1] where the high energy part of the couplet is detectable, but still very small. On the other hand this higher energy c.d. band is also theoretically expected to be weaker than the lower energy one. (iii) A very high intensity couplet which corresponded to the pyridine $\pi b' \leftarrow \pi b$ transition was observed at *ca.* 51,800 cm^{-1}.

Bands (ii) and (iii), as was expected, seem to derive principally from exciton coupling between the long-axis polarised transitions of the two alkylpyridine chromophores. For the known *S* absolute configuration we expected a negative low energy (*B* symmetry) and a positive high energy (*A* symmetry) c.d. band for each of the two transitions. However, as pyridine possesses at least two bands which in the epoxide (I) give rise to exciton coupling, the c.d. is expected to be non-conservative and each electronic transition should have a finite

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[7] A. P. Gray and H. Kraus, *J. Org. Chem.*, 1966, **21**, 399.

rotational strength ($R^A + R^B \neq 0$), the sum of rotational strengths over both transitions still being zero.

The dipole strength of (I) is also expected to differ from twice the value of pyridine and there should be exchange of intensity between the two bands.[1,8,9] The co-ordinate system for (I) was chosen as shown in ref. 1. From Dreiding models the distance R_{21}, taken between the centres of the two pyridine rings, is *ca.* 6·6 Å and the direction-cosines of the transition moments which are long-axis polarised are found to be 0·960, 0·190, and 0·190 for cos x, cos y, and cos z respectively. The transition dipole moment $\mu bb'$ of the high-energy band was taken from the vapour spectrum of pyridine.[10]

Tentatively, only one-half of the dipole strength was used, as both $\pi a' \longleftarrow \pi b$ and $\pi b' \longleftarrow \pi b$ transitions contribute to the absorption, but only the latter contributes to the optical activity and to the intensity transfer of the dimer, and the oscillator strength given in ref. 8 is measured in the interval between 54,000 and 64,000 cm^{-1} where pyridine gives a broad continuous spectrum, almost certainly caused by both the above mentioned transitions.

The dipole moment of the $\pi a' \longleftarrow \pi a$ transition was taken from the spectrum of pyridine in cyclohexane solution; this value after correction for the solvent effect [11] is practically identical with that which was reported in ref. 10, and does not differ notably from that of 4-pyridylmethanol.

After correction of the zero-order excited state wave functions of the dimer by mixing the other excited function having the same symmetry,[1] the rotational strength for the $\pi a' \longleftarrow \pi a$ transition, omitting the very small normalisation factor, is given by equation (1)

$$R_{aa'}{}^{A,B} = \frac{\pi\nu}{2} R_{21} \cdot \mu_{2aa'} x \mu_{1aa'} + \frac{V(\nu_{aa'} + \nu_{bb'})}{h(\nu_{aa'} - \nu_{bb'})} R_{21} \cdot \mu_{2aa'} x \mu_{1bb'} \qquad (1)$$

where V represents the coulombic interaction between the transition-charge-distribution of the excitation $\phi_{1a'} \longleftarrow \phi_{1a}$ and $\phi_{2b'} \longleftarrow \phi_{2b}$ in the individual chromophores and is given by equation (2). This interaction

$$V = \left\langle \phi_{1a'}\, \phi_{1a} \left| \frac{e^2}{r_{1i,2j}} \right| \phi_{2b}\, \phi_{2b'} \right\rangle \qquad (2)$$

energy was calculated using point dipole approximation (3). The dipole strength of the dimer is given, with the

$$V = \mu_1 \cdot \mu_2 / R^3 - 3\,(\mu_1 \cdot R)(\mu_2 \cdot R)/R^5 \qquad (3)$$

same approximations used for equation (2), by equation (4).

$$D_{aa'} = D^A + D^B = 2\mu^2{}_{aa'} + \frac{4|V|\mu_{1aa'} \cdot \mu_{2bb'}}{h\,(\nu_{bb'} - \nu_{aa'})} \qquad (4)$$

Taking into account molecular states in which both groups are excited [8] does not consistently improve the calculated values.

The results obtained are summarised in the Table. After inclusion of configuration interaction both (A and B) transitions contributing to $\pi a' \longleftarrow \pi a$ band system are shifted to lower frequency by $V^2/(E_{bb'} - E_{aa'}) =$ 15 cm^{-1}, and both the corresponding transitions of the $\pi b' \longleftarrow \pi b$ band system are shifted to higher frequency by a similar interval. The dominant contribution to the frequency separation between the first-order corrected transition of the dimer (A and B) derived from both $\pi a' \longleftarrow \pi a$ and $\pi b' \longleftarrow \pi b$ excitation is still the zero-order exciton splitting.

Theoretical and experimental dipole strength D (10^{-36} c.g.s.u.) and rotational strength R (10^{-40} c.g.s.u.) of (−)-(I)

Band system	Exciton component	Theoretical R	Theoretical D	Experimental R	Experimental D
$\pi_{a'} \longleftarrow \pi_a$	B	−23	11	−40	12
	A	+8		0	
$\pi_{b'} \longleftarrow \pi_b$	B	−83	45	−44	49
	A	+98		>0	

Therefore the conclusions of degenerate exciton theory are not changed qualitatively by inclusion of configuration interactions.

The agreement between theoretical and experimental rotational strengths is qualitatively satisfactory; however, the uncertainty about the experimental values, due to the overlap and mutual cancellation of neighbouring bands of opposite signs, makes quantitative comparison difficult. For the B exciton band of the $\pi a' \longleftarrow \pi a$ system, which is the less affected by cancellation, the exciton theory in the rough point dipole approximation gives only 60% of the observed optical activity.

The calculated dipole strengths seem to be in better agreement with the experimental ones, and this could show that the tentative assumptions made about the intensity of the pyridine and epoxide transitions, in the high energy region of the spectrum, were not too unrealistic.

In conclusion, if the directions of pyridine electric transition dipole moments given by molecular orbital theory are used, the absorption and c.d. spectra of (−)-*S*-(I) can be quite satisfactorily interpreted in terms of exciton theory and this gives experimental support to the correctness of polarisations deduced from theory.

EXPERIMENTAL

M.p.s are uncorrected. Absorption and c.d. spectra were measured with a Unicam SP 700 or a Cary 14 spectrophotometer and with a Jouan C.D. II dichrograph respectively, with path lengths of 0·1—10 mm. Optical rotations were measured using a Bendix automatic polarimeter.

trans-1,2-*Di*-4-*pyridyloxiran* (I).—This was obtained following the general method of Mark.[7a,b] The precipitate obtained from the reaction was filtered off, washed with a little benzene, and crystallised from acetone. Pyridine-4-

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[8] I. Tinoco, jun., *Adv. Chem. Phys.*, 1962, **4**, 113.

[9] W. C. Johnson, jun., and I. Tinoco, jun., *Biopolymers*, 1969, **8**, 715.

[10] L. W. Pickett, M. E. Corning, G. M. Wieder, D. A. Semenow, and J. M. Buckley, *J. Amer. Chem. Soc.*, 1953, **75**, 1618.

[11] (*a*) N. Q. Chako, *J. Chem. Phys.*, 1934, **2**, 644; (*b*) A. Mangini, A. Trombetti, and C. Zauli, *J. Chem. Soc.* (*B*), 1967, 153.

carbaldehyde (10 g) gave g.l.c.-pure *trans*-epoxide (3·7 g), m.p. 166—167° (decomp.), M^+ 198 (Found: C, 72·65; H, 5·15; N, 14·1. Calc. for $C_{12}H_{10}N_2O$: C, 72·7; H, 5·1; N, 14·15%).

Resolution of Compound (I).—Compound (I) (2·1 g) was dissolved in the minimum amount of warm acetone, added to a solution of (−)-dibenzoyltartaric acid (3·97 g) in warm acetone, and set aside overnight. The precipitate obtained was composed of two macroscopically different types of crystals which were mechanically separated. One fraction gave, after recrystallisation from acetone, shiny leaflets (2·05 g), m.p. 139—141° (Found: C, 64·7; H, 4·3; N, 5·0. Calc. for $C_{30}H_{21}N_2O_9$: C, 64·75; H, 4·35; N, 5·05%). The other fraction, after recrystallisation from acetone, gave needles (1·9 g), m.p. 145—146° (Found: C, 64·65; H, 4·35; N, 5·0%).

After basification with 20% aqueous sodium hydroxide, extraction with chloroform, and crystallisation from cyclohexane the first fraction gave epoxide (0·9 g), m.p. 98—100°, $[\alpha]_D$ −226·2° (*c* 0·5, H_2O). The fraction with m.p. 145—146° gave, by the same procedure, epoxide (0·9 g), m.p 99—100°, $[\alpha]_D$ +228° (*c* 0·5, H_2O).

Synthesis of (+)trans-*Stilbene Oxide* (II).—This was obtained from (−)-(1*R*,2*S*)-*erythro*-2-amino-1,2-diphenylethanol,[12] $[\alpha]_D$ −16° (*c* 0·6, EtOH), using the method of Read and Campbell.[13] The epoxide had $[\alpha]_D$ +350° (*c* 0·5, C_6H_6), m.p. 68—69° (lit.,[13] 68—69°).

Absolute Configuration of Compound (I).—The quasi-racemate method was employed to obtain the absolute configuration. The reference compound was (+)-*R*-*trans*-stilbene oxide (II). The mixtures were prepared from different amounts of the solutions of (I) and (II) in chloroform, evaporation of the solvent, and homogenisation. The m.p. diagram is shown in Figure 3. Both diastereo-systems form solid compounds. It is known that in similar examples the 'compound' containing the components in opposite configurations has the higher melting point.[14] The (−)-isomer of (I) has therefore the *S* absolute configuration.

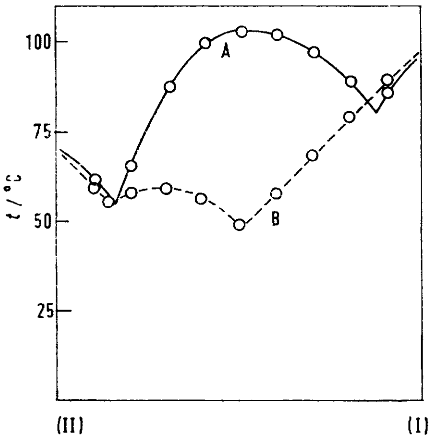

FIGURE 3 M.p. diagram for diastereo-systems (I) and (II) A, M.p. curve for mixtures of (−)-(I) and (+)-(II); B, for (+)-(I) and (+)-(II)

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