Linear Dichroism of Organic Molecules in Electrically Oriented Liquid Crystal Matrices

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A general treatment of the orientation of organic molecules in liquid crystal matrices is given in terms of molecular shape models. Applications of the theory to polarisation measurements of a number of organic molecules in the visible and near u.v. region are reported. The usefulness and limitations of the technique are discussed.

THE assignments and energies of the out-of-plane polarised transitions of a large number of organic molecules are still in question. The linear dichroism spectra of molecules dissolved in an electrically aligned nematic liquid crystal[1] can be particularly useful in detecting and assigning this type of transition. Using this technique we have recently assigned the lowest energy transitions of pyridine 1-oxide as in-plane polarised[2] and have shown that all the transitions in the visible–near i.r. region of some manganese(III) porphyrins and their free bases are polarized in the molecular plane.[3]

The stability and reproducibility of the liquid crystal solvent alignment have been improved by replacing the d.c. electric field previously used by a sinusoidal a.c. one of 1 200 Hz. The theory required to interpret the linear dichroism spectra obtained by this method is developed in terms of a simple model and is applied to a number of aza-aromatic compounds.

EXPERIMENTAL

The compounds studied were dissolved in a compensated nematic mixture[1] of cholesteryl chloride and cholesteryl laurate (1.85 : 1.0 w/w; $T_{\text{nem.}}$ 30 °C). The components of this mixture were purified by column chromatography (silica gel 60, Merck; n-hexane as eluant). The d.c. electric field which was used to orient this mixture in our prevous work[2,3] was replaced by an a.c. one (1 200 Hz) which could be varied up to 16 kV. This resulted in much greater stability and reproducibility[4] and will also allow charged species to be oriented without accompanying electrolysis. Cells were constructed by sandwiching the electrodes (supported in a Teflon frame) between silica plates; the thickness of the electrodes defines the optical path-length of the sample (between 0.05 and 0.5 mm) and their distance apart varied between 0.1 and 0.5 cm. The temperature of the mixture was controlled by a nitrogen stream and was measured with a thermocouple.

The linear dichroism spectra (l.d.) were recorded using a Jouan II dichrograph modified by reducing the sensitivity in order to record (ΔOD/OD) of up to 10^{-1} and by incorporating an Oxley prism[5a,b] (achromatic $\lambda/4$ device) to convert the right and left circularly polarised light into plane polarised components, one parallel and one perpendicular to the optic axis of the sample. The optical density of the solution was at all times less than 1.0 and concentrations were kept as low as possible to avoid aggregation.

THEORY

The direction of the applied electric field defines a direction of orientation or optic axis (o.a.) of the nematic matrix and, provided the symmetry of the orientated molecule is at least C_{2v}, the average orientation with respect to this optic axis is given by the diagonal elements of the Saupe order matrix S_{ii}.[6]

If the light beam is propagated in the y direction (Figure 1) and polarized parallel ($\|$) and perpendicular ($\perp$) to the o.a. (z) and the transition moment μ^{i}_{oa} is oriented at the mean angle θ_i but is free to rotate about z, integration of the μ^{x}_{oa} and μ^{y}_{oa} components of μ^{i}_{oa} over all possible orientation

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[1] E. Sackmann and H. Möhwald, *J. Chem. Phys.*, 1973, **58**, 5407.

[2] R. D. Peacock and B. Samorì, *J.C.S. Faraday II*, 1975, 1909.

[3] R. Gale, R. D. Peacock, and B. Samorì, *Chem. Phys. Letters*, 1976, **37**, 430.

[4] H. Gruler and C. Meier, *Mol. Cryst. Liquid Cryst.*, 1972, **16**, 299; W. Helfrich, *ibid.*, 1973, **21**, 187.

[5] (*a*) A. E. Oxley, *Chem. News*, 1910, **102**, 189; (*b*) W. A. Kizel, Y. I. Krasilov, and V. N. Shamraev, *Optics and Spectroscopy*, 1964, **17**, 248.

[6] A. Saupe, *Mol. Cryst. Liquid Cryst.*, 1972, **16**, 87.

angles ϕ_i results in equation (1).[7] The elements of the order matrix, S_{ii}, may be obtained by a variety of spectroscopic techniques (n.m.r., e.s.r., i.r., and visible–u.v.). There is no difference in principle between S_{ii} determined by any of these methods except, of course, that they will

$$\frac{\Delta\varepsilon_i}{\bar{\varepsilon}} = \frac{3(\varepsilon_{\parallel} - \varepsilon_{\perp})}{(\varepsilon_{\parallel} + 2\varepsilon_{\perp})} = \tfrac{3}{2}(3\cos^2\theta_i - 1) = 3S_{ii} \qquad (1)$$

depend on the extent of orientation of the solvent. It can probably be assumed that in favourable cases we may be able to use the S_{ii} values obtained in one orientation matrix to interpret the l.d. spectra obtained in another.

Because of the approximations involved in this kind of extrapolation, however, an unambiguous determination of the polarisation of the transitions of interest is possible only if the symmetry of the molecule simplifies the problem. We will consider two limiting shape models, the disc and the rod, and then describe the intermediate case, the ellipsoid. The limiting cases have already been discussed [8, 9] and used to interpret the orientation of molecules aligned in stretched polymer films in terms of a ' degree of orientation function '.

(a) *Disc-shaped Molecules* (*Figure* 2a).—The matrix alignment allows free rotation of the solute about its x and z axes but not about y which could lead to the unstacking of the long liquid crystal molecules. This means that only the z axis may be perpendicular to the o.a. when maximum orientation has been achieved and thus $S_{zz}^{\max} = -1/2$. From the spacial degeneracy of the x and y axes $S_{xx} = S_{yy}$ and so from the diagonal sum rule [6] $S_{xx}^{\max} = S_{yy}^{\max} = 1/4$. Thus for a transition polarised in the molecular plane a positive l.d. will be obtained. In fact $\left(\frac{\Delta\varepsilon}{\bar{\varepsilon}}\right)^{\text{in plane}}_{\text{max.}} = 3/4$. For a transition polarised out of the molecular plane a negative l.d. will be obtained, *i.e.* $\left(\frac{\Delta\varepsilon}{\bar{\varepsilon}}\right)^{\text{out of plane}}_{\text{max.}} = -3/2$. Even when the molecules are only partially oriented by the liquid crystal solvent the signs of the l.d. will be the same as at maximum orientation and so in-plane and out-of-plane polarised transitions may be identified.

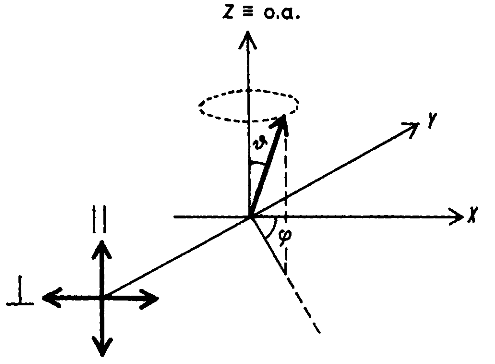

FIGURE 1

(b) *Rod-shaped Molecules* (*Figure* 2b).—In this case the long axis of the molecule (x) will align parallel to the o.a. of the matrix. Free rotation is possible only about the molecular x axis, thus $S_{xx}^{\max} = 1$. As before because of the spacial degeneracy of y and z $S_{yy}^{\max} = S_{zz}^{\max} = -1/2$. In this limiting case, we can distinguish between transitions polarised parallel to the long molecular axis on the one hand (positive l.d.) and the others (out-of-plane and in-plane short axis; negative l.d.) on the other.

(c) *Ellipsoidal Molecules* (*Figure* 2c).—This shape, that of the majority of relatively symmetric organic molecules, is intermediate between that of the disc and the rod. In particular there are no spacial degeneracies. It can easily be seen that $S_{xx} \geqslant 0$ and $S_{zz} \leqslant 0$ but S_{yy} may be positive, negative, or zero, depending on the relative dimensions of the molecule in the x, y, and z directions. In an attempt to measure the anisotropy of a molecule in the xy plane (z being taken as the smallest molecular dimension) the quantity $|S'_x| = \left|\frac{S_{yy} - S_{xx}}{3S_{zz}}\right|$ has been defined.[10] It has the value of 1 for the rod-shape and 0 for the disc. When $|S'_x| = 1/3$ we have the change-over point between disc-like and rod-like behaviour. The data in Table 1 are illustrative of the various cases. We may summarise as follows. (i) In all cases $S_{xx} \geqslant 0$, therefore long-axis in-plane polarised transitions must have positive l.d. (ii) In all cases $S_{zz} \leqslant 0$ therefore out-of-plane polarized transitions must have negative l.d. (iii) Short-axis in-plane polarised transitions may have positive or negative l.d. If nearer to the rod than to the disc shape they will have negative l.d. and *vice versa*. (iv) The function $|S'_x|$ is a reasonably good guide to molecular shape. If it is $>1/3$ we may regard the molecule as rod-shaped and if $<1/3$ as disc-shaped. (v) It is hoped that even if the values of S_{ii} cannot be transferred from system to system the value of $|S'_x|$ can be.

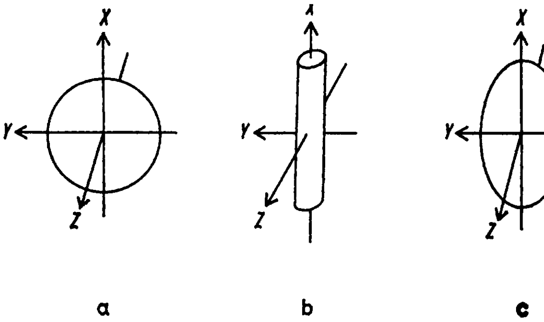

FIGURE 2

Mixed Polarisation.—So far we have not considered absorption bands which are of mixed polarisation either because of vibronically induced mixing of excited states or simply because of the overlapping of transitions, $(\Delta\varepsilon/\bar{\varepsilon})$ will no longer be constant throughout such a band. In fact equation (1) is not valid and should be replaced by the more general (1'). If an absorption band has contributions from

$$\left(\frac{\Delta\varepsilon}{\bar{\varepsilon}}\right) = 3\sum_i \varepsilon_i S_{ii} \Big/ \sum_i \varepsilon_i \qquad (1')$$

only two perpendicularly polarised transition then $\bar{\varepsilon} = 1/3 (\varepsilon_x + \varepsilon_z)$.

Knowledge of the S_{ii} values allows the separation of the two contributions [equation (2)].

$$\varepsilon_x = \frac{3\bar{\varepsilon}S_{zz} - \Delta\varepsilon}{S_{zz} - S_{xx}} \qquad \varepsilon_z = \frac{\Delta\varepsilon - 3\bar{\varepsilon}S_{xx}}{S_{zz} - S_{xx}} \qquad (2)$$

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[7] R. J. Dudley, S. F. Mason, and R. D. Peacock, *J.C.S. Faraday II*, 1975, 997.

[8] B. Nordén, *Chemica Scripta*, 1971, **1**, 145.

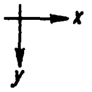
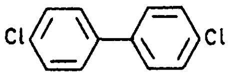
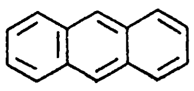
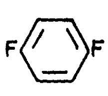
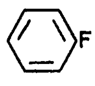
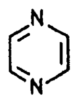
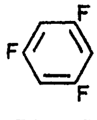
[9] A. Yogev, L. Margulies, B. Stransberger, and Y. Mazur, *J. Phys. Chem.*, 1974, **78**, 1400.

[10] K. G. Orrel and V. Sik, *J.C.S. Faraday II*, 1975, 1360.

RESULTS AND DISCUSSION

The Linear Dichroism Spectra of Some Aza-aromatic Molecules.—(a) *Pyrimidine, pyrazine, and pyridazine.* As a first example of the technique we will consider the l.d. spectra of the three diazabenzenes, pyrimidine, pyrazine, and pyridazine. The S_{ii} values of pyrimidine have been measured[11] by n.m.r. in a magnetically aligned nematic liquid crystal (Table 1) and clearly show that the molecule must, as expected, be classified as disc-like. This will apply to the other two isomers also since they have essentially the same shape, so we expect the l.d. of the $n \longrightarrow \pi^*$ out-of-plane polarized transitions[12] to be negative and that of the $\pi \longrightarrow \pi^*$ in-plane polarized transitions to be positive (the long and short axis polarisation will, of course, be indistinguishable). Figure 3 shows the l.d. and isotropic absorption spectra of the three molecules. The two types of polarisation are clearly differentiated in l.d., the $n \longrightarrow \pi^*$ lying to low energy of the $\pi \longrightarrow \pi^*$ in all cases. The S_{ii} values for all three molecules in our solvent are similar and those for pyrazine are given in Table 2. The orientation is somewhat greater than in the nematic liquid crystal n.m.r. experiment but the $|S'_x|$ values obtained are almost identical, which gives us confidence in using $|S'_x|$ as a criterion for molecular shape.

TABLE 1

	S_{xx}	S_{yy}	S_{zz}	Ref.	$\lvert S_x'\rvert$
$H_2C{=}CH_2$	0.053	−0.027	−0.027	*a*	1
	0.432	−0.197	−0.234	*b*	0.89
	0.33	−0.08	−0.25	*c*	0.54
	0.18	−0.03	−0.15	6	0.46
	0.122	0.006	−0.128	*d*	0.30
	0.056	0.041	−0.097	11	0.05
	0.08	0.08	−0.166	6	0

[a] P. Diehl, S. Sykora, and W. Wullschleger, *Mol. Phys.*, 1975, **29**, 305. [b] W. Nuderberg, P. Diehl, and L. Lunazzi, *Mol. Phys.*, 1973, **26**, 571. [c] S. F. Mason and R. D. Peacock, *Chem. Phys. Letters*, 1973, **21**, 406. [d] E. Halani and D. Canet, *Compt. rend.*, 1972, **275a**, 447.

(b) *The methylpyridines.* It is currently accepted[13] that the absorption spectra of the picolines between 300 and 230 nm is caused by two electronic transitions, an $n \longrightarrow \pi^*$ ($B_1 \longleftarrow A_1$) at lower and a $\pi \longrightarrow \pi^*$ ($B_2 \longleftarrow A_1$) at higher energy. In solution in hydrocarbon solvents the $n \longrightarrow \pi^*$ is hidden under the $\pi \longrightarrow \pi^*$ and the possibility that it has been blue-shifted to higher energy of that transition cannot be discounted. It is important to know the energy order of these two transitions in solution because of the suggestion[14] that there is a second $n \longrightarrow \pi^*$ transition ($A_2 \longleftarrow A_1$) to higher energy of the $\pi \longrightarrow \pi^*$ one. The existence of a second magnetic dipole transition has been assumed in inter-

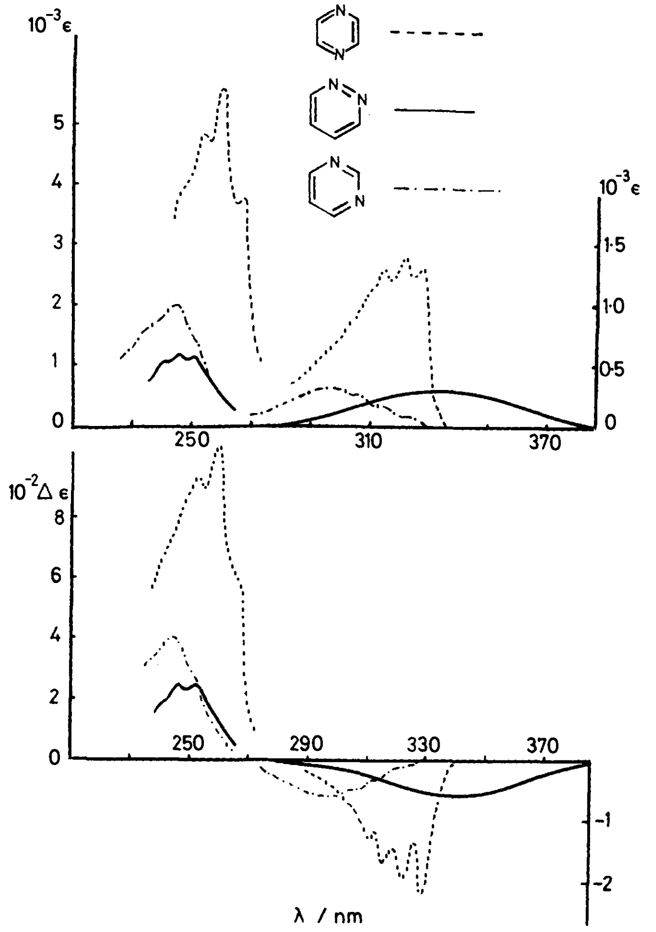


FIGURE 3 The absorption (upper) and linear dichroism (lower) spectra of the isomeric azines

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[11] P. Diehl and C. L. Khetrapal, *Mol. Phys.*, 1968, **14**, 327.

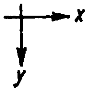
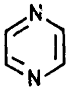
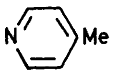
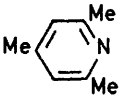
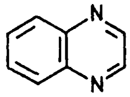
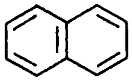
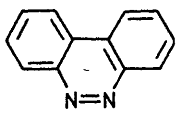
[12] S. F. Mason, *Quart. Rev.*, 1963, **15**, 287.

[13] J. N. Murrell, 'The Theory of the Electronic Spectra of Organic Molecules,' Methuen, London, 1963.

[14] H. E. Smith, L. J. Schaad, R. B. Banks, C. J. Wiant, and C. F. Jordan, *J. Amer. Chem. Soc.*, 1973, **95**, 811; G. Gottarelli and B. Samorì, *J.C.S. Perkin II*, 1974, 1462.

preting the c.d. spectra of (—)-(*S*)-2-, -3-, and -4-pyridylethanols but in only one case [the (—)-(*S*)-4-derivative] is it certain that this is not the $(B_1 \longleftarrow A_1)$ $n \longrightarrow \pi^*$ transition blue-shifted. In the spectrum of pyridine itself in a polythene matrix[15] the $n \longrightarrow \pi^*$ transition has been detected to low energy of the $\pi \longrightarrow \pi^*$ one. We have recently assigned[2] the two bands seen in the l.d. spectrum of 4-methylpyridine as $n \longrightarrow \pi^*$ (270 nm, negative l.d.) and $\pi \longrightarrow \pi^*$ (253 nm positive l.d., short-axis polarised) by assuming that the S_{ii} values for the molecule are similar to these for fluorobenzene. Once this has been done the S_{ii} values for 4-methylpyridine oriented by our method may be calculated and these are given in Table 2. The picolines are near the changeover point between rod-like and disc-like molecules and the best we can say is that out-of-plane and long-axis transitions should have strong negative and positive l.d. respectively and that short-axis transitions should have weak and probably positive l.d. The spectra of the 2- and 3-methylpyridines are given in Figure 4 and that of 2,4,6-trimethylpyridine in Figure 5.

TABLE 2

	S_{yy}	S_{xx}	S_{zz}	Ref.	$\lvert S_x' \rvert$
	0.081	0.063	−0.144	This work	0.04
	0.005	0.08	−0.085	2	0.29
	0.03	0.03	−0.06	This work	0
	0.026	0.094	−0.120	17	0.19
	−0.039	+0.191	−0.152	16	0.50
	−0.040	0.09	−0.051	This work	0.8

The interpretation of the 2- and 3-methylpyridine spectra is fairly easy. The negative l.d. band on the low energy sides of the absorption must correspond to the our-of-plane polarised $n \longrightarrow \pi^*$ transition thus confirming that it is to low energy of the $\pi \longrightarrow \pi^*$ in these two molecules as in 4-methylpyridine and pyridine itself. The positive l.d. then corresponds to the $\pi \longrightarrow \pi^*$ transition.

In 2,4,6-trimethylpyridine the picture is less clear. The l.d. spectrum is all of one sign and so the out-of-plane transition cannot immediately be singled out. The dichroic ratio is constant from the onset of absorption to *ca.* 270 nm implying that there is only one transition (in-plane polarised) present. From this ratio an S_{ii} value of 0.03 is obtained. The molecule is clearly disc-like (*cf.* 1,3,5-trifluorobenzene) and so all three S_{ii} values can be calculated $S_{xx} = S_{yy} = 0.03$ and $S_{zz} = -0.06$. If we assume that only two perpendicularly polarized transitions are under the band envelope we can use equation (2) to separate out the contributions from $\varepsilon_x = \varepsilon_y$ and ε_z. The partitioned spectrum is shown in Figure 5. It is difficult to say whether the *z*-polarised transition is actually to higher energy of the $\pi \longrightarrow \pi^*$ but they are certainly rather close.

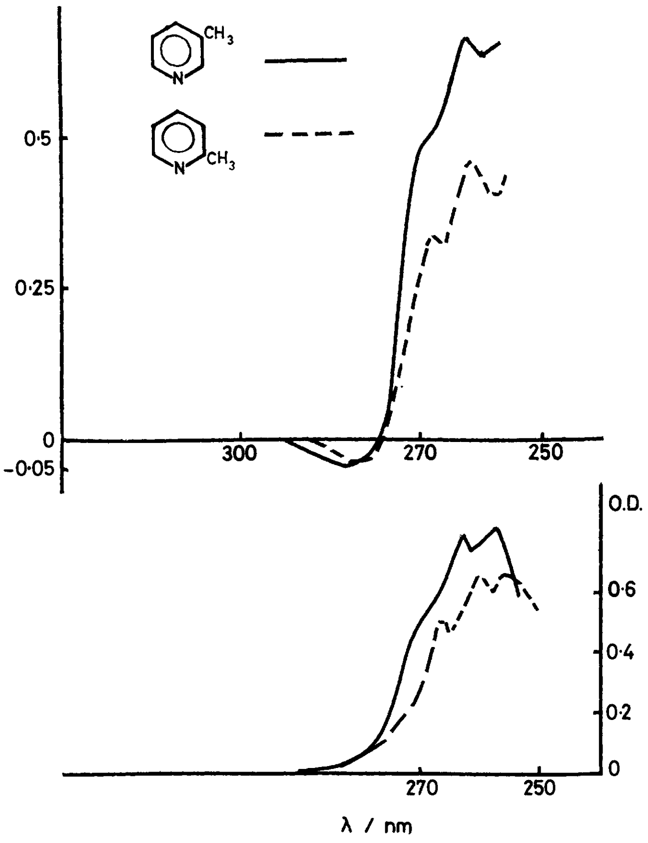


FIGURE 4 The absorption (lower) and linear dichroism (upper) spectra of 2- and 3-picoline

(c) *Naphthalene and quinoxaline.* The absorption spectrum of naphthalene in the compensated mesophase is similar to that recorded in hydrocarbon solvents.

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[15] B. Norden, *Chem. Phys. Letters*, 1973, **23**, 200.

The l.d. spectrum, however, shows a pattern quite different from the isotropic absorption (Figure 6). The S_{ii} parameters[16] for the molecule are given in Table 2 and we can see that naphthalene is nearer to the rod than to the disc shape. Since all the transitions must be $\pi \longrightarrow \pi^*$ (at least in the region of the spectrum accessible to us) they must be in-plane polarised. Positive l.d. will thus indicate long-axis polarisation and negative l.d. short axis.

The low energy part of the spectrum (to 290 nm) is clearly of mixed polarisation. This corresponds to the region where the ^1L_b ($B_{2u} \longleftarrow A_{1g}$) transition is expected to appear. This transition is known to consist of two main vibronic progressions, one (having *ca.* 1/4 of the intensity) is based on the true electronic origin and so is long-axis polarised and the other (*ca.* 3/4 of the intensity) is based on one quantum of a non-totally-symmetric (B_{3u}) vibration and so is short-axis polarised. Since the l.d. is entirely positive in this region, it appears that the progression based on the true origin dominates in l.d. (although the band as a whole clearly is of mixed polarisation). This is perhaps to be expected since from the S_{ii} values it can be seen that for equivalent absorption the associated positive l.d. would be *ca.* 5 times greater than the negative l.d. It is hoped that a careful analysis of this part of the spectrum using equation (2) will reveal both progressions.

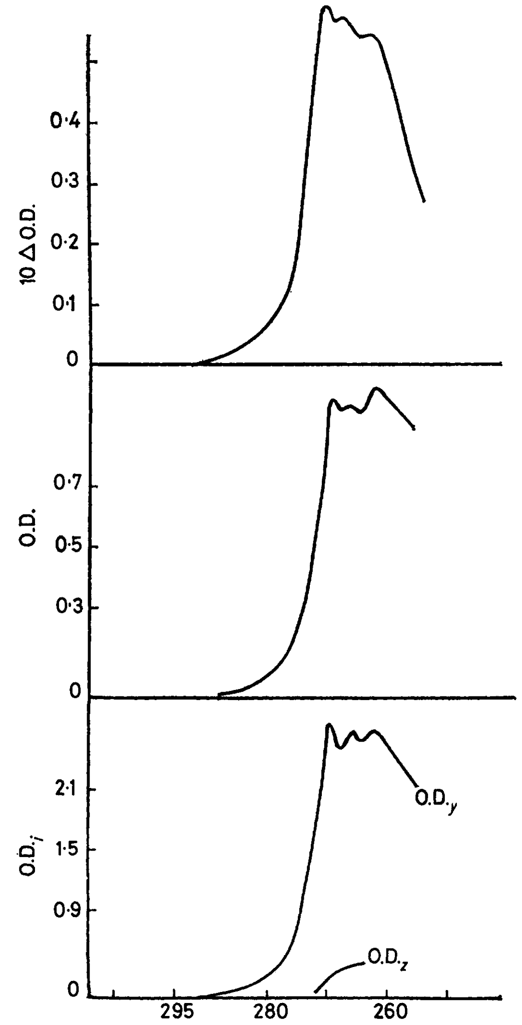

FIGURE 5 The absorption (central) and linear dichroism (upper) spectra and the partitioned spectrum (lower) corresponding to absorptions polarised in the molecular plane (OD$_y$) and perpendicular to it (OD$_z$) of *sym*-collidine

In the next region of the spectrum, caused by the $^1L_a(B_{1u} \longleftarrow A_{1g})$ transition which is short-axis polarised, both positive and negative l.d. occur. The negative feature is likely to correspond to the band origin and the positive polarisation at higher energies presumably is due to progressions built on non-totally-symmetric vibrations (which would be long axis-polarised). This is not an entirely satisfactory explanation since the ^1L_a transition is quite strongly allowed and non-totally-symmetric vibrations would not be expected to be particularly important. It is difficult to investigate the polarisation of this transition by more direct means, however, due to its large intensity and to the absence of host crystals which are transparent in this region.

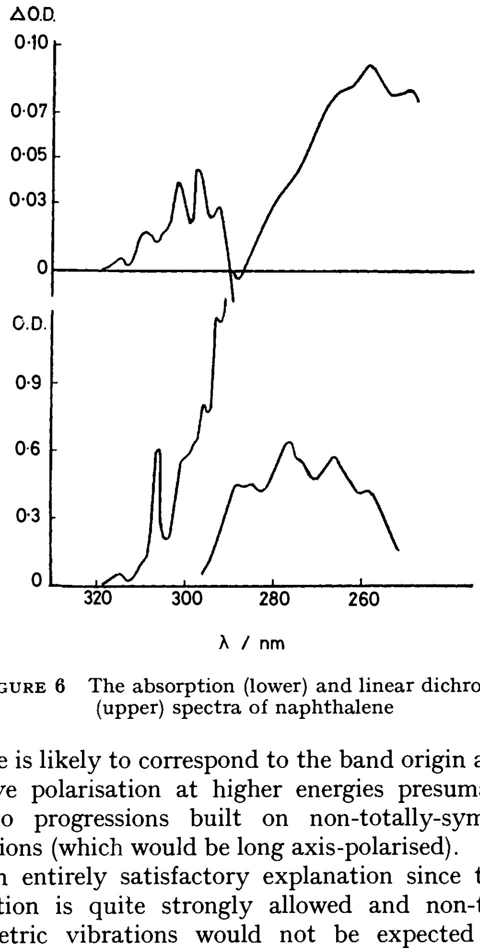

FIGURE 6 The absorption (lower) and linear dichroism (upper) spectra of naphthalene

The S_{ii} values for quinoxaline[17] are given in Table 2. These are different from the corresponding ones for naphthalene than would have been expected and indeed indicate that quinoxaline is a disc-like molecule. We

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[16] J. M. Deveppe, J. Degelaen, and M. Van Meerssche, *J. Mol. Structure*, 1973, **17**, 225.

[17] C. L. Khetrapal and A. C. Kunwar, *Mol. Cryst. Liquid Cryst.*, 1972, **15**, 363.

might at first ascribe this to a very low orientation obtained in the nematic n.m.r. experiment in which they were determined but, as will be seen, the most reasonable interpretation of our l.d., spectrum of quinoxaline (Figure 7) leads to very similar S_{ii} parameters. It is not clear why naphthalene and quinoxaline should orient so differently but it perhaps indicates the need for caution in transferring S_{ii} values between molecules which have similar shapes.

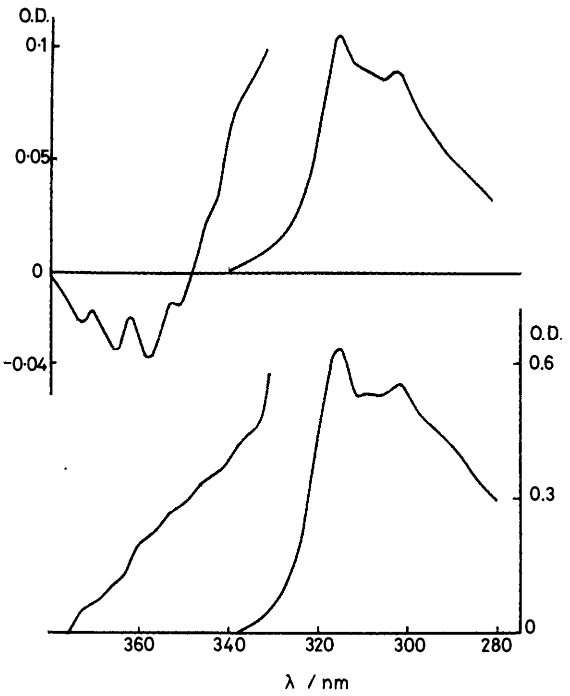

FIGURE 7 The absorption (lower) and linear dichroism (upper) spectra of quinoxaline

In any case the S_{ii} values for quinoxaline indicate negative l.d. for both in-plane polarised transitions and negative l.d. for the out-of-plane ones. The most recent experimental studies [18-20] indicate a $^1B_1$ ($n \longrightarrow \pi^*$) transition between 390 and 350 nm and a long-axis polarised $^1A_1$ ($\pi \longrightarrow \pi^*$) one between 340 and 280 nm. Recent calculations [21] have suggested that the absorption between 340 and 280 nm is caused by two transitions (the equivalent of the ^1L_a and ^1L_b bands of naphthalene) which should be orthogonally polarised. Our l.d. spectrum confirms the experimental assignments given above and seems to rule out two orthogonal polarisations under the higher energy absorption although, unfortunately, the S_{ii} values characterising long- and short-axis polarisation are not sufficiently different to make this certain. The S_{ii} values obtained assuming the assignments just mentioned are $S_{xx} = 0.06$, $S_{yy} = 0.04$, and $S_{zz} = -0.010$ which, as stated above, are similar to those in Table 2.

(d) 9,10-*Diazaphenanthrene*. The S_{ii} values of this molecule have not been reported. It would seem reasonable, at first sight, to regard it as a rod-like molecule. The visible absorption spectrum consists of three bands which have recently been assigned [22,23] as $n \longrightarrow \pi^*$ (395 nm) and $\pi \longrightarrow \pi^*$ short (350 nm) and long (300 nm) axis polarised. If we make the reasonable assumption that the first transition is the $n \longrightarrow \pi^*$ one and the other two are $\pi \longrightarrow \pi^*$ then our l.d. spectrum (Figure 8) unambiguously confirms the polarisation of the $\pi \longrightarrow \pi^*$ transitions since for any shape of molecule long-axis polarisation must have positive l.d. Using these assignments the S_{ii} values given in Table 2 were obtained.

Conclusions.—We hope that we have demonstrated the usefulness (and limitations) of aligned nematic liquid crystal l.d. as a means of assigning the polarisations of the electronic transitions of organic molecules. Obviously in the case of molecules of high symmetry it is often possible to make unambiguous assignments. Thus it is always possible to pick out the out-of-plane polarised transitions of a molecule near the disc-shape limit. Similarly in the case of near rod-shape molecules long-axis transitions may be singled out. It is even better, in this case, if it is known that the transitions are all in-plane polarised (the $\pi \longrightarrow \pi^*$ transitions, say, of the aromatic hydrocarbons) then both short- and long-axis polarisation can be identified. Even where the mole-

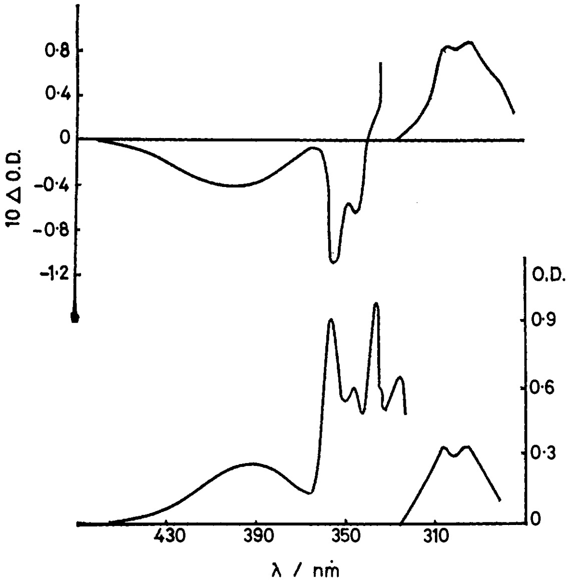

FIGURE 8 The absorption (lower) and the linear dichroism (upper) spectra of 9,10-diazaphenanthrene

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[18] R. H. Clarke, R. M. Hochstrasser, and C. J. Marzzacco, *J. Chem. Phys.*, 1969, **51**, 5015.

[19] R. W. Glass, L. C. Robertson, and J. A. Merritt, *J. Chem. Phys.*, 1970, **53**, 3857.

[20] A. Aminzadeh, V. Fawcett, and D. A. Long, *Chem. Phys. Letters*, 1976, **39**, 116.

[21] H. Baba and I. Yamazaki, *J. Mol. Spectroscopy*, 1972, **44**, 118.

[22] R. M. Hochstrasser and C. J. Marzzacco, *J. Chem. Phys.*, 1966, **45**, 4681.

[23] K. J. Mainusch, P. Polmann, and H. Stegmeyer, *Z. Naturforsch.*, 1973, **28a**, 1476.

cule does not belong to one of the extreme shape types it is often possible, either by using S_{ii} parameters obtained in a different solvent system by n.m.r., *etc.*, or by comparison with another molecule of similar molecular shape, to differentiate between the three polarisations. The method is in many cases the only one available, due to the impossibility of obtaining single crystal or doped crystal spectra.

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