Polarisation Directions of the Near Ultraviolet Band Systems of Disubstituted Benzene Derivatives

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The induced circular dichroism (i.c.d.) spectra of homo- and hetero-disubstituted benzene derivatives and of the monocyclic diazines in a cholesteric liquid crystal solution have been measured for radiation propagated along the helix axis of the plane texture. The polarisation direction of the ^1L_a and ^1L_b benzenoid transitions and, in the case of the diazines, of the $n \longrightarrow {}^1\pi^*$ transition are derived from the i.c.d. spectra through the order matrix elements which express the statistical orientation of the solute molecular axes in the mesophase solution. It is found that the ^1L_b moment near 380 nm is polarised in the direction of the longer in-plane axis in 1,2- and 1,3-homodisubstituted benzenes but is rotated through $\pi/2$ to the shorter in-plane axis for the corresponding heterodisubstituted derivatives, C_6H_4XY, with one substituent *meta*-directing and the other *ortho–para*-directing, which satisfy the induced spectroscopic moment condition, $m_X \simeq -m_Y$. The ^1L_a moment near 230 nm similarly changes polarisation from the shorter in-plane axis in 1,2- or 1,3-$C_6H_4X_2$ to the longer in the corresponding C_6H_4XY with $m_X \simeq -m_Y$. The changes in polarisation direction and other results support a vector addition model for the resultant transition moment in benzene derivatives based upon the assignment of the ^1L_b and ^1L_a bands to the transitions $^1A_{1g} \longrightarrow {}^1B_{2u}$ and $^1A_{1g} \longrightarrow {}^1B_{1u}$, respectively, in the parent hydrocarbon. The i.c.d. spectra confirm that the $n \longrightarrow {}^1\pi^*$ transition of the diazines is polarised perpendicular to the molecular plane.

SUBSTITUTION in the benzene nucleus gives rise to frequency shifts and to intensity changes of the lower energy ^1L_b and the higher energy ^1L_a absorption band in the electronic spectrum which have been related to the symmetry properties of the transition, $^1A_{1g} \longrightarrow {}^1B_{2u}$ and $^1A_{1g} \longrightarrow {}^1B_{1u}$, respectively responsible for the two absorption bands in the parent molecule.[1-5] These two transitions are electronically forbidden in benzene itself as the component electric dipole moments of the excitation connecting the ground state $^1A_{1g}$ with either the $^1B_{2u}$ (Figure 1) or the $^1B_{1u}$ excited state (Figure 2) mutually cancel and give a vanishing resultant in each case. A substituent in the benzene ring alters the magnitude of the component electric dipole transition moment at the position of substitution, so that the mutual cancellation of the components becomes incomplete and each transition, the ^1L_b and ^1L_a, acquires a non-zero moment. The changes in the magnitude of the component transition moment at the position of substitution, termed the 'migration moment' by Sklar[1] or the 'spectroscopic moment' by Platt,[3] are vectorially additive in a di- or a poly-substituted benzene derivative according to the B_{2u} symmetry pattern for the ^1L_b transition (Figure 1) or the B_{1u} pattern for the ^1L_a transition (Figure 2). The observed intensity changes of the ^1L_b band due to the substitution of the benzene nucleus are found to support[3-5] the vector addition model (Figure 1), *e.g.* the intensity enhancement of the ^1L_b benzene band due to *ortho*- or *meta*-homodisubstitution approximately equals that due to the corresponding monosubstitution whereas that arising from the analogous *para*-disubstitution is generally some four times larger.[3-5] Similarly the frequency shifts of the ^1L_b and the ^1L_a bands of benzene due to substituents are satisfactorily accommodated by perturbation theory from the basis that these bands originate, respectively, from the transitions $^1A_{1g} \longrightarrow {}^1B_{2u}$ and $^1A_{1g} \longrightarrow {}^1B_{1u}$ of the parent hydrocarbon.[2,4,5]

The polarisation directions of the ^1L_b and ^1L_a transitions in benzene derivatives have been less extensively investigated than the corresponding band intensities and frequencies although the vector addition model affords distinctive expectations for the orientation of the resultant moment of each of these transitions in a substituted benzene. The intensity changes of the ^1L_b band due to heterodisubstitution in the benzene nucleus show that *meta*-directing substituent groups have a spectroscopic

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[1] A. L. Sklar, *J. Chem. Phys.*, 1942, **10**, 135.
[2] T. Förster, *Z. Naturforsch.*, 1947, **2a**, 149.
[3] J. R. Platt, *J. Chem. Phys.*, 1951, **19**, 263.
[4] J. Petruska, *J. Chem. Phys.*, 1961, **34**, 1111, 1120.
[5] P. E. Stevenson, *J. Chem. Educ.*, 1964, **41**, 234.

moment of opposite sign to that of an *ortho–para*-directing group.[3] That is, a *meta*-directing group substituted in a given position of the benzene ring induces a ${}^1L_b$ spectroscopic moment antiparallel to that produced by a corresponding *ortho–para*-directing group. Accordingly it is expected that a 1,2- or 1,3-heterodisubstituted benzene derivative, C_6H_4XY, with one substituent *meta*-directing and the other *ortho–para*-directing with spectroscopic moments *m* of equal magnitude, such that $m_X = -m_Y$, has a resultant ${}^1L_b$ transition moment directed in the molecular plane perpendicular to the ${}^1L_b$ moment orientation in the corresponding 1,2- or 1,3-homodisubstituted analogue, $C_6H_4X_2$ or $C_6H_4Y_2$. Thus the vector addition model indicates that the ${}^1L_b$ moment is oriented in the direction of the longer in-plane molecular axis (*z*) in 1,2- or 1,3-$C_6H_4X_2$ but is directed along the shorter in-plane axis (*y*) in 1,2- or 1,3-C_6H_4XY with $m_X = -m_Y$ (Figure 1). In each of these benzene derivatives the ${}^1L_a$ moment is expected to have an in-plane orientation perpendicular to the corresponding ${}^1L_b$ moment (Figure 2). If the condition $m_X = -m_Y$ is fulfilled the ${}^1L_b$ and ${}^1L_a$ moments of 1,4-C_6H_4XY vanish whereas the corresponding moments of 1,4-$C_6H_4X_2$ are directed along the shorter (*y*) and longer (*z*) in-plane axis, respectively (Figures 1 and 2).

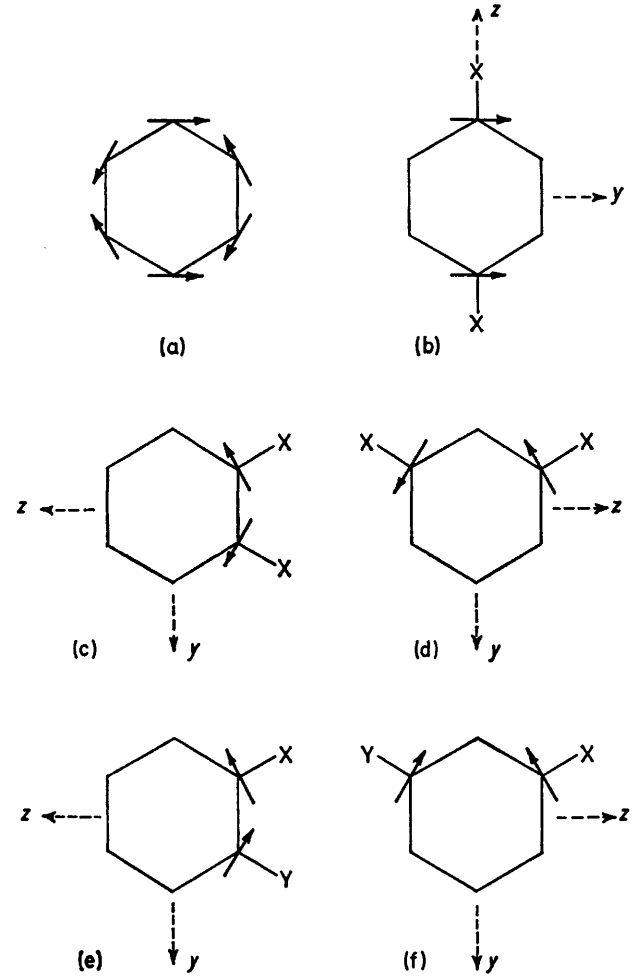

FIGURE 1 The component moments of the ${}^1A_{1g} \longrightarrow {}^1B_{2u}$ π-electron transition of the benzene molecule giving the ${}^1L_b$ band (a), and the changes in those components, the spectroscopic moments, induced at the positions of substitution in (b) 1,4-, (c) 1,2-, and (d) 1,3-homodisubstituted benzene derivatives, and (e) 1,2- and (f) 1,3-heterodisubstituted derivatives C_6H_4XY, with one substituent *meta*-directing and the other *ortho–para*-directing such that their spectroscopic moments are related by $m_X = -m_Y$. The resultant ${}^1L_b$ transition moment is polarised along (b) the *y*-axis, (c) the *z*-axis, (d) the *z*-axis, (e) the *y*-axis, and (f) the *y*-axis

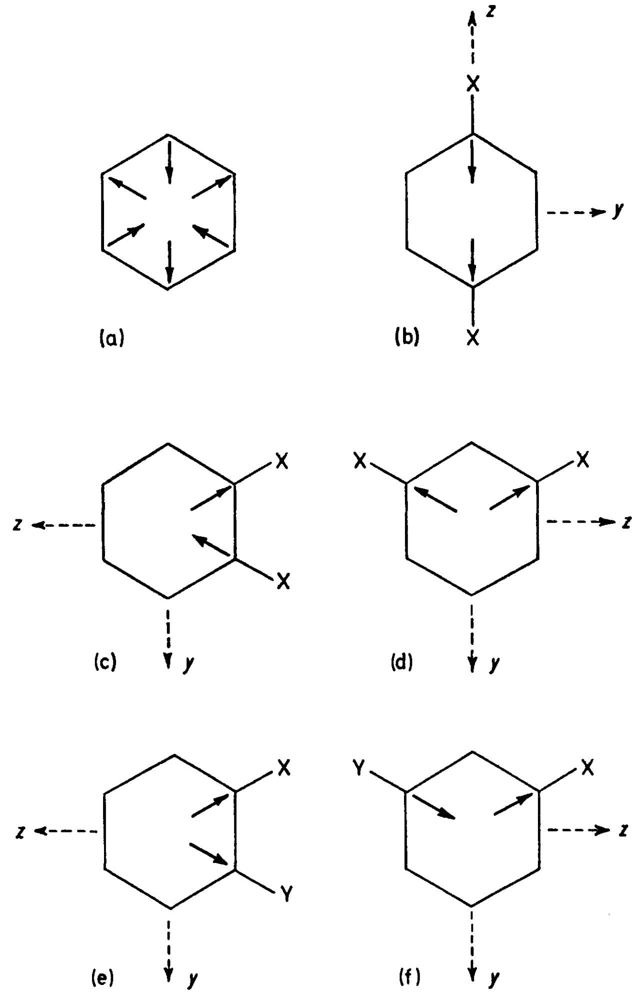

FIGURE 2 The component moments of the ${}^1A_{1g} \longrightarrow {}^1B_{1u}$ π-electron transition of the benzene molecule giving the ${}^1L_a$ band (a), and the changes in those components at the positions of substitution, the spectroscopic moments, in (b) 1,4-, (c) 1,2-, and (d) 1,3-homodisubstituted benzene derivatives, and (e) 1,2- and (f) 1,3-heterodisubstituted derivatives, C_6H_4XY, with the spectroscopic moments, $m_X = -m_Y$. The resultant ${}^1L_a$ transition moment is polarised along (b) the *z*-axis, (c) the *y*-axis, (d) the *y*-axis, (e) the *z*-axis, and (f) the *z*-axis.

Studies of the polarised singe crystal spectra of benzene derivatives are confined largely to homodi- and homopoly-substituted compounds and they are generally limited to the lower frequency region of the ${}^1L_b$ transition.[6] An exception in the latter respect is the quartz and vacuum u.v. single crystal study of 1,4-dimethoxybenzene by

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[6] T. N. Misra, *Rev. Pure and Appl. Chem.*, 1965, **15**, 39.

Albrecht and Simpson,[7] recently confirmed and extended to the case of 1,4-dihydroxybenzene,[8] which show that the ^1L_b and the ^1L_a transition of these derivatives are polarised in the direction of the shorter and the longer in-plane axis, respectively. The ^1L_b moment is found to be directed along the shorter in-plane axis of a number of other benzene derivatives 1,4-disubstituted with *ortho–para*-directing groups from the rotational contour of the 0–0 vibronic band in the vapour-phase spectrum at high resolution.[9]

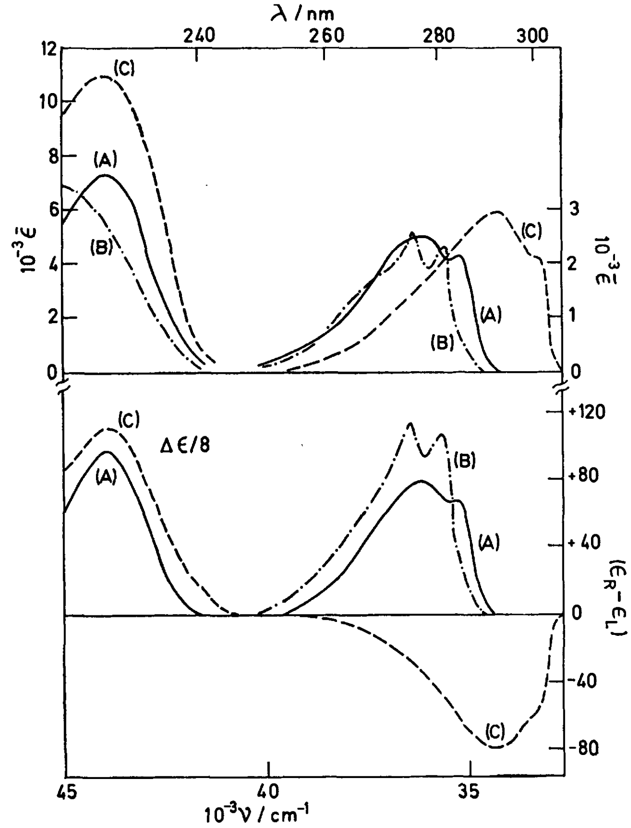

FIGURE 3 The unpolarised absorption (upper curves) and the induced circular dichroism (lower curves) of (A) 1,2-, (B) 1,3-, and (C) 1,4-dimethoxybenzene in the cholesteric plane texture formed by cholesteryl chloride–cholesteryl nonanoate (1 : 1 w/w) at 25 °C

In order to investigate the scope of the vector addition model for the ^1L_b and ^1L_a transition moment directions in substituted benzenes we have determined the induced circular dichroism (i.c.d.) spectra of a range of benzene derivatives in a cholesteric liquid crystal solvent with particular reference to 1,2- and 1,3-disubstituted compounds, C_6H_4XY, where one group is *meta*-directing and the other *ortho–para*-directing with $m_X \simeq -m_Y$. Lists of the spectroscopic moments of the substituents which do not strongly perturb the benzene chromophore show[3,4] that it is not possible to meet the condition $m_X = -m_Y$ exactly. However, the values[3] of +31, +21, −19, and −28 $(\mathrm{l\ mol^{-1}\ cm^{-1}})^{\frac{1}{2}}$ for the spectroscopic moments of the groups, OCH_3, F, C≡N, and CO_2H, respectively, indicate that the methoxybenzoic acids and the fluorobenzonitriles approximately fulfill the desired condition. The i.c.d. spectra of 1,2-, 1,3-, and 1,4-dimethoxybenzene in a cholesteric solvent have been measured (Figure 3) in order to obtain the ^1L_b and the ^1L_a polarisation directions for the 1,2- and the 1,3-homodisubstituted case and to check the method from the known polarisation directions[7,8] for the 1,4-isomer. In addition to the corresponding spectra of 2- and 3-fluorobenzonitrile (Figure 4) and of 2- and 3-methoxybenzoic acid (Figure 5), the i.c.d. spectra of pyridazine, pyrimidine, and pyrazine in a cholesteric solvent have been determined (Figure 6) for the study of an electronic transition polarised along the third molecular axis, perpendicular to the molecular plane. Analyses of the rotational structure observed in the 0–0 vibronic band show that the $n \longrightarrow {}^1\pi^*$ transition of the azabenzenes is polarised perpendicular to the molecular plane.[10,11]

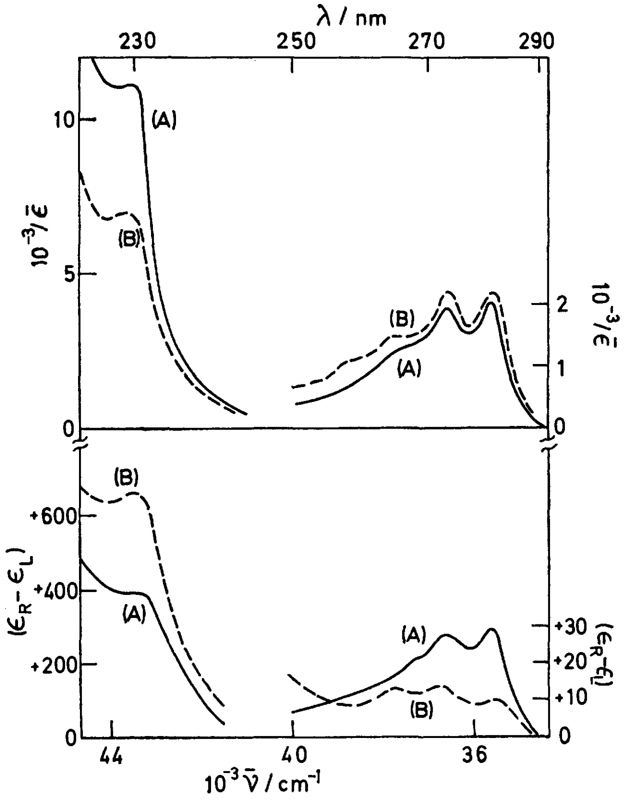

FIGURE 4 The unpolarised absorption (upper curves) and induced circular dichroism (lower curves) of (A) 2- and (B) 3-fluorobenzonitrile in the cholesteric plane texture formed by cholesteryl chloride–cholesteryl nonanoate (1 : 1 w/w) at 25 °C

The plane texture of a cholesteric liquid crystal, in the model first proposed by Mauguin,[12] consists of a stack of nematic layers, each with a monomolecular thickness,

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[7] A. C. Albrecht and W. T. Simpson, *J. Chem. Phys.*, 1955, **23**, 1480.

[8] K. Kaya, K. Fuke, and S. Nagakura, *Bull. Chem. Soc. Japan*, 1974, **47**, 438.

[9] T. Cvitas, J. M. Hollas, and G. H. Kirby, *Mol. Phys.*, 1970, **19**, 305.

[10] S. F. Mason, *J. Chem. Soc.*, 1959, 1269.

[11] K. K. Innes, J. A. Merritt, W. C. Tincher, and S. G. Tilford, *Nature*, 1960, **187**, 500.

[12] C. Mauguin, *Bull. Soc. France Mineral.*, 1911, **34**, 71.

which are skewed through a small angle relative to one another, forming a helical array. Molecules of an anisotropic and achiral solute in a cholesteric mesophase are aligned with the longest molecular axis statistically oriented along the director of the local nematic layer, so that the solute molecules themselves constitute a helical assembly. For radiation propagated along the helix axis of the cholesteric mesophase, the solute molecules exhibit an i.c.d. $(\varepsilon_L - \varepsilon_R)$ which is proportional to the corresponding linear dichroism of the solute $(\varepsilon_\parallel - \varepsilon_\perp)$ for radiation polarised parallel and perpendicular to the director of a nematic layer.[13-15] The major contribution to the i.c.d. at the transition wavenumber $\bar{\nu}_j$ of an anisotropic solute in a cholesteric mesophase with a helical pitch length P is given by expression (1) [15] where

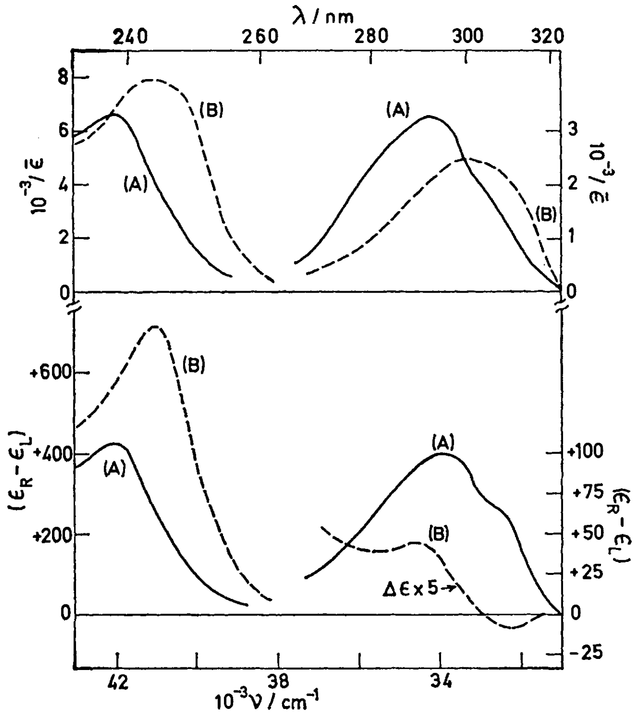

FIGURE 5 The unpolarised absorption (upper curves) and induced circular dichroism (lower curves) of (A) 2- and (B) 3-methoxybenzoic acid in the cholesteric plane texture formed by cholesteryl chloride–cholesteryl nonanoate (1 : 1 w/w) at 25 °C

$$(\varepsilon_L - \varepsilon_R)_j = [P\bar{\nu}_j^3\Delta n(\varepsilon_\parallel - \varepsilon_\perp)_j]/[2(\bar{\nu}_j^2 - \bar{\nu}_0^2)] \quad (1)$$

Δn is the linear birefringence $(n_\parallel - n_\perp)$ of each nematic layer, with a mean refractive index n, and $\bar{\nu}_0$ is the wavenumber of the cholesteric pitch-band $(\bar{\nu}_0 = 1/Pn)$ at which left- or right-circularly polarised radiation is reflected, depending upon the left- or the right-handed helical twist angle of the nematic layers in the cholesteric liquid crystal. Equation (1) applies to a right-handed mesophase, reflecting right-circularly polarised light at $\bar{\nu}_0$. For a left-handed cholesteric plane texture reflecting left-circular radiation at $\bar{\nu}_0$ the sign of the i.c.d. is reversed and becomes $(\varepsilon_R - \varepsilon_L)_j$ in equation (1) and in expressions derived from it.

A minor contribution to the i.c.d. of an anisotropic solute in a cholesteric mesophase, and the sole contribution in the case of an isotropic solute, arises from the differential radiation field strength in a chiral medium of left- and right-circularly polarised light incident upon the medium with equal field amplitudes.[15,16] The differential field i.c.d. effect is proportional to the circular birefringence of the chiral solvent and it is relatively small for the markedly anisotropic benzene derivatives studied. Neglect of a correction for the differential field effect gives rise to no ambiguities in the determination of the ^1L_b and the ^1L_a moment direction in benzene derivatives from the major dichroism i.c.d. effect.

As the absorption bands of the substituted benzenes considered lie in the u.v. region, the choice of a cholesteric solvent with a pitch band in the i.r. region for i.c.d. measurements allows the reduction of equation (1) to expression (2). The i.c.d. spectra recorded (Figures

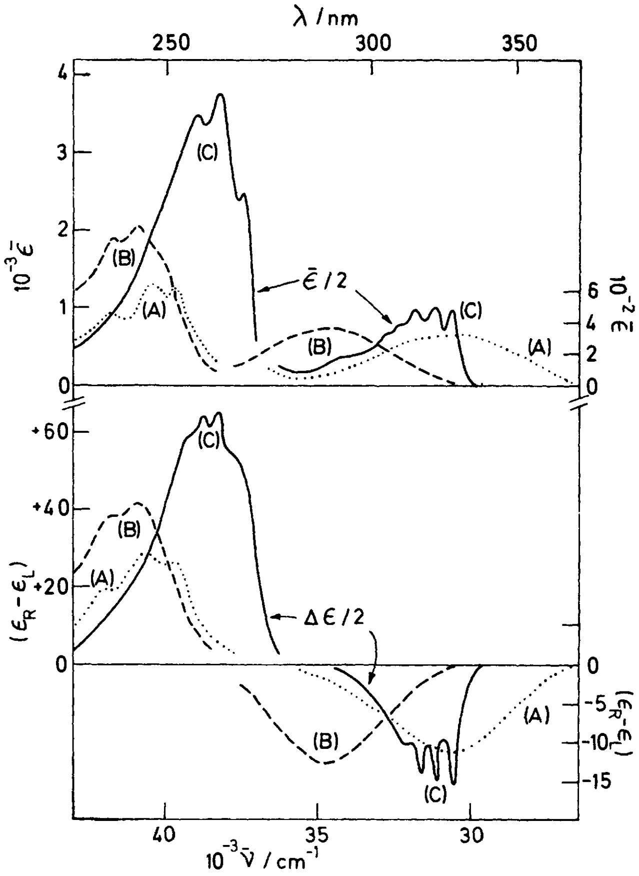

FIGURE 6 The unpolarised absorption (upper curves) and induced circular dichroism (lower curves) of (A) 1,2-diazine (pyridazine), (B) 1,3-diazine (pyrimidine), and (C) 1,4-diazine (pyrazine)

$$(\varepsilon_L - \varepsilon_R)_j = P\Delta n\bar{\nu}_j(\varepsilon_\parallel - \varepsilon_\perp)_j/2 \quad (2)$$

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[13] E. Sackmann and J. Voss, *Chem. Phys. Letters*, 1972, **14**, 528.

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

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

[16] S. F. Mason and R. D. Peacock, *J.C.S. Chem. Comm.*, 1973, 712.

TABLE 1

The wavelength maximum (λ_j) and the order matrix element (S_{jj}) of the polarisation direction of the ^1L_b and the ^1L_a transition moment in disubstituted benzene derivatives. The polarisation axes of the transitions are those illustrated in Figures 1 and 2

	^1L_b			^1L_a		
Substituents	λ_j/nm	S_{jj}	Pol.$_j$	λ_j/nm	S_{jj}	Pol.
1,2-$(CH_3O)_2$	278	+0.132	z	227	+0.043	y
1,3-$(CH_3O)_2$	274	+0.187	z	222	~0	y
1,4-$(CH_3O)_2$	294	−0.105	y	227	+0.307	z
1,2-F(CN)	282	+0.059	y	230	+0.126	z
1,3-F(CN)	282	+0.018	y	230	+0.168	z
1,2-$(CH_3O)(CO_2H)$	294	+0.129	y	238	+0.238	z
1,3-$(CH_3O)(CO_2H)$	290	+0.017	y	244	+0.357	z
	312	−0.004	x			

TABLE 2

The wavelength maximum (λ_j) and the order matrix element (S_{jj}) of the polarisation direction of the ^1L_b and the $n \longrightarrow \pi^*$ transition moment in the monocyclic diazines. The polarisation axes of the transitions are those illustrated in Figures 1 and 2 with the C–X groups replaced by aza-nitrogen atoms

	$n \longrightarrow {}^1\pi^*$			^1L_b		
	λ_j/nm	S_{jj}	Pol.$_j$	λ_j/nm	S_{jj}	Pol.$_j$
1,2-Diazine	328	−0.15	x	247	+0.07	z
1,3-Diazine	290	−0.14	x	246	+0.07	y, z
1,4-Diazine	328	−0.145	x	260	+0.065	y

3—6) were obtained with a solvent composed of a mixture of cholesteryl chloride with an equal weight of cholesteryl nonanoate. The mixture forms a cholesteric plane texture with a pitch band at 6 900 cm^{-1} where left-circularly polarised radiation is reflected, and for this solvent equation (2) serves as a good approximation to equation (1). Mixtures of cholesteryl esters [17] and of the esters with cholesteryl chloride [18] have a mean refractive index n of 1.50 and a linear birefringence Δn of 0.05 through which, with the derived pitch length P of 0.97 μm, the i.c.d. spectra of the benzene derivatives studied are quantitatively related to the corresponding linear dichroism spectra by equation (2).

The determination of the polarisation direction of the ^1L_b and the ^1L_a transition moments in the substituted benzenes considered from the linear dichroism spectra requires a knowledge of the mean orientation of the solute molecules relative to the director of the local nematic layer in the cholesteric solvent. A measure of the average degree of alignment is provided by the Saupe [19] order matrix with the elements (3) where θ_j is the mean angle

$$S_{ij} = (1/2)\langle 3\cos\theta_i\cos\theta_j - \delta_{ij}\rangle \qquad (3)$$

between the j axis of the solute molecule and the nematic director, and i, j = x, y, or z. For molecules of C_{2v} or D_{2h} symmetry, *i.e.* the homodisubstituted benzene derivatives, only the diagonal elements of the order matrix are non-zero and only two of the latter elements are independent, owing to the sum rule (4). The 1,2-

$$S_{xx} + S_{yy} + S_{zz} = 0 \qquad (4)$$

and 1,3-heterodisubstituted analogues, C_6H_4XY, strictly speaking have only C_s symmetry, and for molecules of this type three elements of the order of matrix are independent. However, the choice of the spectroscopic moments, $m_X = -m_Y$, affords the 1,2- and 1,3-C_6H_4XY molecules studied an effective C_{2v} chromophoric symmetry and the sizes of the substituents X and Y in a given derivative do not preclude an approximate C_{2v} steric symmetry. Accordingly the homo- and the hetero-disubstituted benzene derivatives are considered alike to have only two independent elements in the order matrix.

A solute statistically oriented in a nematic layer absorbs radiation polarised parallel and perpendicular to the nematic director with the respective extinction coefficients, $\varepsilon_\parallel$ and $\varepsilon_\perp$, which are given by relations (5) and (6) [14] where ε_{iso} is the corresponding extinction coefficient

$$\varepsilon_\parallel = \varepsilon_{\text{iso}} + (2/3) \sum_{j=x,y,z} \varepsilon_j S_{jj} \qquad (5)$$

$$\varepsilon_\perp = \varepsilon_{\text{iso}} - (1/3) \sum_{=x,y,z} \varepsilon_j S_{jj} \qquad (6)$$

for the solute randomly oriented in an isotropic solution [equation (7)]. The mean extinction coefficient $\bar{\varepsilon}$ of the

$$\varepsilon_{\text{iso}} = (1/3) \sum_{j=x,y,z} \varepsilon_j \qquad (7)$$

solute in a nematic layer or the corresponding cholesteric plane texture for unpolarised radiation differs from $\bar{\varepsilon}_{\text{iso}}$ on account of the statistical orientation and it is given by equation (8).

$$\begin{aligned}\bar{\varepsilon} &= (1/2)[\varepsilon_\parallel + \varepsilon_\perp] \\ &= \varepsilon_{\text{iso}} + (1/6) \sum_{j=x,y,z} \varepsilon_j S_{jj}\end{aligned} \qquad (8)$$

Except for cases of accidental degeneracy, an electronic transition in a solute molecule with C_{2v} or D_{2h} symmetry giving rise to absorption at the frequency $\bar{\nu}_j$ is polarised along only one of the molecular axes, and in a nematic or cholesteric solution the particular polarisation direction is characterised by the order matrix element S_{jj} of that axis. The i.c.d. and unpolarised spectrum of the solute in a cholesteric mesophase give the order-matrix element S_{jj} of the polarisation axis of the electronic transition at $\bar{\nu}_j$ through relation (9), obtained from equations (2), (5), (6), and (8).

$$S_{jj} = 2(\varepsilon_L - \varepsilon_R)_j/[3P\Delta n\bar{\nu}_j\bar{\varepsilon}_j - (\varepsilon_L - \varepsilon_R)_j] \qquad (9)$$

Values of the order matrix element S_{jj} obtained from equation (9) for the polarisation axis of the ^1L_b and of the ^1L_a transition in the disubstituted benzene derivatives studied, and of the $n \longrightarrow {}^1\pi^*$ and of the ^1L_b transition in the monocyclic diazines, are recorded in Tables 1 and 2, respectively. Literature values of the order matrix elements S_{jj} of the diazines [20] and of representative

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[17] J. L. Fergason, *Mol. Cryst. Liquid Cryst.*, 1966, **1**, 293.

[18] I. Teucher, K. Ko, and M. M. Labes, *J. Chem. Phys.*, 1972, **56**, 3308.

[19] A. Saupe, *Mol. Cryst. Liquid Cryst.*, 1966, **1**, 527.

[20] R. C. Long, jun., and J. H. Koldstein, *Mol. Cryst. Liquid Cryst.*, 1973, **23**, 137.

disubstituted benzenes[21,22] in thermotropic nematic liquid crystals, obtained by n.m.r. methods, are listed in Table 3.

Benzene derivatives generally are found to align in a thermotropic nematic solvent with the longer in-plane axis, the z-axis in the sterically based convention adopted here (Figures 1 and 2), at the smallest mean angle to the nematic director, and with the axis perpendicular to the molecular plane, the x-axis (Figures 1 and 2), at the largest average angle to the director[19-23] (Table 3). That is, the matrix elements lie in the order, $S_{zz} > S_{yy} > S_{xx}$, with the present axis convention. The i.c.d. and unpolarised absorption of the ^1L_b and ^1L_a bands of the disubstituted benzenes provide the two in-plane elements, S_{zz} and S_{yy}, and these are identified, giving the polarisation direction of the corresponding transition (Table 1) by reference to the above magnitude-order of the elements and by a comparison with the elements for analogous benzene derivatives estimated by n.m.r. spectroscopy (Table 3).

TABLE 3

The order matrix elements (S_{jj}) of the monocyclic diazines and of the dicyano- and difluoro-benzene derivatives in thermotropic nematic solvents determined by n.m.r. methods. The molecular axes are those illustrated in Figures 1 and 2, the C–X groups being replaced by aza-nitrogen atoms in the case of the diazines

	$C_6H_4F_2$ [a]			$C_6H_4(CN)_2$ [b]			$C_4H_4N_2$ [c]		
Positions	S_{xx}	S_{yy}	S_{zz}	S_{xx}	S_{yy}	S_{zz}	S_{xx}	S_{yy}	S_{zz}
1,2	−0.14	+0.03	+0.11	−0.169	+0.040	+0.129	−0.099	+0.064	+0.035
1,3	−0.12	+0.02	+0.10	−0.171	−0.009	+0.180	−0.092	+0.028	+0.064
1,4	−0.15	−0.03	+0.18	−0.190	−0.110	+0.300	−0.097	+0.041	+0.056

[a] From ref. 21. [b] From ref. 22. [c] From ref. 20.

The results obtained for the polarisation direction of the ^1L_b and the ^1L_a transition in the disubstituted benzenes investigated (Table 1) support the vector addition model for the spectroscopic moments induced by substitution[3] based upon the respective $^1B_{2u}$ and $^1B_{1u}$ symmetry character of the excited state of those transitions in the benzene molecule (Figures 1 and 2). In agreement with the single crystal spectroscopic studies,[7,8] the i.c.d. method shows that the ^1L_b and the ^1L_a transitions of 1,4-dimethoxybenzene are polarised along the shorter and the longer in-plane axis, respectively, whereas the corresponding transitions of the 1,2- and the 1,3-isomer are conversely polarised in the direction of the longer and the shorter in-plane axis, respectively (Figures 1 and 2, Table 1). On passing from a 1,2- or a 1,3-homodisubstituted derivative to a heterodisubstituted analogue, C_6H_4XY, with spectroscopic moments, $m_X \simeq -m_Y$, the moments of both the ^1L_b and the ^1L_a transition are found to rotate through $\sim\pi/2$ (Table 1), from z- to y-polarisation for the ^1L_b transition (Figure 1), and from y- to z-polarisation for the ^1L_a transition (Figure 2). The experimental verification of this singular theoretical prediction provides strong support for the vector addition model of substituent-induced transition moments with B_{2u} parent symmetry for the ^1L_b and B_{1u} symmetry for the ^1L_a band.

An unexpected finding is that the longer wavelength absorption band of 3-methoxybenzoic acid is due to more than one electronic transition, as is shown by the change in the sign of the associated i.c.d. absorption at 303 nm (Figure 5). The composite nature of the band is confirmed by a measurement of the linear dichroism spectrum of 3-methoxybenzoic in a nematic mixture of cholesteryl chloride and cholesteryl laurate (1.85 : 1 w/w),[14] oriented by an electric field of 5 kV cm^{-1}, where the dichroism $(\varepsilon_{\parallel} - \varepsilon_{\perp})$ changes from negative above 300 nm to positive at shorter wavelengths. The order matrix elements derived from the two regions of the i.c.d. spectrum associated with the longer wavelength absorption band of 3-methoxybenzoic acid (Table 1) suggest that the ^1L_b $\pi \longrightarrow \pi^*$ transition with y-polarisation is overlaid at the lower frequency band edge by a weaker transition with x-polarisation, possibly the $n \longrightarrow \pi^*$ transition of the conjugated carboxy-group. The element S_{xx} for 3-methoxybenzoic acid in the cholesteric solvent studied has a value in the region of —0.37, from the sum rule [equation (4)], and the value of —0.004 obtained from the i.c.d. adsorption at 312 nm indicates that the intensity of the x-polarised transition is smaller than that of the ^1L_b transition which it overlaps (Figure 5, Table 1).

The i.c.d. associated with the ^1L_a absorption of the monocyclic diazines is inaccessible, owing to the onset of absorption due to the cholesteric solvent below 230 nm, but the order matrix elements of these benzene analogues are provided by the i.c.d. spectra of the ^1L_b and the $n \longrightarrow {}^1\pi^*$ transition, which have a mutually orthogonal polarisation (Figure 6). The element obtained from the i.c.d. of the $n \longrightarrow {}^1\pi^*$ transition is large and negative in each case (Table 2), indicating that the transition is polarised perpendicular to the molecular plane, as was first demonstrated by an analysis of the rotational structure observed in the corresponding vapour-phase spectra of the diazines.[11]

The steric difference between the two in-plane axes of the monocyclic diazines is small and, while the present i.c.d. measurements show that the ^1L_b transition of the diaza-analogues of benzene is polarised in the molecular plane, they do not distinguish between the two possible polarisation directions in the case of pyrimidine. The order matrix element for the ^1L_b moment direction of pyrimidine may refer equally to the y- or to the z-polarisation axis which have the same S_{jj} value from the

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i.c.d. measurements (Table 2). However the ^1L_b transition moment direction of pyridazine and pyrazine is associated with the smaller of the two in-plane order matrix elements in each case (Table 2) and a comparison with the corresponding S_{jj} values determined by n.m.r. methods (Table 3) suggests that the ^1L_b moment lies along the z- and the y-axis, respectively. The ^1L_b polarisation direction expected from the vector addition model (Figure 1) is the z-azis for pyridazine (1,2-diazine) and the y-axis for pyrazine (1,4-diazine).

EXPERIMENTAL

Materials.—The benzenoid solutes and components of the cholesteric solvent were obtained from commercial sources and purified by crystallisation or distillation. Cholesteryl chloride and cholesteryl nonanoate were recrystallised from ethanol at 0 °C in order to remove diene and other light absorbing impurities. A mixture of cholesteryl chloride with an equal weight of cholesteryl nonanoate forms at 25 °C a cholesteric plane texture between silica plates separated by a 10—50 μm spacer. The texture is retained with a benzenoid solute (~0.1M), the solution reflecting left-circularly polarised light at 1.45 μm.

Spectra.—Unpolarised and c.d. spectra were measured with a Cary 17 and a Jouan CD 185 spectrometer, respectively, the radiation being propagated along the helix axis of the cholesteric solution, normal to the silica plates, in each case. The linear dichroism spectrum of 3-methoxybenzoic acid was obtained with a solution (0.01M) in a mixture of cholesteryl chloride and cholesteryl laurate (1.85 : 1 w/w),[14] nematically aligned perpendicular to the propagation direction of the radiation by the application of a 2 kV potential to electrodes 4 mm apart in a sandwich cell with a 0.4 mm pathlength. The difference between the absorption of light polarised parallel and perpendicular to the electric field direction was measured with a laboratory-constructed spectrometer incorporating a Morvue photoelastic modulator used in the periodic half-wave retardation mode.

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