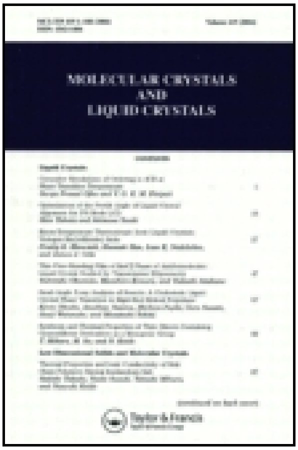

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Applications of the Modulated Liquid Crystal-Linear Dichroism (I. C.-I. d.) to Spectro- and Stereo-chemical Problems-Part 3[1]

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Applications of the Modulated Liquid Crystal-Linear Dichroism (l. c.-l. d.) to Spectro- and Stereo-chemical Problems–Part 3[1†]

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The instrument, apparatus, and some new details of the set-up for measurements using l. c.-l. d. techniques are reported.

Some applications of l. c.-l. d. information previously published by the author are collected and reviewed in order to give some examples of the usefulness of the technique in solving spectro- and stereo-chemical problems. The manner in which l. c.-l. d. information about the symmetry of electronic states can be applied both to assign electronic transitions and demonstrate that a molecule that is achiral in its electronic ground state can become chiral in an excited state, is here presented. Distortions induced in solute molecules by liquid crystalline solvents can be demonstrated by l. c.-l. d. and stereochemical models of induction of cholesteric mesophase have been proposed on the basis of l. c.-l. d. orientational information.

INTRODUCTION

A sample is said to exhibit linear dichroism (l. d.) if it absorbs light to different degrees depending on its linear polarization. The l. d. is usually defined as the differential absorption of two perpendicularly plane-polarized components of an electromagnetic radiation. l. d. spectra can be recorded by static or modulated techniques.

[†] Presented at the Ninth International Liquid Crystal Conference, Bangalore, December 6–10, 1982.

MEASUREMENT TECHNIQUES

The most sensitive and widely used *static-method* consists of separate recordings of the spectra for the two components, parallel (∥) and perpendicular (⊥) to the sample optic axis, by producing linearly polarized light in a "normal" spectrophotometer by means of a polarizer and by rotating either the polarizer or the sample. The independently accumulated errors, mostly due to the sample or polarizer rotations, and the sensitivity, at least 10^3-fold lower than that for the modulated methods, makes static techniques suitable for strongly dichroic signals and well-oriented samples only.

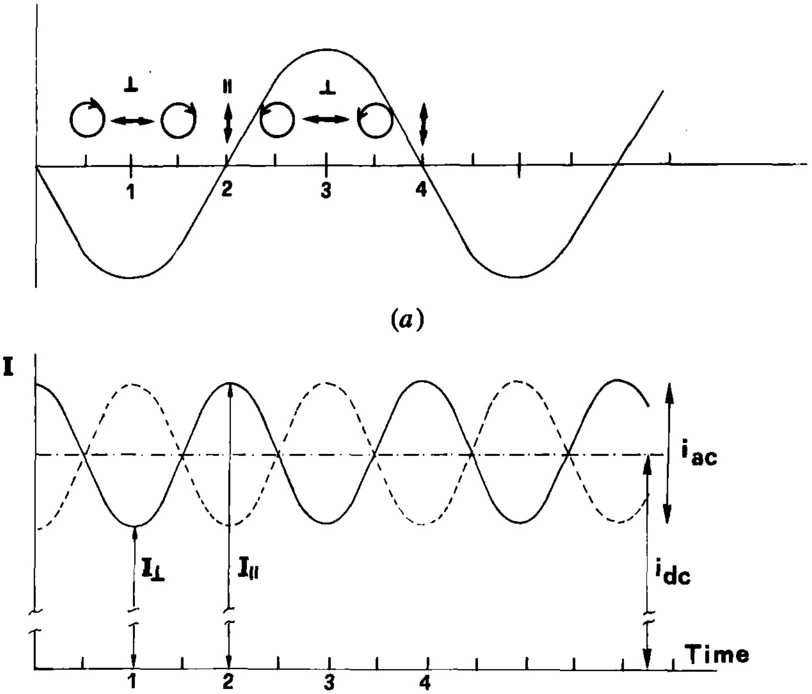
The modulated techniques involve directly-run differential l. d. spectra (l. d. = $E_{\parallel}(\lambda) - E_{\perp}(\lambda)$ where $E_{\parallel}(\lambda)$ and $E_{\perp}(\lambda)$ are the optical densities for the two plane polarized components) and the polarization state of the light beam is varied periodically in time. The monochromatic polarized light is produced by a monochromator, a linear polarizer and a polarization modulator oriented with its principal axis at 45° to that of the polarizer. The modulator consists of a block of isotropic, fused quartz made birefringent through the application of a periodic stress by a piezoelectric transducer, and acts as a $\lambda/2$ retarding element. The state of modulated polarization of the light beam passing through it and the corresponding relative intensity (I) of the beam transmitted through the sample at different modulation phases are shown in Figures 1a and 1b respectively. If the sample is isotropic, its absorption does not depend on polarization of the light: **I** is therefore, constant with the modulation phases and a direct current signal (i_{dc}) is produced by the detector. On the other hand, if the sample is linearly dichroic, the intensity of the transmitted beam will vary in phase with the light-modulation period (Figure 1a) and an alternating current (i_{ac}) at the dector will be superimposed on the i_{dc}. The solid and dashed curves of Figure 1 correspond to the cases $E_{\parallel}\langle E_{\perp}$ and $E_{\parallel}\rangle E_{\perp}$ respectively. The signal processing is set up to take the d.c. and the ratio of the a.c. to d.c. signals. From Eqs. 26 and 28 of Ref. 2

$$i_{dc}(\lambda) = \frac{1}{2}[T_{\parallel}(\lambda) + T_{\perp}(\lambda) + J_0(\delta_0)(T_{\parallel}(\lambda) - T_{\perp}(\lambda))] \tag{1}$$

$$\frac{i_{ac}(\lambda)}{i_{dc}(\lambda)} = \frac{4}{\pi}\frac{J_2(\delta_0)\tanh(\text{l.d.})}{1 + J_0(\delta_0)\tanh(\text{l.d.})}, \tag{2}$$

and the l.d. and "average absorption" become respectively

$$\text{l.d.} = E_{\parallel}(\lambda) - E_{\perp}(\lambda) = \frac{2}{\ln 10}\tanh^{-1}\frac{S}{K + J_0(\delta_0)S} \tag{3}$$



(a)

(b)

FIGURE 1 The modulation signal and the relative polarization of the light beam (1a); the periodic corresponding intensity (I) of the beam transmitted through a linearly positive ($I_{\|} < I_{\perp}$, dashed line) and negative ($I_{\|} > I_{\perp}$, full line) dichroic sample (1b). The resulting alternating (i_{ac}) and direct (i_{dc}) currents at the detector can be related to the l. d. intensity and to the "average absorption" by Eqs. 2 and 5.

$$[E_{\|}(\lambda) + E_{\perp}(\lambda)]/2 = \text{l.d.}/2 + \log \frac{1 + 10^{-\text{l.d.}} + J_0(\delta_0)(10^{-\text{l.d.}} - 1)}{2i_{dc}(\lambda)} \tag{4}$$

where $J_2(\delta_0)$ and $J_0(\delta_0)$ are the Bessel functions of the programmed modulator phase shift δ_0, $T_{\|}(\lambda)$ and $T_{\perp}(\lambda)$ and the transmissions of the two plane components, and S is the recorded l.d. signal. The experimental evaluation methods of Eq. 3 are described in Ref. 1.[3a] If the sample is rotated to an orientation which gives zero l.d. signals, Eq. 4 is simplified into the very compact and useful relation

$$[E_{\|}(\lambda) + E_{\perp}(\lambda)]/2 = -\log i_{dc}(\lambda) \tag{5}$$

which provides the "average absorption" directly from measurement of the direct current.[3b] All the commercial dichrographs able to run circular dichroism (c.d.) spectra by a modulated method can be easily converted to l.d. measurements. In the case of non-photoelastic modulators, conversion of the two right- and left-circularly polarized components is achieved better by a $\lambda/4$ achromatic device.[4] L.d. attachments for piezoelastic modulators are now also commercially available.

Liquid crystalline solvents provide the safest and most effective way of imparting to any molecule the partial orientation required to run its l.d. spectrum. The good transparency to U.V. radiation assured by bicyclohexyl derivatives like nematic ZLI-1167 (E. Merck), allows l.d. spectra of the solute molecules to be recorded down to 200 nm. Orientation of the sample can be obtained by the usual orienting techniques such as cell surface coating[1] and electric[4] or magnetic fields.

l.c.-l.d. SPECTRAL INTERPRETATION

9,10-Diazaphenanthrene molecules, oriented with respect to two plane-polarized components as depicted in Figure 2, are expected to display negative linear dichroism bands, centered at 350 and 390 nm, corresponding to the short-axis in-plane (a) and out-of-plane (b) polarized transitions respectively, and a positive l.d. corresponding to the long-axis polarized band (c). The shape of the l.d. spectra is in fact determined by the angular deflections of the averaged orientations of the directions of the transition moment with respect to the two polarization planes of the incident radiation. If the molecular orientation inside the sample is known, the directions of the transition moment within the molecular frame are easily obtained, or, on the other hand, if the transition moment directions are known, information about the molecular orientation preferred, is accessible.

Qualitative interpretations, like those mentioned above for 9,10-diazaphenanthrene, are normally suitable for polarization studies if the solute symmetry simplifies the task, and are based on orientational predictions by a "shape-model" approach.[1,4]

Quantitative handling of the results is expressly required when overlapping of differently polarized absorptions does occur, either owing to overlapping transitions or to vibronically-induced mixing of excited states. By a technique similar to that used in the evaluation of the composition of a mixture on the basis of its absorption spectrum, reduction procedures for the data allow determination of the S_{uu} order parameters and $A_u(\lambda)$ absorption components along the u-molecular axis. Linear combinations (Eq. 6)[1]

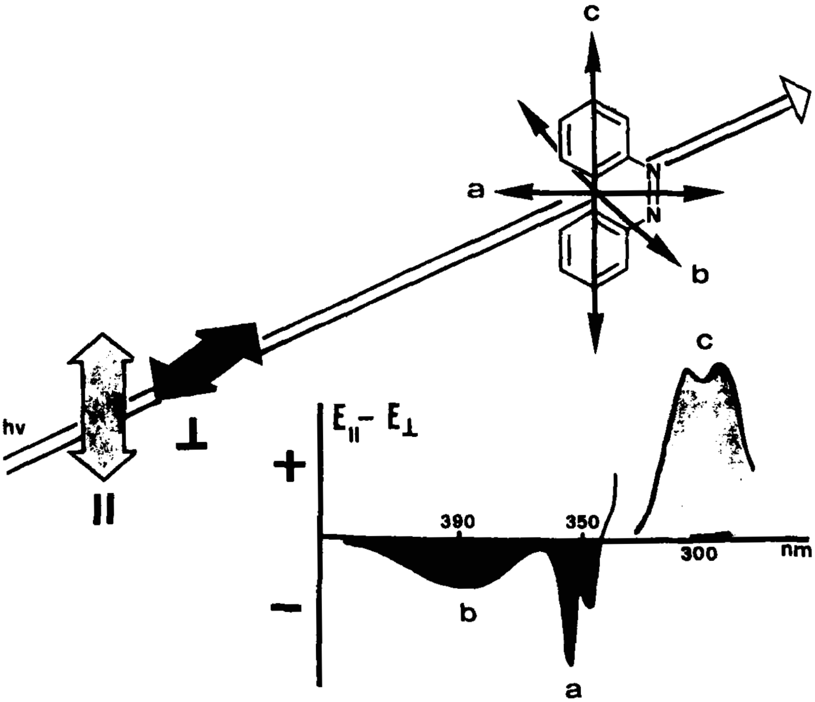


FIGURE 2 The l. d. ($E_{\parallel} - E_{\perp}$) spectrum sketched in the lower part corresponds to the depicted orientation of 9,10 diazaphenanthrene with respect to two, labelled parallel (||) and perpendicular (⊥), plane polarized light components. The (a), (b) and (c) are the directions of the short-axis in-plane, out-of-plane, and long-axis transition polarizations respectively.

of the l.d. and "average absorption" spectra are computed by a trial-and-error method (see Figure 3) in order to get the different $d' = d'_u$ values for which the contributions of the u polarized transitions to the l.d. spectrum relatively disappear

$$[E_{\parallel}(\lambda) - E_{\perp}(\lambda)] - \frac{d'}{2}[E_{\parallel}(\lambda) + E_{\perp}(\lambda)] = \sum_u S_{uu}A_u(\lambda) - \frac{d'}{3}\sum_u A_u(\lambda) + \frac{1}{2}\sum_u A_u(\lambda)S_{uu} \qquad (6)$$

The S_{uu} order parameters are obtained by Eq. 7.

$$S_{uu} = \frac{2d'_u}{6 - d'_u} \qquad -2 < d' < +2 \qquad (7)$$

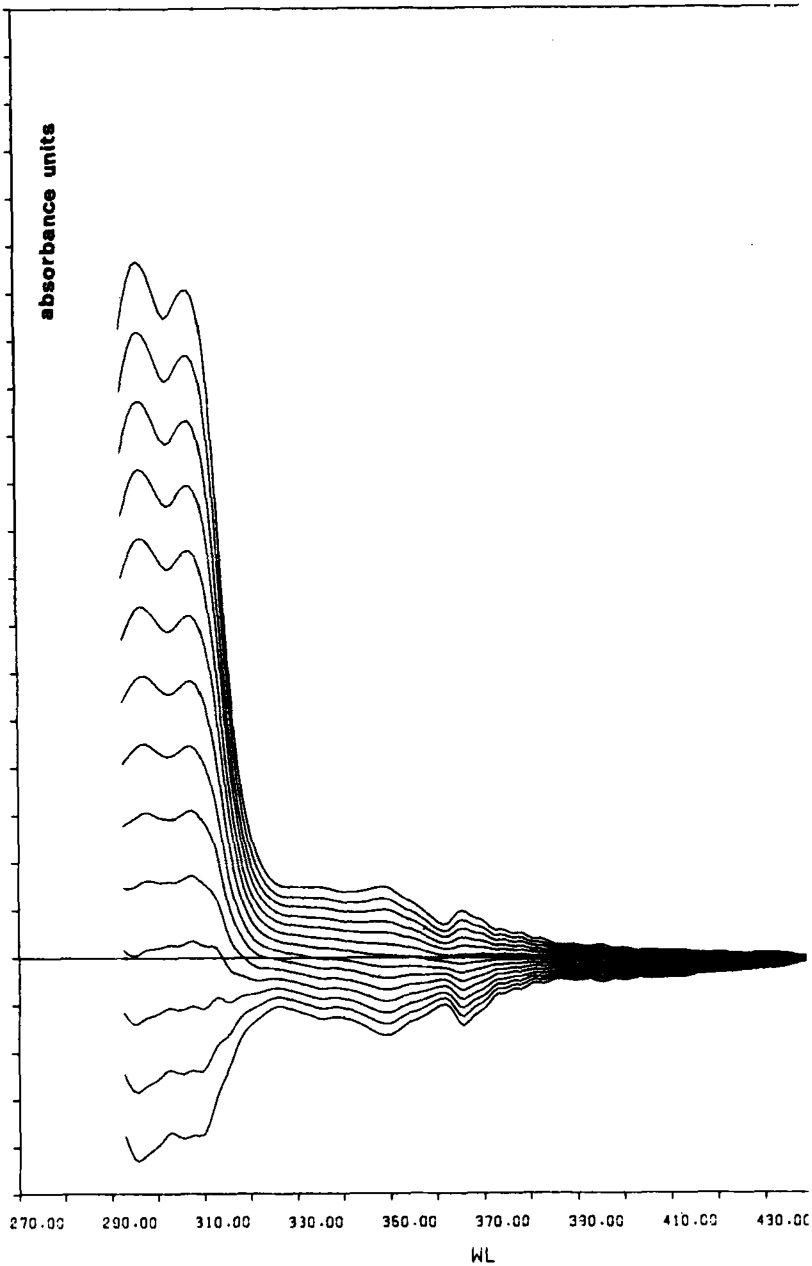
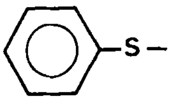


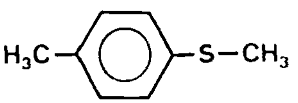
FIGURE 3 An example of plotted solutions of Eq. 6 from l. d. and absorption spectra of 9,10 diazaphenanthrene. For $d' = 0.5$, the contributions of the (c) long-axis polarized transition, centered at about 300 nm, are the closest to zero. The d'_c value is thus considered to be 0.5 and $S_{cc} = 0.18$ is in this case obtained.

SOME APPLICATIONS OF THE L.C.-L.D. INFORMATION REGARDING THE SYMMETRY OF ELECTRONIC STATES

Interpretations of the circular dichroism (c.d.) spectra of chiral compounds expressly require knowledge of the polarizations of the transitions under investigation. We are all aware that any chiral molecule can be depicted as a structure wherein the different chromophores are spirally framed (Figure 4) and that its c.d. spectra can be analyzed by taking into account the electrostatic coupling of the transition-charge-distributions within the different chromophores.[5] In the exciton approach, theoretical c.d. predictions are available provided that the directions of the transition moments of the chromophores are known. By l.c.-l.d., the transition charge distributions of any single chromophore are studied and the resulting information is composed within the global chiral structure of the molecule to compute its overall transition charge distributions.

It is very helpful to this end to use an artifice that we have labelled "*substitution approach*."[1] l.c.-l.d. spectra of the same chromophore variously oriented with respect to the light beam can allow the polarization of all the transitions investigated to be assigned. By adding, for example, a methyl group at the *para*-position of the phenylthio-chromophore (I), methyl *p*-tolyl sulphide (II), for example, is provided with a long-axis more elongated than that of unsubstituted thioanisole and so is more effectively aligned with the direction of the sample orientation: the long-axis polarized transitions can be easily distinguished from those associated with the short-axis (in-plane and out-of-plane) on the basis of the different signs of their l.d. signals, positive for the former, negative for the latter. The out-of-plane polarizations could be easily recognized by their negative l.d. using a disc-shaped derivative of the same phenylthio-chromophore: methyl mesityl sulphide (III) is a very suitable model structure. The assignments of all the transitions in the near-U.V. for the thioanisole and the first experimental evidence of the general sequence ${}^1L_b$, ${}^1L_a$, ${}^1B_b$, ${}^1B_a$, theoretically forecast for the *p*-disubstituted benzenes by Mc. Glynn *et al.*,[6] were achieved by these l.d. data.


(I)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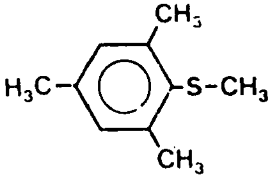

(III)

A chromophore can be "dressed" by substituents with small spectroscopic effects (the methyl group is normally the most suitable) in order

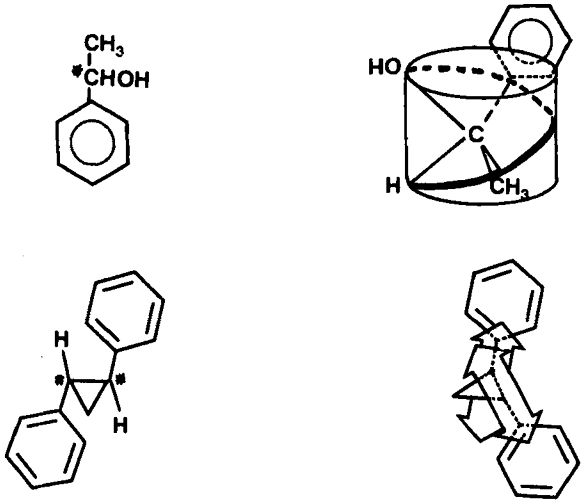
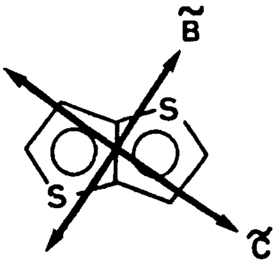


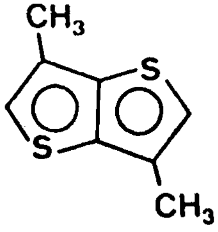
FIGURE 4 Spiral or propeller models of chiral molecules.

to get a disc- or rod-like overall shape of the resulting substituted molecule. The C_{2V} symmetry of the phenylthio-chromophore rules out rotation of the transition moment because of its different substitution patterns.

The disc-shape and orientation of thiophthen (IV) has allowed disclosure of a weak new band between the two equally-positively signed l.d. bands of the $\tilde{B}$ and $\tilde{C}$ transitions.[1] A positive and a negative l.d. for the $\tilde{C}$ and $\tilde{B}$ bands, respectively, have been achieved by methyl-disubstitution of thiophthen (V) along the $\tilde{C}$ transition moment direction: the assignments of the two bands have been obtained in this way (see Figure 6, Ref. 2). In this case the symmetry of (IV) and (V) does not help to rule out transition moment rotations that may be due to the methyl substitution, and to this end we have been obliged in this case to apply to a theoretical MO–CI description of the B_u states involved in the $\tilde{B}$ and $\tilde{C}$ transitions. By taking into



(IV)



(V)

account local perturbations in the oscillating charges of the one-electron transitions relevant in the C.I. descriptions of the states (see Figure 4, Ref. 2), we demonstrated how the l.d. of both thiophthen (IV) and 3,6-dimethylthieno [3,2-*b*]-thiophen (V) can be correlated in order to get a complete assignment of the U.V.-visible transitions of the thiophthen chromophore.

The l.c.-l.d. spectrum of 9,9′-Spiro[9*H*-fluorene] (S. B. F.) has allowed an experiment to be planned and performed which has demonstrated how *chirality can be a property of some states of a molecule only*, i.e., how an "achiral" molecule can become chiral in an excited state.[7] Since the middle of the last century,[8] it has been well known that the non-superposability of an object and its mirror image is the necessary condition for optical activity. In other words chirality requires pure rotational symmetries (I, O, T, D_p, C_p).

S. B. F., which is constituted by two perpendicular fluorene units linked by a spiro-junction, (see Figure 5) belongs to the D_{2d} symmetry group and, therefore, is expected to be achiral. On the other hand, on the basis of the Jahn-Teller theorem, S. B. F. is expected to be unstable with the D_{2d} geometry in a degenerate electronic state, but stable with a D_2, and hence chiral, geometry. The E-degeneracy of the lowest energy excited states of S. B. F. has been demonstrated by the negative l.d.'s of the corresponding bands, down to 240 nm, of the spectrum of S. B. F. dissolved and oriented by a ZLI-1167 mixture. The band assignments to E states, xy polarized, was based on the assumption that the preferred S. B. F. orientation was that depicted in Figure 5. The correctness of this assumption was further confirmed by the MCD spectrum of SBF dissolved in an isotropic solvent where the degeneracy of the above transitions was clearly displayed by a sequence of A terms.[9] Hence SBF, when dissolved in an isotropic medium, in its first excited state behaves as a racemic mixture of two degenerate conformational enantiomers with P and M geometry (see Figure 6). A chiral medium can discriminate between the P and M structures and stabilize one with respect to the other, thus allowing recording of the c.d. of the transitions to the single chiral states. This goal was achieved by using *l*-diethyl tartrate as chiral solvent and a preferential stabilization of the P enantiomeric forms resulted.

SOME APPLICATIONS OF THE L.C.-L.D. INFORMATION REGARDING THE ORIENTATION OF SOLUTE MOLECULE

Distortions induced in solute molecules by the anisotropic solvation within liquid crystalline solutions can be revealed by the l.c.-l.d. technique with

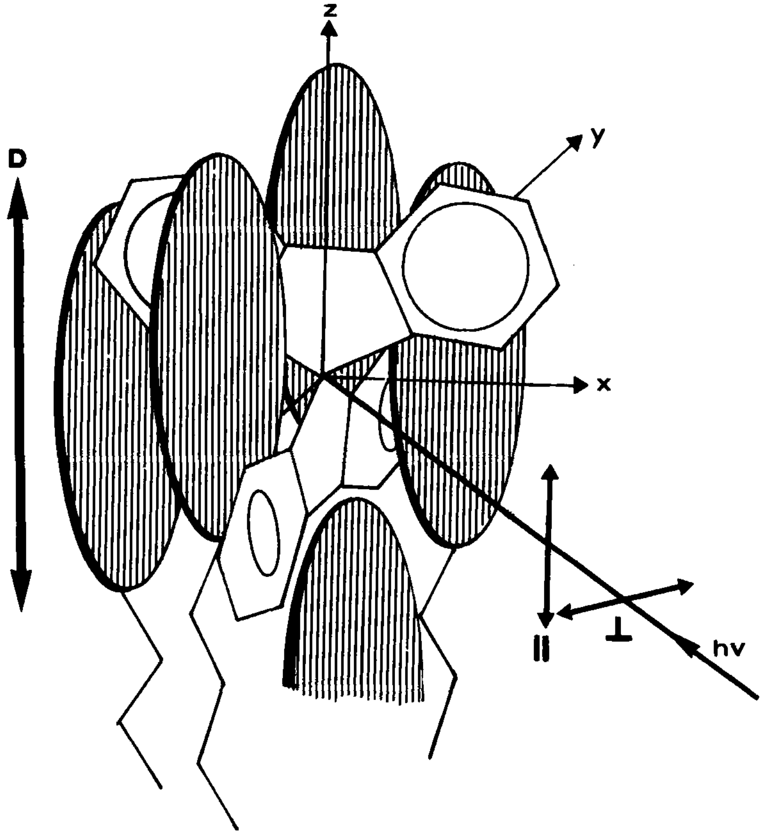


FIGURE 5 Preferred orientation of a 9,9′-Spiro [9*H*-fluorene] molecule with respect to the director (**D**) of a macroscopically aligned nematic solution. The plane perpendicularly polarized components of the light beam are depicted also.

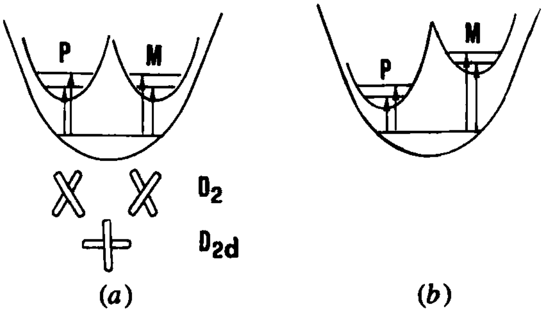
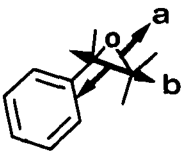


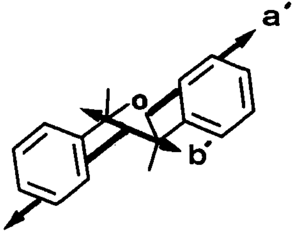
FIGURE 6 Adiabatic potential curves for the ground (D_{2d} symmetry) and excited (D_2 symmetry) states of S. B. F. in isotropic (a) and chiral (b) media. The *P* and *M* excited-state conformational enantiomers, degenerate in case (a), can be discriminated by a chiral solvent (b) and the c. d. signals of the transitions to the single chiral states can now be recorded.

a very simple trick. A cubic molecule is isotropic and cannot choose preferential orientations in a liquid crystalline solvent: therefore no l.d. can be exhibited by such a molecule. But if the anisotropic solute-solvent intermolecular interactions can cause deformations to give a lower symmetry, preferred orientations and optical anisotropy also result. The sigmoid, double-signed l.c.-l.d. spectrum of cubic $W(CO)_6$ dissolved in an oriented, compensated-cholesteric solvent, can be interpreted by a model of uniaxial distortion of the original O_h symmetry towards a trigonal (D_{3d}) or tetragonal (D_{4h}) geometry.[10] Theoretical l.d. predictions for the different distorted geometries have been obtained by an exciton approach, mainly based on symmetry considerations.

Stereochemical models of induction of cholesteric mesophases rely on orientational information. We are all aware that a chiral guest molecule dissolved in a nematic mesophase will exert a twisting power on its close surroundings and macroscopic cholesteric structures will be induced. The local chiral perturbation exerted by the solute is amplified in the bulk by the long-range molecular correlations of the solvent. As equal amounts of enantiomeric guest substances of equal optical purity induce helical structures with opposite chirality and identical pitch, the chiralities of cholesteric phases induced by solute molecules with similar structures can be compared in order to correlate the relative or absolute configurations of the solutes. The configurational correlations must be based on knowledge of the preferred orientations of the chiral solute molecules within the mesomorphic solvent. On this basis, the low twisting power, $\beta = -1.2$ (MBBA), of the chiral oxirane (VII) compared with $\beta = -45$ (MBBA) for (VIII) can be justified on the basis of the different orientational properties of the two molecules. The order parameters $S_{aa} = +0.16$, $S_{bb} = +0.09$ and $S_{a'a'} = +0.31$, $S_{b'b'} = -0.13$ obtained by l.c.-l.d. measurements for (VII) and (VIII) respectively, clearly display preferred disk-like-orientation of the former and rod-like-orientation of the latter.[11] The mutual orientational fluctuations of the solute and solvent molecules are thus reduced for

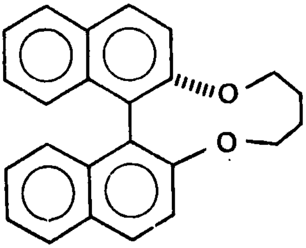


(VII)



(VIII)

(VIII) with respect to (VII): the solute-solvent molecular packing and the amplification in the bulk of the local chiral perturbations will thus be more effective in the former. The model of induction, proposed on this basis, in which the chirality is transferred from the chiral inducer to the nearest neighbor molecule through chiral conformations has been further confirmed by the β's obtained using biphenyl nematic liquid crystals and the l.c.-l.d.'s of variously bridged biaryl molecules[12] like (IX). The axis joining the two naphthyl groups was preferentially parallel to the nematic director (similarly to the S. B. F. behavior depicted in Figure 5) and hence to the biphenyl axis of the solvent.[12] The biphenyl nematic solvents [E7 or PCB(5CB)][†] are expected to be racemic mixtures of chiral non-planar conformational enantiomers. The chiral biaryl dopant can stabilize those conformations of the closest solvent molecules having the same twisted chirality. Macroscopic chiral structures are built by gradually transferring the induced chirality from the nearest neighbor molecules to the next and so on.



(IX)

The temperature dependence of the l.c.-l.d. signals, i. e., of the molecular order parameters, provides wider information regarding the orientational properties of the solute molecules investigated. Theoretical simulations of the observed curves have been attempted in order to identify molecular parameters (like shape or polarizability) able to provide a basis for making quantitative predictions of the molecular orientational biaxiality.[13]

Recent studies of reactivity in liquid crystalline media have demonstrated that tightly ordered Smectic B solvents are able to exert relevant catalytic effects by "driving" the solute, reactant molecules towards collisions with the critical orientations required for reaction to take place.[14–16] The preferred orientations of the reactant molecules in mesomorphic solvents can be studied by the l.c.-l.d. technique.[15]

[†] BDH Chemicals Ltd., Poole, England.

Acknowledgment

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3. (a) In Eq. 5 of Ref. 1, a bracket in the numerator was not shown: the correct form is

$$J_0(d_0) = -\frac{K[S^+_{\max} + S^-_{\max}]}{2S^+_{\max} \cdot S^-_{\max}}$$

(b) Both in Ref. 1 and $10[E_{\|}(\lambda) + E_{\perp}(\lambda)]/2$ has been labelled "isotropic absorption" because the sample is so oriented with respect to the two planes of polarization of the light beam that it behaves as an isotropic material (l. d. = 0). This definition, as privately observed by J. Michl (Salt Lake City), may create confusion with the "absorption of an isotropic sample" $E_{is}(\lambda) = [E_{\|}(\lambda) + 2E_{\perp}(\lambda)]/3$: that is why we now use the notation "average absorption" instead.
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