# The Liquid Crystal–Linear Dichroism (L.c.–L.d.) of Organic Molecules by a Modulation Technique. Part 2.[1] The Phenylthio and Thiophthen Chromophores studied by an ' L.d. Substitution Approach '

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A new development of the l.c.–l.d. technique is presented. The correlation of the experimental measurements and the reduction equations, which display absorption components along the molecular axes, are reported in terms of the quantities recorded by the modulated techniques. To illustrate the application of l.c.–l.d. in assigning the polarizations of electronic transitions, two model applications to a high symmetry (phenylthio) and a low-symmetry (thiophthen) chromophore are presented. In order to characterise the polarizations of the electronic transitions detected, the orientations of the chromophore are variously modified on the basis of a 'substitution approach'. New assignments of the transitions of the phenylthio chromophore are proposed. The l.c.–l.d. spectra of the thiophthen chromophore indicate a new band, previously unreported, and support published theoretical results.

THE interaction between plane-polarized light and matter can give rise to an electronic excitation only when the plane of polarization of the radiation is non-perpendicular to the transition dipole moment of the electronic transition investigated. In oriented samples, the intensity of the absorption of plane-polarized light can give information about the orientation of the investigated molecule in the sample or the transition moments in the molecular framework.

Electronic spectroscopy of isotropic solutions obviously does not provide such stereochemical information which, being linked to the intrinsic linear anisotropy of the absorption of light, can be investigated by l.d. techniques, *i.e.* by studying how two perpendicularly plane-polarized radiations are differently absorbed by an oriented sample.

The l.d. technique has been reviewed by Norden [2] with particular emphasis on biological applications. Thulstrup and Michl have critically analysed [3] l.d. studies of organic molecules dissolved in stretched polymeric films. The use of nematic liquid crystalline matrices has not previously been so widespread owing to the general low transparency to u.v. light and, perhaps, to the required knowledge of the different mesomorphic phases and of their ability to be oriented by electric, magnetic, or surface fields. Liquid crystals containing non-aromatic ring systems [4] now provide mesophases transparent to u.v. light down to 200 nm and easily orientable by a very simple chemical coating of the cell, and these can be used for l.d. studies.[5]

It is thus possible to avoid using cholesteric mixtures oriented by very high electric fields.[1,6] L.d. attachments to commercial dichrographs now allow polarization studies by modulation techniques with a scale sensitivity up to $10^{-5}[E_{\parallel}(\lambda) - E_{\perp}(\lambda)]$/mm [where $E_{\parallel}(\lambda)$ and $E_{\perp}(\lambda)$ are the optical densities for the two perpendicularly polarized radiations] and avoid the lower transparency to u.v. light of the achromatic $\lambda/4$ prism [1,7] inserted in non-photoelastic modulated dichrographs.

In this paper, besides the calibration of the technique, two applications are presented where two chromophores, of $C_{2v}$ and $C_{2h}$ symmetry, are studied by changing their orientation in the liquid crystalline matrix by means of modification of their molecular shape by methyl substitution, on the basis of a general method which can be labelled the ' substitution approach '.

## EXPERIMENTAL

The compounds were dissolved in the nematic phase ZLI 1167 (E. Merck, Därmstadt), a mixture of bicyclohexyl derivatives.

The oriented samples were obtained by coating the walls of a 10 μm cell by *N*-methyl-3-aminopropyltrimethoxysilane [8] (Dow Corning) or by poly(vinyl alcohol) [9] and then by rubbing with tissue paper. The surface treatment lasts for many samples and its persistence and efficiency can be preliminarily checked by a polarized microscope before recording the l.d. spectra. The copper cell-holder, heated at 37 °C † (the liquid crystalline solvent is smectic below 32 °C), allows rotation of the sample on a plane perpendicular to the direction of propagation of the light with an accuracy of *ca.* 0.2° ‡ (control of the rotation to 1° is sufficient).

The l.d. spectra have been recorded by a JASCO-J 500A spectropolarimeter–DP 500 data processor whose l.d. attachment is commercially available but, until now, without any calibration device.

## METHOD

*Calibration of the Measurements.*—The l.d. of an anisotropic sample can be measured by static methods, *i.e.* by producing linear polarized light in a normal spectrophotometer by means of a polarizer, or by dynamic methods, *i.e.* by using a piezoelastic modulator in order to produce a high frequency alternating sequence of two perpendicularly plane-polarized radiations.[10,11]

The sensitivity of the latter methods is at least $10^3$-fold higher than that of the former but the ' true ' l.d. is a rather complex function of the positive or negative recorded signal *S*. The intensity equation 28 of ref. 11 can be converted into a signal expression, such as equation (1). The l.d.

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† °C = K − 273.15.
‡ 1° = (π/180) rad.

$$\text{l.d.} = \frac{2}{\ln 10}\tanh^{-1}\frac{S}{K + J_0(\delta_0)\,S} \qquad (1)$$

symbol stands for the difference $[E_{\parallel}(\lambda) - E_{\perp}(\lambda)]$. The $K$ constant collects all the numeric factors such as the electrical attenuation factors described in ref. 10 and the $J_2(\delta_0)$ Bessel function which, with a maximum around the programmed modulator phase shift $\delta_0 = \pi/2$ (see Figure 2 of ref. 10), can be considered constant. The $K$ constant and the $J_0(\delta_0)$ Bessel function values, which are required in order to estimate the l.d. by equation (1), are determined by the instrumental signal processing and by the programmed half-wave retardation amplitude of the modulator, respectively. While the $K$ constant needs to be determined only periodically, the $J_0(\delta_0)$ function, unlike $J_2(\delta_0)$, has a steep variation around the programmed maximum phase shift $\delta_0 = \pi/2$,[10] and hence its value must be checked for every investigated transition by means of a very simple experimental method.

Corresponding to the wavelength of an absorption maximum, the sample is first rotated until the maximum positive signal ($S^{+}_{\text{max.}}$) is reached and afterwards the sample is rotated by $\pi/2$ and the maximum negative signal ($S^{-}_{\text{max.}}$) is therefore determined. The l.d. spectra corresponding to the two above orientations are recorded and then corrected by equations (1), (4), and (5).

The absolute values of $S^{-}_{\text{max.}}$ and $S^{+}_{\text{max.}}$ are different and $|S^{-}_{\text{max.}}| > |S^{+}_{\text{max.}}|$ as expected from the presence of a negative $J_0(\delta_0)$ value in the denominator of equation (1).

The intense l.d. spectra of reference single crystals of anthracene and naphthalene previously recorded by the static method on a Cary 15 spectrophotometer allowed the calibration of the modulation technique, *i.e.* the determination of the $K$ constant, as follows. By equation (1), the difference between the $S^{+}_{\text{max.}}$ and $S^{-}_{\text{max.}}$ values can be

$$S^{+}_{\text{max.}} - S^{-}_{\text{max.}} = \frac{K\tanh(\text{l.d.}^{+}_{\text{max.}}\ln 10/2)}{1 - J_0(\delta_0)\tanh(\text{l.d.}^{+}_{\text{max.}}\ln 10/2)} - \frac{K\tanh(\text{l.d.}^{-}_{\text{max.}}\ln 10/2)}{1 - J_0(\delta_0)\tanh(\text{l.d.}^{-}_{\text{max.}}\ln 10/2)} \qquad (2)$$

expressed in term of equation (2). For $\tanh \text{l.d.}^{+}_{\text{max.}} = -\tanh \text{l.d.}^{-}_{\text{max.}}$, equation (2) becomes (3). The $K$ value [*]

$$S^{+}_{\text{max.}} - S^{-}_{\text{max.}} = \frac{2K\tanh(\text{l.d.}^{+}_{\text{max.}}\ln 10/2)}{1 - J_0^{2}(\delta_0)\tanh^{2}(\text{l.d.}^{+}_{\text{max.}}\ln 10/2)} \qquad (3)$$

can be computed by equation (4) which has been obtained by assuming that $1 - J_0^{2}(\delta_0)\tanh^{2}(\text{l.d.}^{+}_{\text{max.}}\ln 10/2) = 1$. The

$$K = \frac{S^{+}_{\text{max.}} - S^{-}_{\text{max.}}}{2\tanh(\text{l.d.}^{+}_{\text{max.}}\ln 10/2)} \qquad (4)$$

$J_0(\delta_0)$ values are hence computed by equation (5) and their

$$J_0(\delta_0) = -\frac{K}{2}\,\frac{S^{+}_{\text{max.}} + S^{-}_{\text{max.}}}{S^{+}_{\text{max.}} \cdot S^{-}_{\text{max.}}} \qquad (5)$$

variation around the expected value of $-0.3$ is precisely determined for every transition over the investigated spectral range.

The signs of the recorded l.d. signals with respect to the $Z$ optical axis of the sample (*i.e.* the rubbing direction) are then defined by its orientation with respect to the two directions of polarization of the light.

## RESULTS AND DISCUSSIONS

Our treatment of the experimental data follows very strictly the general approach of Thulstrup and Michl[3] even though the orientation distribution functions and the experimental quantities used by us are different.

The Saupe order parameters ($S_{uu}$) are preferred owing to their particular efficiency in treating l.d. results[6,12] and their widespread use in the liquid crystal field.[13] The reduction equations obtained for the static technique by Thulstrup and Michl[3] are expressly modified in order to obtain more direct and easier processing of the experimental data of the modulated technique: in fact $[E_{\parallel}(\lambda) - E_{\perp}(\lambda)]$ and $[E_{\parallel}(\lambda) + E_{\perp}(\lambda)]/2$, *i.e.* the isotropic absorptions of the oriented sample,[14] are the quantities directly recorded by the instrument.

*Phenylthio: an Example of a High-symmetry Chromophore*.—The symmetry of the chromophore, which is responsible for the electronic transitions under investigation, is considered high when it belongs to a symmetry group (*e.g.* $C_{2v}$) where the $i$ directions of the three perpendicular transition moments are lying, or can be assumed to lie, along the $u = x, y, z$ axis which define the orientation of the whole molecule with respect to the $Z$ optical axis of the sample through a diagonal tensor $S_{uu}$. In this case the 'degree of dichroism' for an isolated vibronic transition is given by equation (6).

$$\frac{E_{\parallel}(\lambda) - E_{\perp}(\lambda)}{E_{\parallel}(\lambda) + E_{\perp}(\lambda)} = \frac{3\,S_{uu}}{2 + S_{uu}} \qquad (6)$$

In the general case of absorption bands with mixed polarization, either owing to vibronically induced mixing of excited states or simply owing to overlapping transitions, formula (7) must be used where $A_u(\lambda)$ is the

$$\frac{E_{\parallel}(\lambda) - E_{\perp}(\lambda)}{E_{\parallel}(\lambda) + E_{\perp}(\lambda)} = \frac{3\Sigma_u A_u(\lambda) S_{uu}}{2\Sigma_u A_u(\lambda) + \Sigma_u A_u(\lambda) S_{uu}} \qquad i = u = x, y, z \qquad (7)$$

absorption component along the $u$-axis. Reduction procedures for the data allow the determination of the $S_{uu}$ values and the $A_u(\lambda)$ spectra. Linear combinations [equation (8)] of $[E_{\parallel}(\lambda) - E_{\perp}(\lambda)]$ and $[E_{\parallel}(\lambda) + E_{\perp}(\lambda)]$ are computed by a trial and error method (t.e.m.) in order to get the different $d' = d_u'$ values for which the contribution of the $u$-polarized transitions to the l.d. spectrum respectively disappear [equation (8)].

$$[E_{\parallel}(\lambda) - E_{\perp}(\lambda)] - \frac{d'}{2}[E_{\parallel}(\lambda) + E_{\perp}(\lambda)] = \Sigma_u S_{uu} A_u(\lambda) - \frac{d'}{3}\left[\Sigma_u A_u(\lambda) + \frac{1}{2}\Sigma_u A_u(\lambda) S_{uu}\right] \qquad (8)$$

This t.e.m. procedure is very clearly presented in ref. 15. The order parameters $S_{uu}$ are obtained by equation (9).

$$S_{uu} = \frac{2\,d_u'}{6 - d_u'} \quad -2 \leqslant d' \leqslant +2 \qquad (9)$$

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[*] If the recorded signal is expressed as $S = l.s.10^{3}$ where $l$ is the deflection (cm) of the pen and $s$ the sensitivity of the instrumental selector, $K$ 22.5 ± 0.5 is obtained by inserting, in equation (4), the absolute values of the reference static measurements $|\text{l.d.}_{\text{max}}|$ for $\text{l.d.}^{+}_{\text{max}}$.

The $A_u(\lambda)$ spectra can be computed by equations (10)—(12) when only two components contribute to the l.d. spectra as happens in particular (a) *for 'planar' molecules* without out-of-plane transitions [equations (10a—c) where $x$, $y$, $z$ are the out-of-plane, the short in-plane, and the long in-plane axes respectively]; (b) *for disc-shaped molecules* where the in-plane $z$ and $y$ axes are orientationally degenerate and hence, being $S_{zz} = S_{yy} = -1/2\ S_{xx}$, out-of-plane $x$-polarized components with negative l.d. can be resolved; (c) *for rod-shaped molecules* where $S_{yy} = S_{xx} = -\frac{1}{2}S_{zz}$ and the long-axis $z$-polarised components can be obtained by equation (12).*

$$A_x(\lambda) = 0 \tag{10a}$$

$$A_z(\lambda) = \frac{[E_{\|}(\lambda) - E_{\perp}(\lambda)](2 + S_{yy}) - 3\ S_{yy}[E_{\|}(\lambda) + E_{\perp}(\lambda)]}{2(S_{zz} - S_{yy})} \tag{10b}$$

$$A_y(\lambda) = \frac{3\ S_{zz}[E_{\|}(\lambda) + E_{\perp}(\lambda)] - [E_{\|}(\lambda) - E_{\perp}(\lambda)](2 + S_{zz})}{2(S_{zz} - S_{yy})} \tag{10c}$$

$$A_x(\lambda) = \frac{3[E_{\|}(\lambda) + E_{\perp}(\lambda)]S_{zz} - [E_{\|}(\lambda) - E_{\perp}(\lambda)](2 + S_{zz})}{6S_{zz}} \tag{11a}$$

$$[A_y(\lambda) + A_z(\lambda)] = \frac{3[E_{\|}(\lambda) + E_{\perp}(\lambda)]S_{zz} - [E_{\|}(\lambda) - E_{\perp}(\lambda)](S_{zz} - 1)}{3S_{zz}} \tag{11b}$$

$$A_z(\lambda) = \frac{3[E_{\|}(\lambda) + E_{\perp}(\lambda)]S_{zz} + [E_{\|}(\lambda) - E_{\perp}(\lambda)](4 - S_{zz})}{6S_{zz}} \tag{12a}$$

$$[A_x(\lambda) + A_y(\lambda)] = \frac{3[E_{\|}(\lambda) + E_{\perp}(\lambda)]S_{zz} - [E_{\|}(\lambda) - E_{\perp}(\lambda)](2 + S_{zz})}{3S_{zz}} \tag{12b}$$

The majority of relatively symmetric organic molecules are ellipsoidally shaped, which is an intermediate case between the two limiting shape models, the disc and the rod.

At $S_{yy} = 0$ we have a turning point between disc-like ($0 \leqslant S_{yy} \leqslant 1/4$) and rod-like molecules ($-1/2 \leqslant S_{yy} \leqslant 0$) whose l.d.s make easily available the identification of out-of-plane and long-axis polarized transitions respectively.

On the basis of the above models, the chromophore under investigation can be 'dressed' by substituents with small spectroscopic effects (*e.g.* methyl) in order to get an overall shape of the resulting molecule able to induce a disc- or a rod-like orientation.

The identification of the different polarizations of the transitions obtained by this 'substitution approach' implies that the effects of the substituents both on the molecular orientation in the matrix and on the direction of the polarizations of the transitions are under control.

Regarding the problem of orientation a disc-like molecule is expected to assume a molecular packing in the matrix which prevents the orientation of its molecular plane perpendicular to the local director, and the orientation axis of a rod-like molecule is expected to lie in the direction of the molecular long-axis.

The effect of substitution on the direction of the transition moments is generally ruled out on the basis of symmetry considerations or by the 'spectroscopic moments' theory [17,18] as applied below to the thiophthen chromophore.

The phenylthio chromophore is an example of a high-symmetry chromophore: it can be considered a $C_{2v}$ monosubstituted benzene chromophore in spite of the very low $G_4$ symmetry [19] of methyl phenyl sulphide (I).

The l.c.–l.d. and the isotropic absorption spectra of (I) reported in Figure 1 have a different shape in the 290 and 215 nm regions, where negative contributions overlapped with the strong positive l.d. of the long-axis polarized transitions can be immediately suggested.

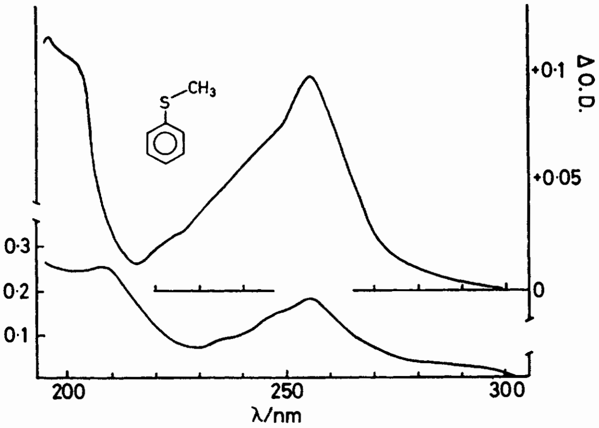

FIGURE 1 Isotropic absorption (lower) and l.c.–l.d. (upper) spectra of an oriented sample of thioanisole (I) in the liquid crystalline matrix

The alignment of the $z$ preferential orientation direction of methyl phenyl sulphide along the long axis of the phenyl ring does not seem as safe as in all the mono-substituted benzenes belonging to the $C_{2v}$ symmetry group because of the non-linear molecular structure and the possible non-planar conformations of the methylthio-group with the phenyl ring.[19-22]

Therefore the spectra of methyl *p*-tolyl sulphide (II) reported in Figure 2 have been recorded in order to analyse a better rod-like-shaped molecule and thus to get a higher long-axis orientation, *i.e.* a better resolution of the long-axis from the short-axis and out-of-plane components in the l.c.–l.d. spectrum.

The presence of out-of-the-chromophoric-plane transitions has been further ruled out by the identical shapes of the l.c.–l.d. and the isotropic absorption spectra of methyl mesityl sulphide (III) (see Figure 3), whose disc-like shape is expected to give a clear resolution of out-of-plane polarized components [23] [see also equation (11)].

The negative contributions to the l.c.–l.d. of (II) are hence assigned to short-axis $y$ polarizations. Applying

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* The different $x$ or $z$ labelling of the non-degenerate axis in disc- and rod-shaped molecules makes equation (11) different from equation (12). When the t.e.m. reduction procedure displays orientational degeneracy of two molecular axes, as in a molecule such as 9,9′-spirobifluorene [16] where neither a disc- nor a rod-shaped structure is evident, the computation of the $A_u$ (λ) spectra can be worked out by either equation (11) or (12) according to the labelling of the non-degenerate molecular axis.

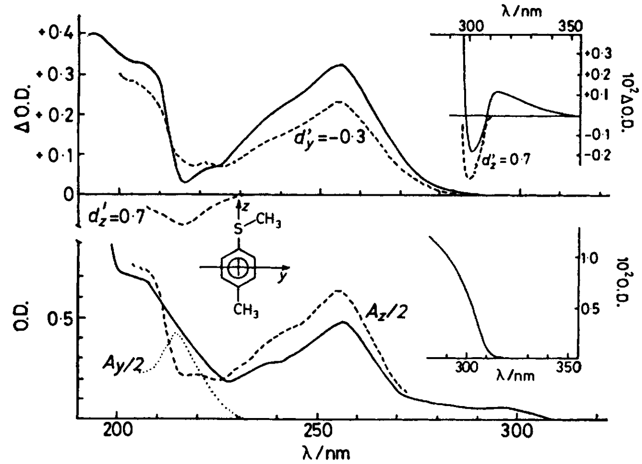

FIGURE 2 Isotropic absorption (lower, solid line) and l.c.–l.d. (upper, solid line) spectra of an oriented sample of methyl *p*-tolyl sulphide (II) in the liquid crystalline matrix. Absorption components (lower, dashed and dotted line) along the *z* and *y* molecular axes computed by the t.e.m. reduction and by equation (10). The reduced spectra (upper, dashed line) $[E_{\|}(\lambda) - E_{\perp}(\lambda)] - \frac{d'}{2}[E_{\|}(\lambda) + E_{\perp}(\lambda)]$ in arbitrary units, for $d_z' = 0.7$ and $d_y' = -0.3$, display and resolve the negative and positive l.d. contributions of polarizations along the short- and long-molecular axes respectively

the t.e.m. reduction procedure of equation (8) to the l.d. spectrum the *z*- and *y*-polarized contributions disappear for $d_y' = -0.3$ and $d_z' = 0.7$. $S_{yy} = -0.11$ and $S_{zz} = 0.26$ obtained by equation (9) are very close to $S_{yy} = -0.103$ and $S_{zz} = 0.286$ of *p*-chlorothioanisole determined by n.m.r. by Veracini.[22]

Having ruled out the presence of out-of-plane transitions the $A_y(\lambda)$ and $A_z(\lambda)$ spectra reported in Figure 2 can be computed by equation (10).

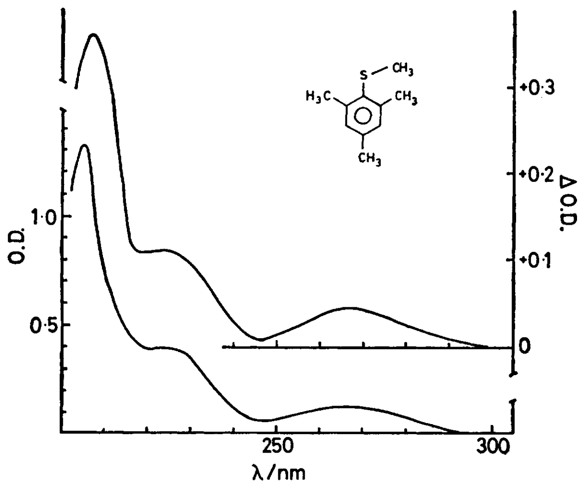

FIGURE 3 Isotropic absorption (lower) and l.c.–l.d. (upper) spectra of an oriented sample of methyl mesityl sulphide (III) in the liquid crystalline matrix

Although the excited states of the investigated transitions certainly contain considerable charge-transfer (c.t.) character [24–26] we prefer to assign all the bands to benzenoid transitions following the line of the general and systematic approach of McGlynn *et al.*[27] to the spectroscopy of substituted benzenes. Their $^1L_b$, $^1L_a$, $^1B_b$, $^1B_a$ general computed sequence of the excited states of *p*-disubstituted benzenes, reported in Figure 2 of ref. 27, finds complete experimental evidence in our resolved l.c.–l.d. spectrum of (II), where alternately short- and long-axis polarizations clearly result.

Any slight deviation of the molecular preferential orientation direction from the long-axis of the phenyl ring can influence the relative intensities of the reduced $A_z(\lambda)$ and $A_y(\lambda)$ spectra, but cannot affect the new assignments of the transitions, on the basis of the actual $C_{2v}$ chromophore symmetry.

*Thiophthen: an Example of a Low-symmetry Chromophore.*—When the *i* transition dipole moments do not lie along the $u = x, y, z$ axes of the orientational system with diagonal tensor $S_{uu}$, the symmetry of the chromophore is low and the absorption components $A_i$ are obviously linked to the $A_u$ values by the relative direction cosines by equation (13). For an isolated vibronic

$$A_u(\lambda) = A_i(\lambda)\cos^2\phi_u{}^i \qquad (13)$$

transition the ' degree of dichroism ' is given by equation (14). For the general case of absorption bands

$$\frac{E_{\|}(\lambda) - E_{\perp}(\lambda)}{E_{\|}(\lambda) + E_{\perp}(\lambda)} = \frac{3\Sigma_u S_{uu}\cos^2\phi_u{}^i}{2 + \Sigma_u S_{uu}\cos^2\phi_u{}^i} \quad u = x, y, z \qquad (14)$$

with mixed *i* polarization equation (15) must be used.

$$\frac{E_{\|}(\lambda) - E_{\perp}(\lambda)}{E_{\|}(\lambda) + E_{\perp}(\lambda)} = \frac{3\Sigma_i\Sigma_u A_i(\lambda)S_{uu}\cos^2\phi_u{}^i}{2\Sigma_i A_i(\lambda) + \Sigma_i\Sigma_u A_i S_{uu}\cos^2\phi_u{}^i} \qquad (15)$$

The t.e.m. reduction procedures following equation (16)

$$\begin{aligned}[E_{\|}(\lambda) - E_{\perp}(\lambda)] - d'/2[E_{\|}(\lambda) + E_{\perp}(\lambda)] &= \\ \Sigma_i A_i(\lambda)S_{ii} - d'/3[\Sigma_i A_i(\lambda) + \tfrac{1}{2}\Sigma_i A_i(\lambda)S_{ii}] &= \\ \Sigma_i\Sigma_u A_i(\lambda)S_{uu}\cos^2\phi_u{}^i - d'/3[\Sigma_i A_i(\lambda) &+ \\ \tfrac{1}{2}\Sigma_i\Sigma_u A_i(\lambda)S_{uu}\cos^2\phi_u{}^i] & \qquad (16)\end{aligned}$$

allow the computing of the single $d' = d_i'$ values for which the contributions of the *i* polarized transitions to the l.d. spectrum disappear and hence the estimate of the order parameter $S_{ii}$ is given by equation (17). The

$$S_{ii} = \frac{2\,d_i'}{6 - d_i'} \qquad -2 \leqslant d_i' \leqslant +2 \qquad (17)$$

relationship which links $S_{ii}$ to $S_{uu}$ cannot allow the deter-

$$S_{xx}\cos^2\phi_x{}^i + S_{yy}\cos^2\phi_y{}^i + S_{zz}\cos^2\phi_z{}^i = S_{ii} \qquad (18)$$

mination of the $\phi_u{}^i$ values without the aid of other techniques, *e.g.* i.r.–l.d., or the introduction of various approximations of theoretical treatments in order to estimate the $S_{uu}$ values.

The u.v. spectrum of thieno[3,2-*b*]thiophen (thiophthen) (IV), a planar molecule with $C_{2h}$ symmetry, has recently been reinvestigated in the vapour and crystal phase.[28,29] The two intense $\pi \longrightarrow \pi^*$ absorption systems centred in the vapour phase at *ca.* 265 and 255 nm and, labelled $\tilde{B}$ and $\tilde{C}$, have been assigned on the basis of *ab-initio* CI computations to two allowed transitions to $B_u$ excited states, polarized in the molecular plane along the $L$ and $M$ directions respectively [29] (see Figure 4).

Although the polarization ratio of the $\tilde{B}$ and $\tilde{C}$ absorption systems cannot be estimated to a high degree of accuracy in the polarized spectra of a single crystal of (IV), the intensity distributions along the crystallographic *a* and *b* axes are different for the two transitions and are in possible agreement with the computed $L$ and $M$ polarizations. Theoretical computations of crystal energy levels and polarization ratios of the $\tilde{B}$ transition on the basis of the experimental data in the crystal phase allowed us to deduce the $L_{\text{exp}}$ polarization.[28] By this approach an out-of-plane polarization fitted the experimental data as well, but this assignment was rejected as incompatible with $\pi \longrightarrow \pi^*$ transitions on the grounds of the intensity of the transition and the similarity of (IV) with naphthalene and naphthalene-like molecules. This assignment is clearly confirmed by the l.c.-l.d. spectrum reported in Figure 5 where the in-plane polarization of $\tilde{B}$ band is clearly shown.

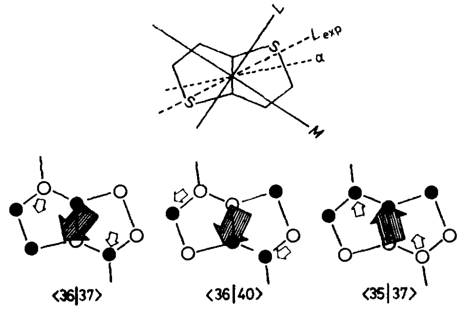

FIGURE 4 Directions of the electronic transition dipoles computed in ref. 29 for the ${}^1B_u \leftarrow A_g$ transition of the thiophthen chromophore (IV) (upper). Charge distributions of the one-electron (36→37, 36→40, 35→37) transitions relevant in the CI description [29] of the ${}^1B_u$ singlet excited states (lower). The hatched arrows sketch the direction of the electric transition moments and the blank ones gives the relative phase and the directions of the local perturbations induced by the methyl substituents in the oscillating transition charges

The l.c.-l.d. spectrum of (IV) also discloses the presence of a weak band which, having a polarization different from those of $\tilde{B}$ and $\tilde{C}$ absorption systems, could be assigned to a new, previously never displayed, transition. The contributions of the B and C transitions disappear at the same time in the t.e.m. reduction procedure which displays the new band: this orientational degeneracy of the directions of polarizations of the two bands could be due to a rod-like orientation of (IV) where an α axis of preferred orientation (see Figure 4) bisects the angle between the $L$ and $M$ directions or to a disc-shaped behaviour. Hence the new band could be polarized either out-of-plane or in the molecular plane along a short-axis direction.

The polarized absorption spectrum reported in ref. 29 actually shows in the corresponding small regions, where we have clearly displayed the new band, a slight variation in the general trend of higher intensity along *a* than along *b* crystallographic axis. The computed states of Table III of ref. 29 allow a reasonable assignment of the new band which can be labelled $\tilde{D}$: the dipole-forbidden $\pi \longrightarrow \pi^*$ singlet transition to an $A_g$ state, expected to occur just between the two $\tilde{B}$ and $\tilde{C}$ transitions, could become allowed by vibronic interaction. In order to remove the orientational degeneracy of the directions of polarization of the $\tilde{B}$ and $\tilde{C}$ transitions in the molecular plane the thiophthen chromophore must be converted into a rod-like molecule where one of the two $L$ or $M$ axes lies closer to the molecular orientation axis than the other. 3,6-Dimethylthieno[3,2-*b*]thiophen (V) [30] has a molecular shape which is expected to induce a preferred orientation along a direction nearly collinear with the $M$ axis and thus the resulting l.d. must be positive and negative for transitions polarized along the $M$ and $L$ directions, respectively. Its l.c.-l.d. spectrum, reported in Figure 6, has just the shape which is expected on the basis of the proposed experimental and theoretical calculations,[29] provided that the directions of the polarization are not affected by the methyl substituents. On the basis of the schematic representations of the MOs and by the description of the electronic states of Figure 6 and Table III of ref. 29, the 'polarization diagrams' of the $\langle\phi_{gr}|\phi_{ex}\rangle$ charge distributions of the three one-electron transitions ($36 \longrightarrow 37$, $36 \longrightarrow 40$, $35 \longrightarrow 37$) which are relevant in the CI description of the $B_u$ singlet excited states are obtained and reported in Figure 4. The directions of the local perturbation at the 3- and 6-positions induced by

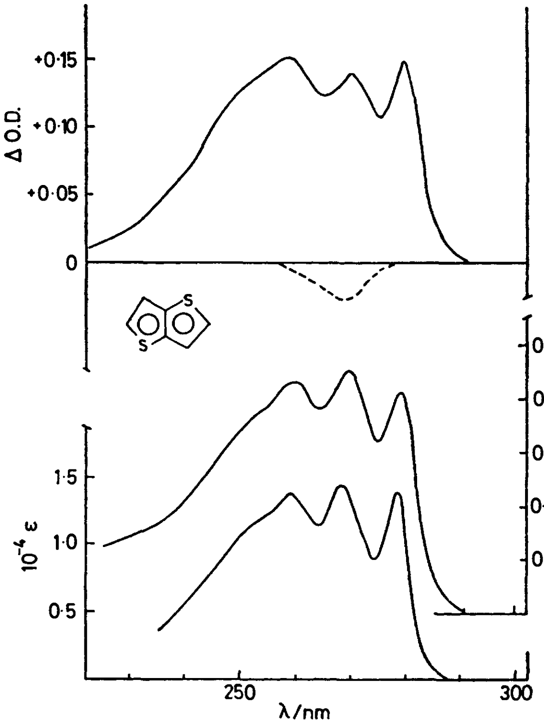

FIGURE 5 Isotropic absorption spectra of a cyclohexane (lower, left side scale) and of an oriented liquid crystalline (middle, right side scale) solution of thieno[3,2-*b*]thiophen (IV). The l.c.–l.d. spectrum is reported in the upper part (solid line) with the $[E_{\|}(\lambda) - E_{\perp}(\lambda)] - 0.37\,[E_{\|}(\lambda) + E_{\perp}(\lambda)]/2$ curve (dashed line, arbitrary units) which clearly displays the presence of the new band

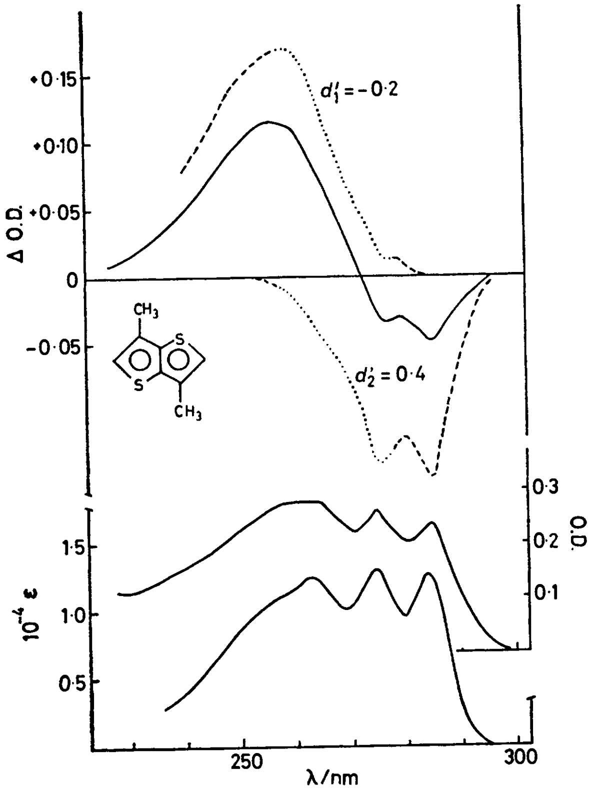

FIGURE 6 Isotropic absorption spectra of a cyclohexane (lower, left hand side scale) and of an oriented liquid crystalline (middle, right hand side scale) solution of 3,6-dimethylthieno[3,2-*b*]-thiophen (V). The l.c.–l.d. spectrum is reported in the upper part (solid line) with the $[E_{\parallel}(\lambda) - E_{\perp}(\lambda)] + 0.2\,[E_{\parallel}(\lambda) + E_{\perp}(\lambda)]/2$ and $[E_{\parallel}(\lambda) - E_{\perp}(\lambda)] - 0.43\,[E_{\parallel}(\lambda) + E_{\perp}(\lambda)]/2$ curves (arbitrary units, dashed and dotted, see text) which display the opposite-signed l.d. contributions of the *B* and *C* transitions

the two methyl groups in the oscillating charges associated with the above three different one-electron transitions can be considered practically collinear with the electric transition moment of the unsubstituted derivative (IV). Hence the changes in magnitude of the component transition moments at the position of substitution can affect the resulting intensity but not the polarization of the transition. Furthermore, the intensity of the $\tilde{B}$ and $\tilde{C}$ transitions is so high as to be expected to remain unaffected by the presence of the two methyls: this expectation has been confirmed by the isotropic spectra of (IV) and (V) in cyclohexane reported in Figures 5 and 6 whose integrated intensities are practically the same.

The t.e.m. reduction procedure [see equation (16)] in the region where neither the weak $\tilde{D}$ band nor overlapping of the different transitions are expected to be present gives $d'_1 = -0.2$, $S_{11} = -0.06$, and $d'_2 = +0.43$, $S_{22} = +0.15$ for the $\tilde{B}$ and $\tilde{C}$ transitions respectively. In the region where the l.c.–l.d. spectrum of (IV) displays the presence of the $\tilde{D}$ transition, the t.e.m. reduction can be performed only by neglecting the contributions of this latter band: the computed values are thus reported in Figure 6 by dotted lines whose shape can in principle be affected by this approximation.

The complete solution of the problem, *i.e.* the knowledge of the two $\phi_u{}^i$ values, requires the estimate of the two $S_{uu}$ order parameters by other techniques: in fact in this case equation (18) gives rise to the $\tilde{B}$ and $\tilde{C}$ transitions to a problem with two equations (19) and four unknowns. Nevertheless even if all the unknowns cannot

$$\begin{cases} S_{zz}\cos^2\phi_z{}^1 + S_{yy}\sin^2\phi_z{}^1 = S_{11} \\ S_{zz}\cos^2\phi_z{}^2 + S_{yy}\sin^2\phi_z{}^2 = S_{22} \end{cases} \qquad (19)$$

be estimated without the aid of other spectroscopic or theoretical techniques, it has been shown how the ' substitution approach ' in the case of a low-symmetry chromophore can both easily allow the discovery of the presence of out-of-plane transitions, when a disc-like orientation is expected, and clearly resolve in-plane polarized transitions, when rod-like behaviour in the liquid crystalline matrix is induced by the substituents.

*Conclusions.*—Our first use of the l.c.–l.d. method was formerly presented in Part 1 with selected applications in order to give a general idea of the usefulness and limitations of the technique. With the same purpose the relevant experimental improvements now achieved are reported in this paper with model applications to a high- and to a low-symmetry chromophore. In order to identify all the different polarizations of the electronic transitions, the molecular shapes, and thus the orientations in the liquid crystalline matrix of the chromophores, are variously modified on the basis of a general method labelled the ' substitution approach '. By the l.c.–l.d. results reported in this paper new assignments of the transitions of the phenylthio-chromophore have been suggested and the presence of a new band, previously not identified, has been demonstrated in the thiophthen chromophore.

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