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Liquid Crystals

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All-trans 2,7-dialkylperhydrophenanthrene as a solvent for measurements of helical twisting power and linear dichroism

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All-trans 2,7-dialkylperhydrophenanthrene as a solvent for measurements of helical twisting power and linear dichroism

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The values of twisting power of a chiral bridged binaphthyl and (+)-trans-stilbene oxide in a rigid hydrocarbon perhydrophenanthrene nematic are much smaller than in conformationally flexible nematics, indicating the importance of the solvent structure for cholesteric induction. The perhydrophenanthrene phase constitutes an excellent solvent for linear dichroism measurements of anthracene but it is unable to orient 9,9′-spirobifluorene.

1. Introduction

The ability of chiral solutes to twist a nematic solvent, referred to as the helical twisting power, is currently defined as $\beta = (p.c.r)^{-1}$, where p is the pitch of the induced cholesteric, c is the concentration of the dopant and r its enantiomeric excess. In the field of stereochemistry, the phenomenon of cholesteric induction allows several applications ranging from the detection of traces of chiral compounds [1–3] to configurational [4] and conformational [5] analysis. In general, the values of β observed are higher in liquid crystal solvents which have a structural similarity with the chiral inducer [4].

Molecular models for the origin of the twisting power in thermotropic nematics are essentially of two types: in the first, the molecules of the nematic are considered as achiral and the chiral guest prevents parallel stacking of the host by means of different intermolecular interactions with the molecules in its neighbourhood [6, 7]. In the second model, the chiral guest favours chiral non-planar conformations of the solvent molecules adjacent to it; these again induce chiral conformations in the near neighbour molecules of the solvent and so on [8, 9]. In particular, chiral biaryls were shown to induce cholesteric phases in biphenyl-type liquid crystals, mainly with a mechanism of this type (cf. figure 1). Analogous mechanisms with undistorted or distorted micelles were proposed by Radley and Saupe [10] to explain cholesteric induction in amphiphilic nematics. In the case of thermotropics, the second model is able to explain the transfer of chirality to the bulk of the solvent and solvent effects. Furthermore, it seems more appropriate in the case of high values of the twisting power where a very low concentration of chiral dopant is able to induce a compact cholesteric structure. Both models have been supported by studies of the orientation of the solute by linear dichroism [6–9] and N.M.R. measurements [11].

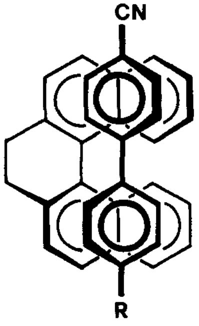
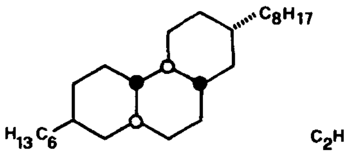
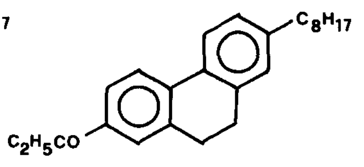


Figure 1. Interaction of a chiral biaryl with a biphenyl-type liquid crystal.



(1)



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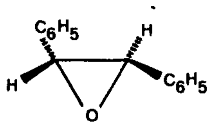
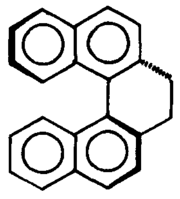


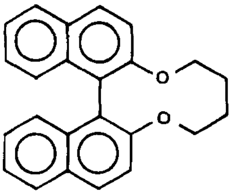
(+)-1R,2R

(3)

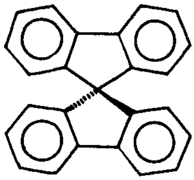


(+)-S

(4)



(5)



(6)

Recently, we have synthesized [12(a, b)] a new class of nematic liquid crystals based on the rigid all-trans perhydrophenanthrene core bearing trans alkyl groups in positions 2 and 7. While most available nematic derivatives contain a central core or highly polarizable substituents which can adopt non-planar chiral conformations (for example, biphenyls, Schiff bases and azoxy derivatives), the all-trans perhydrophenanthrene nucleus is strictly rigid and lacking polar or polarizable groups. Furthermore gauche chiral conformations of the alkyl side chains are unlikely to be highly populated and to have important effects on the solute–solvent interactions. Measurements of the twisting power in nematics of this type should give information as to the relative importance of the two mechanisms.

2. Results and discussion

In the present work we have utilized the all-trans 2-hexyl-7-octylperhydrophenanthrene (**1**) (racemic compound), which is nematic in a relatively large range (T_{CN} 75°C–T_{NI} 91·5°C). The values of β were also measured in several commercially available liquid crystals and in particular in the dihydrophenanthrene ketone (**2**) [12 (c)], related with (**1**), but containing aromatic nuclei and a ketonic polar group. This bridged biphenyl solvent can adopt conformations of opposite chirality but their interconversion is certainly not as easy as in open chain biphenyls.

In the table the values of the twisting powers of R-(+)-trans-stilbene oxide (**3**) and of S-(+)-9,10-dihydrodibenzo-[c,g]-phenanthrene (**4**) in various nematic solvents (including (**1**) and (**2**)) are reported. Derivatives (**3**) and (**4**) were selected; as in previous works they were shown to interact specifically with Schiff bases [8] and biphenyl-type liquid crystals [9] respectively. Both derivatives showed very high values of β and were considered to induce cholesteric phases following a mechanism of the second type. As a comparison the values of β in other solvents are also reported. While the handedness of the induced cholesterics are the same in all solvents, the values of β in solvent (**1**) are much smaller; that of trans-stilbene oxide (**3**) undergoes a twentyfold decrease and that of the bridged binaphthyl (**4**) an approximately fourfold one with respect to the maximum values observed in MBBA and K 15 respectively.

Twisting powers of optically active compounds (**3**) and (**4**) in different nematic liquid crystals.

	$\beta/\mu m^{-1}$‡	
Solvent†	(**3**)	(**4**)
(**1**)§	$-1\cdot7\pm0\cdot8$	$+19\pm5$
(**2**)§	-29 ± 7	$+27\pm6$
MBBA	-37 ± 3	$+37\pm3$
K 15	-34 ± 3	$+76\pm5$
E 7	-32 ± 2	
Phase IV	-28 ± 2	
ZLI 1167		$+42\pm3$

† MBBA: 4-methoxybenzylidene-4′-n-butylaniline from Reidel–de Haan; K 15: 4-cyano-4′-n-pentylbiphenyl from BDH; E 7: a mixture of 4-cyano-4′-aryl and 4′-n-alkylbiphenyl from BDH; Phase IV: 4-methoxy-4′-n-butylazoxybenzene from Merck; ZLI 1167: a mixture of 4-cyano-4′-n-alkylbicyclohexane from Merck.

‡ βs were measured at the same reduced temperature (T/T_{NI} = 0·96); a positive value of β corresponds to a right-handed cholesteric (P).

§ Owing to the small quantity of liquid crystal solvents available and the irregular shape of the disclination lines always observed with these solvents, the error in the determination of the twisting power is greater than in the other cases.

Although the values of the twist elastic constant K_{22} for solvents (**1**) and (**2**) are not known, it seems unlikely that the differences of β observed are related to this parameter [13]. At the same reduced temperature the differences of K_{22} among the most widely investigated liquid crystals (MBBA, K 15, PCH) are in all cases smaller than the variation of β with the solvent observed here and in other cases [13]. The values measured in (**2**) are higher than those in (**1**) and smaller than in 4-cyano-4′-n-pentylbiphenyl. This was somehow expected as the dihydrophenanthrene molecule is non-planar but the rotation about the biphenyl axis is considerably hindered by the aliphatic bridge. These data therefore support the major importance of a mechanism of the second type.

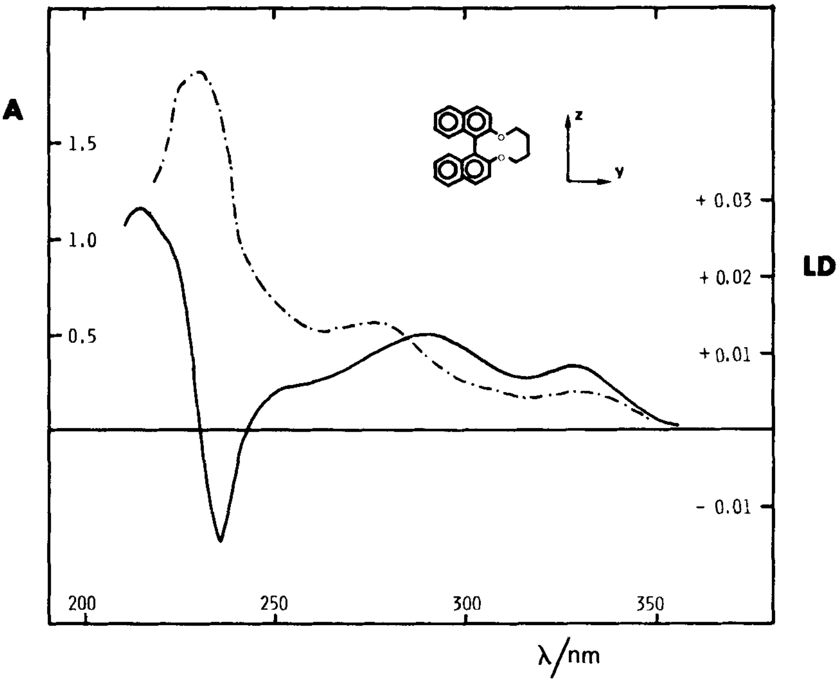


Figure 2. The average absorption [$(A_\parallel + A_\perp)/2$, —·—·—] and linear dichroism [$A_\parallel - A_\perp$, —] spectra of an oriented sample of compound (5) in the nematic (1) recorded at $T = 353\,K$.

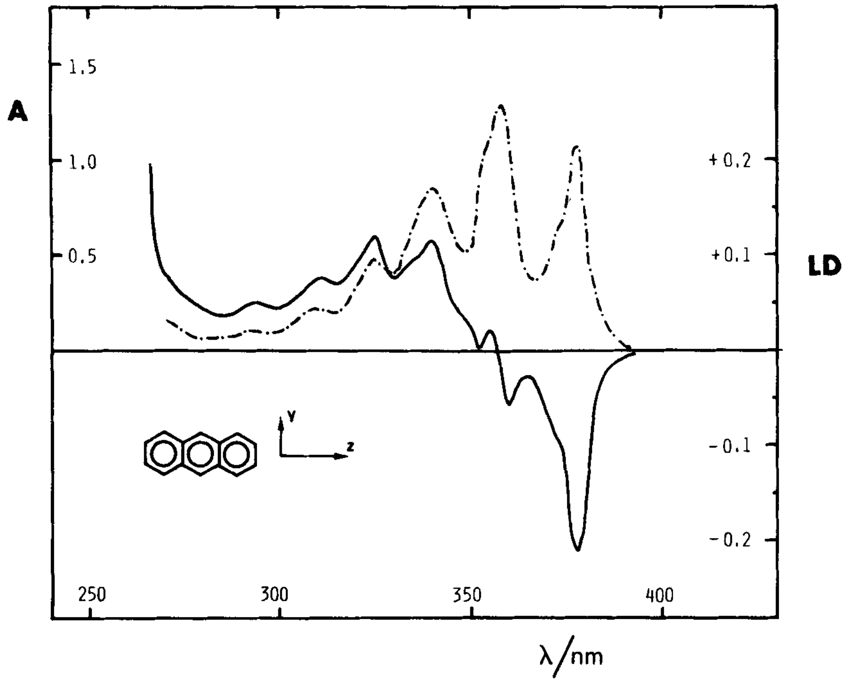


Figure 3. The average absorption [$(A_\parallel + A_\perp)/2$, —·—·—] and linear dichroism [$A_\parallel - A_\perp$, —] spectra of an oriented sample of anthracene in the nematic (1) recorded at $T = 353\,K$.

As the value observed for derivative (**4**) in the nematic (**1**), even if the smallest of the group of solvents, is not negligible, we have measured the linear dichroism of the structurally similar racemic bridged binaphthyl ether (**5**) in the same solvent, in order to detect its possible orientation in this nematic matrix; this is shown in figure 2. In the nematic phase ZLI 1167 (a mixture of bicyclohexyl derivatives) this molecule is oriented with the twofold symmetry axis perpendicular to the nematic director [9]. Although the orientational order is about one order of magnitude smaller than in ZLI 1167 (the order parameters, S_{zz}, are 0·25 in ZLI 1167 and 0·015 in the nematic (**1**)), the linear dichroism spectrum in (**1**) is easily measured. With respect to the spectrum observed in ZLI 1167 there is a marked decrease in the intensity of the negative band at *c.* 240 nm and a relative increase of the two positive bands at *c.* 290 and 330 nm; the effect of temperature variations is negligible. As a reference we have measured the LD of anthracene in ZLI 1167 and in perhydrophenanthrene (**1**); this is shown in figure 3. The two spectra are very similar as are the order parameters (in ZLI 1167: $S_{zz} = 0{\cdot}18$, $S_{yy} = 0{\cdot}08$, $S_{xx} = 0{\cdot}09$; in phase (**1**): $S_{zz} = 0{\cdot}22$, $S_{yy} = 0{\cdot}08$, $S_{xx} = 0{\cdot}15$, the location of the axes is given in figure 3. We have further measured the LD spectrum of 9,9′-spirobifluorene (**6**) whose LD spectrum in ZLI 1167 is reported in the literature [14], but we were unable to detect any dichroic absorption.

These facts seem to be associated with the rigidity of the perhydrophenanthrene nucleus as we now show.

(*a*) Anthracene is planar and its shape is compatible with that of the solvent which results in its strong alignment.

(*b*) In the bridged binaphthyl ether (**5**), the dihedral angle between the two naphthalene planes should be between 30° and 50°, in consequence solvent (**1**) has difficulty in fitting to the non-planar structure of the solute because of the rigidity of its central core. The orientational order is therefore lower and different to that observed in ZLI 1167 which is flexible and can adapt its conformation to accommodate the steric requirement of the solute. The relative decrease of the negative band at *c.* 240 nm (which corresponds to a transition precisely polarized along the twofold symmetry axis) with respect to the two positive bands at 290 and 330 nm (which are connected to transitions which are polarized perpendicularly to the twofold axis) observed in phase (**1**) clearly indicate a modification of the alignment with respect to the solvent ZLI 1167.

(*c*) In 9,9′-spirobifluorene (**6**) the dihedral angle between the two fluorene planes is 90° and the rigid solvent (**1**) is again unable to interact efficiently with this solute, hence no detectable LD is observed. However the spirobifluorene (**6**) is aligned by the flexible bicyclohexyl phase ZLI 1167 which can adopt non-planar conformations allowing close contact and efficient interaction with the solute.

Returning to the twisting power of the binaphthyl derivative (**4**), the small but non-negligible value observed in the perhydrophenanthrene phase could be connected with the contributions from the first mechanism type. There is in fact a strong similarity between the structure of the solvent and that of the lower or upper moiety of the bridged binaphthyl (**3**). The molecules of the solvent could associate with the two planar parts of the solute from the two opposite sides, as is shown in figure 4. This configuration is certainly not the dominant one, but its contribution is consistent with

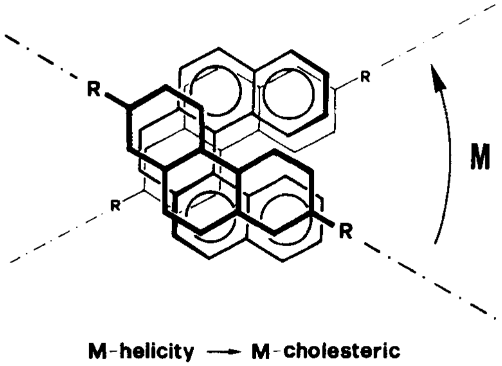


Figure 4. Association of the nematic solvent (**1**) with a bridged binaphthyl solute.

the variations observed in the LD spectrum. The cholesteric handedness deduced is also in agreement with the observed value.

In conclusion, the decrease of the values of β on passing from flexible liquid crystals to the rigid perhydrophenanthrene (**1**) indicates the predominant importance of mechanism 2 for the formation of the cholesteric mesophases induced by derivatives (**3**) and (**4**). In the case of (**4**) the residual value of β could be connected with a contribution from the first mechanism.

3. Experimental

Values of the cholesteric pitch were determined utilizing the lens version [15] of the Grandjean–Cano method. The diameters of the concentric circles were measured with a micrometric scale inserted in the ocular of a standard Zeiss microscope. The temperature stability was $\pm 0{\cdot}3^\circ$C.

The LD spectra $[A_\parallel - A_\perp]$ and the average absorption spectra $[(A_\parallel + A_\perp)/2]$, where $A_\parallel$ and $A_\perp$ are the optical densities of two plane-polarized components parallel and perpendicular to the sample optical axis respectively, were recorded with a JASCO J-500A spectropolarimeter equipped with an LD attachment [16(a, b)].

The aligned samples were obtained by dissolving the compounds in the nematic phases and inserting the solutions in a 10 μm thermostatted cell, the windows of which were previously coated with a surface coupling agent and rubbed with tissue paper in order to give the necessary alignment of the nematic.

The reduction procedure which allows the determination of the order parameters is described in [16(a, b)].

Derivative (**4**), optically pure, was provided by Professor S. F. Mason (London); R-(+)-trans-stilbene oxide, $[\alpha]_D = +350$ ($c = 0{\cdot}5$, benzene), 94 per cent e.e., was prepared as described by Read and Campbell [17].

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