50. A Liquid-Crystal Study of Heptalene

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(21.I.87)

The chiral structure of heptalene is characterised, for a given configuration, by helicities, which are opposite in the direction (x) of the central C(5a)–C(10a) bond and in the direction (y) of a line perpendicular to it, passing through the C(3)- and C(8)-atoms. These two helicities can be experimentally established and differentiated by the handedness of the cholesteric mesophases induced in a biphenyl-type liquid crystal (LC) by chiral heptalenes with substituents favouring the x or y orientation along the nematic director of the LC.

Introduction. – Cholesteric liquid crystals (LC) are described as being comprised of helical aggregates of chiral molecules. As helical structures, they are characterized by handedness and pitch length. Addition of traces of a chiral solute to an achiral nematic mesophase induces the formation of a helical cholesteric macrostructure [1]. The ability of the chiral solute to twist the nematic phase (twisting power, β) is currently defined as

$$\beta = (p \cdot c \cdot r)^{-1}$$

where p is the pitch length [μm], c the concentration (mole of solute per mole of solvent), and r the enantiomeric purity of the chiral dopant. The signs + and – indicate right-handed (P) and left-handed (M) helices, respectively [2]. The value of β is constant in a large interval of concentrations and changes considerably with the nature of the nematic solvent [3].

For high values of β, low concentrations of the chiral dopant can induce a compact cholesteric structure. In this case, a mechanism of cholesteric induction proposed [3] [4] involves the chiral guest favouring chiral non-planar conformations of the solvent molecules adjacent to it, which in turn induce chiral conformations in contiguous molecules of the solvent and so forth. In this way, the chiral information of the dopant is transferred to a large number of host molecules.

In the field of stereochemistry, the phenomenon of cholesteric induction allows several applications ranging from the characterization of polarimetrically not detectable optical activities and chiralities to configurational and conformational analysis [5] [6].

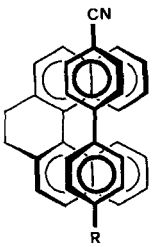


Fig. 1. *Mode of interaction of a chiral binaphthyl and a biphenyl LC molecule*

In particular, it was found that biaryls having (*P*)-helicity induce cholesteric (*P*)-helices in a biphenyl-type LC (*cf. Fig. 1*), *i.e.* the induced helix is homochiral with the guest helicity [4]. Biphenyl-type LC's were found to be a sensitive probe for the configuration of biaryls. They are particularly useful regarding the appropriate spatial orientation of the chiral guest due to the compatibility of the two structures and to the presence of only one single bond, around which rotation of one benzene ring with respect to the other is possible, while for other LC's such as (*E*)-4-butyl-*N*-(4-methoxybenzylidene)aniline (MBBA) the conformational problem is much more complex.

Heptalenes constitute a new class of chiral derivatives. They have recently been resolved [7], their absolute configurations have been determined, and their skeletal features are deduced in detail from X-ray diffraction studies [8]. Heptalenes with substituents in the angular positions (C(1), C(5), C(6), C(10)) have, in solution (*cf.* [8]), a rigid, highly twisted, non-planar structure with C_2 or nearly C_2 symmetry of the C skeleton. The configurations of heptalenes ((*P*) or (*M*)) are attributed according to their helicity along the C(5a)–C(10a) bond [7].

The stereochemistry of heptalenes seems particularly attractive for an LC investigation as, for a given configuration, the heptalene skeleton has helicities which are opposite in the *x* and *y* directions *(Fig. 2), i.e.* the heptalene skeleton has the topological feature of a C_2-loop or propeller (*cf.* Fig. 1 in [8]).

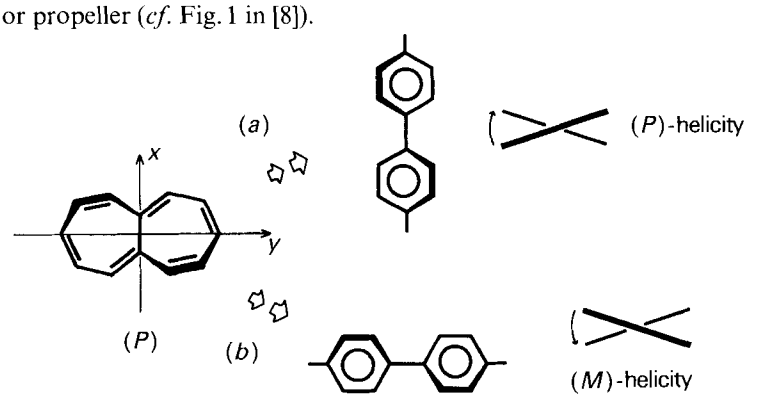


Fig. 2. *Results of the assumed modes of interaction of a* (P)*-heptalene and a biphenyl LC molecule with the nematic director parallel to the* x *axis* (a) *or* y *axis* (b) *of the* (P)*-heptalene*

It is known that, generally, a solute in a LC solvent prefers an orientation with the long axis of the solute parallel to the nematic director [9]. Substituents increasing the molecular dimensions of the heptalene nucleus in the *x* direction should, therefore, favour orientations of the *x* axis along the nematic director and the biphenyl probe should 'feel' the *x* helicity. On the other hand, heptalenes bearing substituents increasing the molecular dimensions along the *y* axis should induce the helicity characteristic of this direction in the biphenyl LC's.

These considerations are clearly supported by a molecular modeling study (*cf.* [10]) of the anticipated interactions. *Fig. 3* shows stereographic projections of the optimum superposition of biphenyl with the heptalene skeleton of dimethyl (*P*)-8-(*tert*-butyl)-5,6,10-trimethylheptalene-1,2-dicarboxylate [8] in the *x* and *y* directions. The twist angles induced in the biphenyl for optimal superposition amount to 65° for the *x* direction and

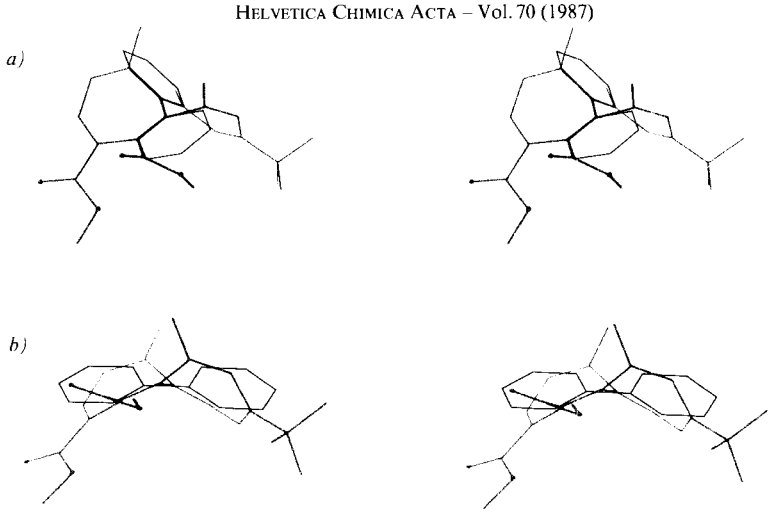
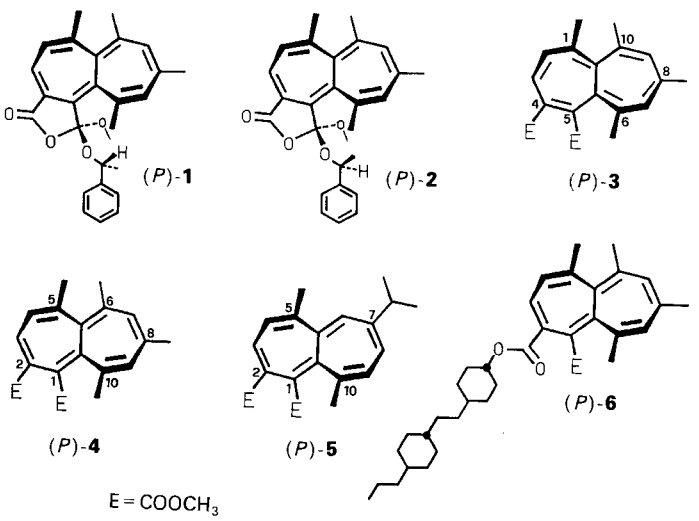


Fig. 3. *Stereographic view of the optimum superposition of biphenyl* (red) *with dimethyl (P)-8-(tert-butyl)-5,6,10-trimethylheptalene-1,2-dicarboxylate* (green) *along the* x (a) *and* y (b) *axis of the heptalene skeleton*

−59.5° for the *y* direction. They correspond very well to the average twist angles in the heptalene around the central C(5a)–C(10a) bond of −115° (including C(1), C(6), and C(5), C(10), respectively) and 65° (including C(1), C(5), and C(6), C(10), respectively) and are near to the minimum twist angle (about 40°) of undistorted biphenyls in solution (see [11] and literature cited therein).

Results and Discussion. – The twisting powers of the heptalenes **1–6** in the nematic biphenyl LC E7[1]) are reported in the *Table*. Obtained absolute values range from *ca.* 1 to 27 μm^{-1}. In particular, derivatives **1**, **2**, and **6** bearing the longest substituents display the



[1]) LC E7 = Eutectic mixture of 4'-aryl- and 4'-alkyl-4-biphenylcarbonitriles.

Table. *Twisting Powers β of Heptalenes* **1–6** *in the LC E7 at Room Temperature*

Compound	Configuration	β [μm^{-1}]
1	*P*	+ 23
2	*P*	+ 19
3	*P*[a])	+ 10
4	*P*[a])	+ 1.5
5	*P*	– 0.6
6	*P*[a])	– 27

[a]) In fact, the enantiomer was measured.

highest values. For **1** and **2**, the β values are very similar, indicating, as pointed out in [5], that the rigid twisted core is important, and that, on the other hand, the orientationally flexible chiral centres play only a little rôle in the cholesteric induction. Both **1** and **2** induce cholesteric (*P*)-helices, *i.e.* the helicity is homochiral with the chirality along the *x* axis. In fact, their substituents increase the molecular dimension mainly along the *x* direction, and this should favour an *x* orientation along the nematic director. On the other hand, derivative **6** has an extended substituent situated mainly in the *y* direction (clear indication by the molecular models); accordingly, its twisting power is opposite and reflects the helicity along the *y* axis.

The high values of β for **1**, **2**, and **6** are easily attributed to their definite alignment imposed by the long-chain substituents added to the heptalene nucleus; the latter can *per se* be compared to an oval disk in which the *x* and *y* orientations are nearly equivalent [12] [13].

Accordingly, the values observed for derivatives **3**, **4**, and **5**, in which the heptalene nucleus has relatively simpler substituents, are smaller. They reflect opposite contributions from the *x* and *y* helicities which, to a certain extent, cancel each other. In particular, both derivatives **3** and **4** have CH_3 groups at C(10) and C(6) (*x* direction), while derivative **5** has an H-atom at C(6) and a comparatively larger i-Pr group at C(7) (mainly *y* direction). It is surprising but gratifying that **5** has a twisting power opposite to those of **3** and **4**. The latter have β's reflecting the *x* helicity, while the β of **5** indicates, instead, the *y* helicity.

The difference between the values observed for **3** (β = 10) and **4** (β = 1.5), whose structures differ only in the position of the double bonds, was unexpected. A possible explanation is that derivative **3** is slightly flatter [8] than **4**, allowing a better contact of the biphenyl LC with the chiral inducer [5][2]). However, the polar interactions between the LC solvent and the solute may also change with the torsion angle between the two ester groups (about 0° in **3** in contrast to about 33° in **4**).

To confirm the interpretation of the variation of β with the structure, we have measured the linear dichroism (LD) spectra of racemic **4**, **5**, **6** in the nematic phase *ZLI 1167* (a mixture of bicyclohexyl derivatives) *(Fig. 4)*. This nematic phase is transparent down to *ca.* 200 nm, and it has been verified that the validity of the obtained data concerning the orientation in this LC solvent can indeed be extended to biphenyl-type LC's [4].

[2]) The twist angles induced in biphenyl by an optimum superposition with dimethyl (*P*)-8-(*tert*-butyl)-1,6,10-trimethylheptalene-4,5-dicarboxylate in the *x* and *y* directions of the heptalene skeleton are indeed slightly smaller (63,5° and –58°, respectively) than for the interaction with the double-bond-shifted isomer of the heptalene (*cf. Fig. 3*).

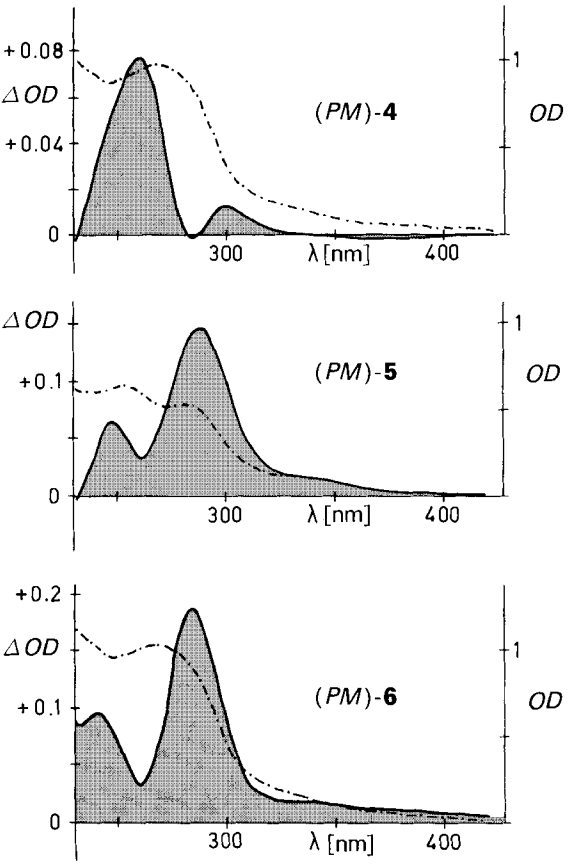


Fig. 4. *Linear dichroism* ( ) *and absorption* (-----) *spectra of* (PM)-**4**, (PM)-**5**, *and* (PM)-**6** *in the nematic phase* ZLI 1167 (see text), *recorded at 40°*

Precise interpretation of the spectra in terms of polarisation of the electronic transitions is difficult due to the lack of information about the transitions involved. Furthermore, due to the low symmetry of the heptalene nucleus, there are no symmetry-determined directions in which the transition moments are predictable. The similarity of the LD spectra of **5** and **6**, however, is striking. On the other hand, the LD spectrum of **4** is very different: the low-energy band is of opposite sign and the band at *ca.* 285 nm is also negative. The LD spectra indicate, therefore, that the alignment of **5** and **6** is similar and different from that of **4**. All these observations strongly support the interpretation of the signs and intensities of the twisting powers as reported above.

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Experimental Part

General. Pitch values were measured at r.t. with the 'lens' version of the *Grandjean-Cano* method [14] using a *Zeiss Standard 16* microscope. Helical handedness was determined from the sign of the rotatory power [15] and from the sense of the spiral-like disclination observed under circular boundary conditions [16]. The LD and absorption spectra were recorded by a modulated technique with a *JASCO J-500A* spectropolarimeter equipped with LD attachment. The liquid crystalline matrix was obtained by using a bicyclohexyl nematic phase, transparent to the UV light (*ZLI 1167* from *Merck*) and a surface coupling agent, in order to get linearly anisotropic samples (for experimental details, see [13]).

*Synthesis of 1-Methyl 2-{*trans*-4-[(*trans*-4-Propylcyclohexyl)ethyl]cyclohexyl}(PM)-5,6,8,10-Tetramethylheptalene-1,2-dicarboxylate* (PM-**6**). *trans*-4-[(*trans*-4-Propylcyclohexyl)ethyl]cyclohexanol (0.6 g, 2.4 mmol)[4]) was dissolved in dry THF (15 ml), and *ca.* 5 mg of 80% NaH in mineral oil was added under stirring. After 30 min, (*PM*)-**4** (0.10 g, 0.35 mmol) [7] was introduced and the soln. stirred in the dark during 65 h at 55°. The usual workup (*cf.* [7] [8]) yielded a crystalline residue which was extracted with pentane (*ca.* 5 ml). The excess cyclohexanol remained undissolved. The residue of the filtrated pentane extract was further purified by prep. TLC (silica gel, hexane/Et_2O 7:3) to yield 0.027 g (14%) of the desired (*PM*)-**6**, which was recrystallized from Et_2O/pentane. Yellow crystals, m.p. 133–135°. R_f (hexane/Et_2O, 7:3) 0.50. ^{1}H-NMR (250 MHz, $CDCl_3$): 0.8–1.37, 1.67–1.79, 1.94 (3*m*, 30 aliphat. H, including *t*, *J* = 7, for $CH_3CH_2CH_2$ at 0.865); 1.743 (*s*, CH_3–C(6)); 1.946 (*s*, CH_3–C(8)); 1.993 (*s*, CH_3–C(5)); 2.041 (*s*, CH_3–C(10)); 3.684 (*s*, CH_3OOC–C(1)); 4.671 (7-lines *m*, CHO); 5.997 (*s*, H–C(9)); 6.137 (*s*, H–C(7)); 6.259 (*dq*-like, *J*(4,3) = 6, H–C(4)); 7.505 (*dq*-like, *J*(3,4) = 6, H–C(3)). MS (70 eV): 546 (100, $M^{+\cdot}$), 531 (3), 514 (2), 506 (2), 487 (2), 312 (18), 295 (10), 280 (49), 265 (19), 253 (32), 235 (15), 214 (17), 207 (16), 193 (25), 184 (84).

*Synthesis of (+)-(M)-***6**. The same procedure as described for (*PM*)-**6** was applied by reacting 0.49 g (1.94 mmol) of the 4-substituted cyclohexanol[3]) with 0.10 g (0.35 mmol) of (+)-(*M*)-**4** ($[\alpha]_D^{20} = 1300°$ (acetone, $c = 1.14 \cdot 10^{-3}$), $p = 0.97$ [7]). (+)-(*M*)-**6** (34 mg, 17%) was obtained as a yellow oil[4]). $[\alpha]_D^{20} = 683°$ (acetone, $c = 2.67 \cdot 10^{-4}$). ORD (cyclohexane): 418/2424 (*P*), 375/0, 295/–16300 (*T*), 276/–4100 (*P*), 273/–4530 (*T*), 265/–2315 (*P*), 253/0. CD (cyclohexane): 378.6/21.15 (max.), 358.7/21.59 (min.), 326.7/23.43 (max.), 279.2/–42.51 (max.), 261.8/–30.25 (min.), 251.6/–33.86 (max.), 222.7/10.97 (max.).

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[3]) We thank Dr. *R. Buchecker, F. Hoffmann-La Roche & Co. AG,* Basel, for a sample of this alcohol.
[4]) The oil of (+)-(*M*)-**6** seemed to contain still traces of the TLC solvent.