

INDUCTION OF CHOLESTERIC MESOPHASES IN NEMATIC LIQUID CRYSTALS, AND CORRELATION OF ABSOLUTE CONFIGURATIONS OF SOME CHIRAL OXIRANES AND THIIRANES

G. GOTTARFELLI*, P. MARIANI and G. P. SPADA
Istituto di Scienze Chimiche, Facoltà di Farmacia, Università di Bologna, Italy

B. SAMORI
Istituto di Chimica degli Intermedi, Università di Bologna, Italy

A. FORNI
Istituto di Chimica Organica, Università di Modena, Italy

and

G. SOLLAJADIE* and M. HIBERT
Ecole Nationale Supérieure de Chimie, Université Louis Pasteur, Strasbourg, France

(Received in the U.K. 4 June 1982)

Abstract—It is shown that the presence of two chirally-distorted aromatic groups is the principal factor determining the twisting power of optically-active *trans*-stilbene oxide and analogous molecules in nematic liquid crystals. The absolute configuration of a series of chiral oxiranes and thiiranes can be correlated by comparing their twisting powers in MBBA, this liquid crystal method being in some cases complementary to CD spectroscopy.

Induced cholesteric mesophases are generated by the addition of small quantities of chiral compounds to nematic liquid crystals (LC).^{1,2} The twisting power of a chiral dopant can be defined as:^{3,4}

$$\beta_{\omega} = (p C r)^{-1}$$

where p is the pitch (μm), C is the concentration (mol of solute per mol of solvent) and r the enantiomeric purity of the dopant.

The parameter β_{ω} and its sign ($(+)$ for a P-helix and $(-)$ for an M-helix of the induced cholesteric mesophase) characterises the chiral solute in a way similar to the use of specific optical rotation $[\alpha]$. However, the physical origin of the two quantities is entirely different. The origin of the optical rotation depends, in fact, on the interactions of light with molecules while the twisting power originates from interactions between molecules of solute and solvent. The classical rotatory power, its dispersion as a function of λ (ORD) and Circular Dichroism (CD) has been widely employed in chemistry for characterizing chiral molecules and obtaining information about the relative and absolute configurations. The quantity β should give information in the same area. The variations of β with the molecular structure of the inducing chiral compound and, for a given compound, with the liquid crystal used as a solvent, must actually afford information concerning the mechanism of induction. That should also allow the formulation of an interaction model between solute and solvent, able to predict the handedness of the induced cholesteric mesophase and the relative magnitude of the twisting powers of a series of solutes having related structures. Such a model should allow the passage from a purely correlative use of β to the determination of absolute configurations based on a firmer background.

Continuing previous work on chiral alcohols⁵ and optically active deuterium derivatives,⁶ we now report some results obtained by doping nematic LCs with variously substituted oxiranes and thiiranes.

RESULTS AND DISCUSSION

Pitch values were determined by means of the Grandjean-Cano method which is based on the observation of the discontinuity lines appearing when a cholesteric LC is inserted in a cell of variable thickness.^{7,8}

The handedness of the helices was determined by means of the elegant method recently described by Heppke and Oestreicher⁹ where the cholesteric solution is placed between a glass plate with planar alignment (parallel rubbing) and a lens with concentric surface alignment (circular rubbing). With these boundary conditions, a P-cholesteric originates a left-handed double spiral and a M-cholesteric a right-handed one.

The sign of the rotatory power of the cholesteric mesophase^{10,11} always confirmed the assignments based on the double spiral method.

Table 1 reports the twisting powers of variously substituted oxiranes and thiiranes of type A in MBBA.

Compounds 1-10 clearly show a correlation between their stereochemistry and the sign of the twisting power: compounds 1 to 10 having the absolute configuration depicted in Figure A (Table 1) induced in MBBA M-cholesteric mesophases (left-handed helix).

The higher values for twisting power are obtained when two aromatic rings are directly bonded to the 3-membered ring (compounds 1-3) and are in a *trans*-configuration. These values are considerably higher than those observed for chiral alcohols⁵ and other variously substituted derivatives.¹² The twisting power diminishes by replacing one aromatic group with a methyl (compound 4) or by moving the aromatic group away from the 3-membered ring (compounds 5-8). The replacement of one group by hydrogen (compound 9) or by a methyl having a *cis* configuration (compound 10) reduces considerably the value of β_{ω} .

Compounds 11 and 12 containing only methyl groups show a dramatic decrease of β_{ω} and sign inversion.

These variations of β_{ω} according to the dopant structure as well as the very high intrinsic values indicate that the structure of the *trans*-diaryl derivatives interacts best

Table 1. Twisting powers of compounds of type A in MBBA^a

	H	H ¹	H ²	X	Absolute Config.	Twisting Power ^b β ₀	Helical Hand ^{c,d}
1	H	H	H	C	1R,2R	-26	M
2	4-Py ^e	4-Py	H	O	1R,2R ^f	-42	M
3	H	H	H	S	1R,2R ^f	-26	M
4	H	CH ₃	H	O	1R,2R	-8.5	M
5	H	HCO ^g	H	O	1R,2S ^{e,f}	-14	M
6	4-THF ^h	HCO ^g	H	C	1R,2S ^{e,f}	-13.5	M
7	H	2-THF ^h	H	O	1R,2S ^{e,f}	-11.5	M
8	H	4-THF ^h	H	D	1R,2S ^{e,f}	-9.5	M
9	H	H	H	C	1R	-1.2	M
10	H	H	CH ₃	O	1R,2S ^f	-0.9	M
11	CH ₃	CH ₃	H	O	1R,2R	-0.5	P
12	CH ₃	CH ₃	H	S	1R,2R ^f	-0.5	P

a) MBBA-*p*-methoxybenzylidene-*p*-*n*-butylaniline

b) Values corrected to 100% optical purity

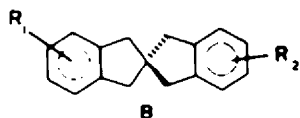
c) Pyridyl

d) Thienyl

e) The absolute configuration is still that of structure A, nomenclature 2S resulting from the priority of the ArCO group.

f) The measurement was carried out on the enantiomer.

with the MBBA molecules. However, the presence of two aryl groups at approximately the same distance as in 1, 2 and 3 is not sufficient to give high values of the twisting power. 2,2'-spiroindanes **B**, recently studied by Korte *et al.*¹¹ showed low values of β in a MBBA/EBBA mixture. The reason seems to be that in these molecules the 2-phenyl groups are perpendicular to each other while in substituted oxiranes and thiranes the two phenyl groups are not



In the course of our report we give indications that the presence of two chirally distorted aryl groups at a distance approximately similar to those in MBBA introduces a molecular asymmetry (similar to a biphenyl asymmetry) and a structural similarity to MBBA which are both important factors in determining the twisting powers.^{4,12}

Determination of the orientation of the inducing chiral molecules inside the mesomorphic solvent by linear dichroism (LD)

Any structural interpretation of the induction of cholesteric mesophases must be based on the knowledge of the orientation of the chiral inducing molecules with

respect to the local nematic directors. Dichroic techniques are very useful for this purpose. Circular Dichroism (CD) studies using light propagating along the helical axis of macroscopically oriented cholesteric samples can be safely performed only when any linear anisotropy has been avoided in the planes perpendicular to the direction of propagation of the circularly polarized light. In induced cholesteric samples, this requirement is expected to be fulfilled only when the pitch is very short.

When a circularly or linearly polarized beam experiences both circular and linear anisotropy through the sample, the interpretation of the circular or linear dichroism data becomes so complex that it discourages any expectation of stereochemical information.¹³ For this reason, instead of studying the CD of the induced cholesterics, racemic mixtures of the investigated inducing molecules were added to the nematic solvent in order to avoid any induction of net helicity in the sample, i.e. of circular anisotropy, and to measure its linear anisotropy in terms of LD.

The LD spectra of guest molecules oriented by nematic solvents transparent in the UV-visible region can yield two types of information: (a) if the main orientation of the guest molecule is known, data concerning the electronic states involved becomes available¹⁴ or (b) if the polarisations of the transitions are known, their orientation with respect to the nematic director is obtained.

When no mixed polarisations are present, a very simple relationship¹⁷ links the LD $(E_p(\lambda) - E_s(\lambda))$ to the absorption from non-polarized light $\frac{1}{2}(E_p(\lambda) + E_s(\lambda))$ and to the Saupe order parameter $S_{\mu\mu}$ of the $\mu = x, y, z$ molecular axes (eqn 1):

$$\frac{E_p(\lambda) - E_s(\lambda)}{E_p(\lambda) + E_s(\lambda)} = \frac{3S_{\mu\mu}}{2 + S_{\mu\mu}} \quad (1)$$

$E_p(\lambda)$ and $E_s(\lambda)$ are the optical density of the two perpendicularly plane polarized radiations.

Provided the symmetry of the molecule is, or can be safely considered, high¹⁷ (e.g. C_{2v}), the polarisation of the transition or the orientation of the molecular axes can be determined easily and directly from the sign of the LD following a "shape model" approach.¹⁸ The solute molecules are considered to have orientational properties, inside a nematic solvent, which are intermediate between those of two limiting shape models, a disk and a rod.

Knowledge of the polarisation of the transitions in the aromatic chromophore of the epoxide derivatives leads one to expect a rod and a disk-like orientation, respectively, for 2 and 9 from their double- and single-signed LD spectra (Figs 1 and 2)

The LD spectrum of 2 shows (Fig. 1) a negative and a positive band, corresponding respectively to the short and long-axis polarized transitions of the pyridine chromophore. The lower and higher energy transitions

are polarized along directions which can be considered as molecular short and long axes (b) and (a) (see chart 1).

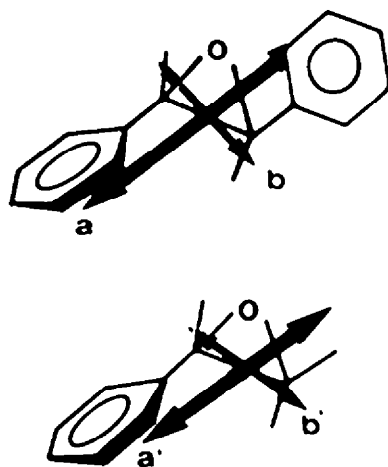


Chart 1

Thus they are expected to give origin to an LD spectrum shaped like that reported in Fig. 1 if the molecules of 2 have a rodlike orientation inside the nematic matrix.

The preferred orientation of the long and short molecular axes parallel and perpendicular to the optical axis of the sample, i.e. to the nematic director of the solvent, can be quantitatively expressed by the values of the

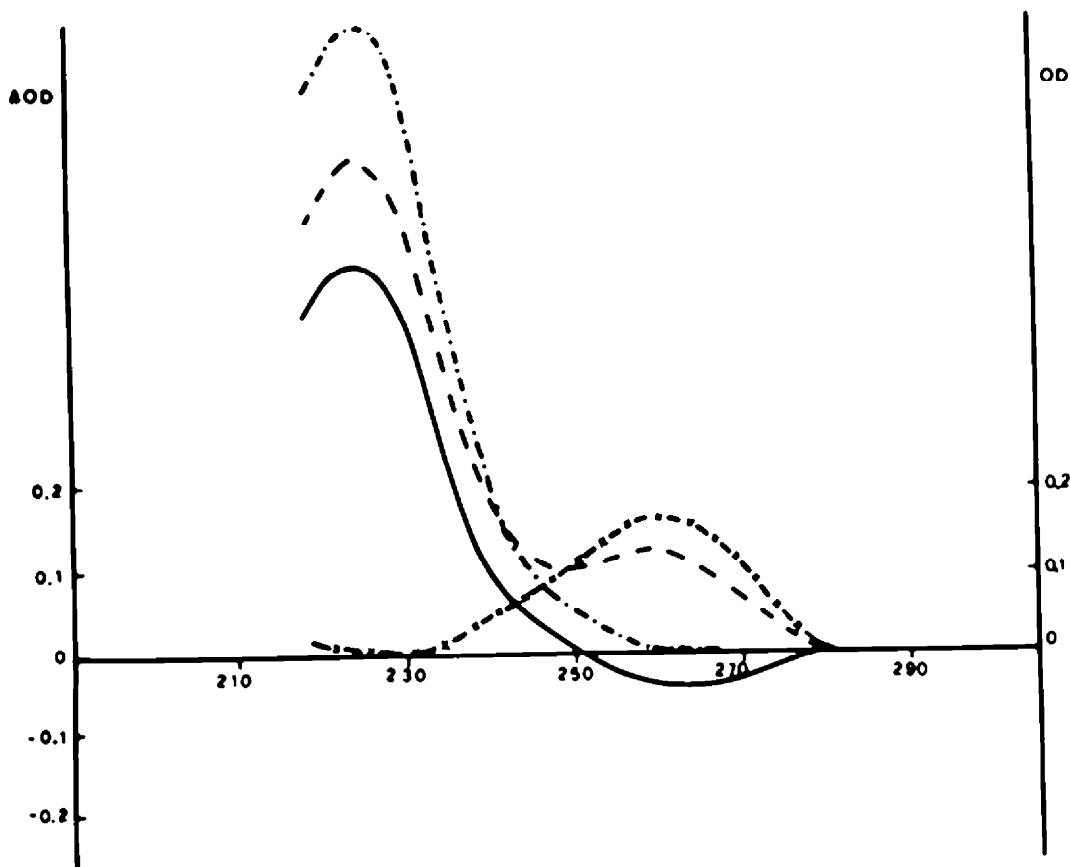


Fig 1 The absorptions (----) and LD (—) spectra of racemic 2 oriented in ZLI 1167 (nematic liquid crystal) at 42°. The absorption components $A_1/2$ (- - -) and $(A_1 + A_2)/2$ (· · ·) computed by a reduction technique¹⁷ assuming a molecular rod-like orientation along the $z = a$ molecular axis (see chart 1)

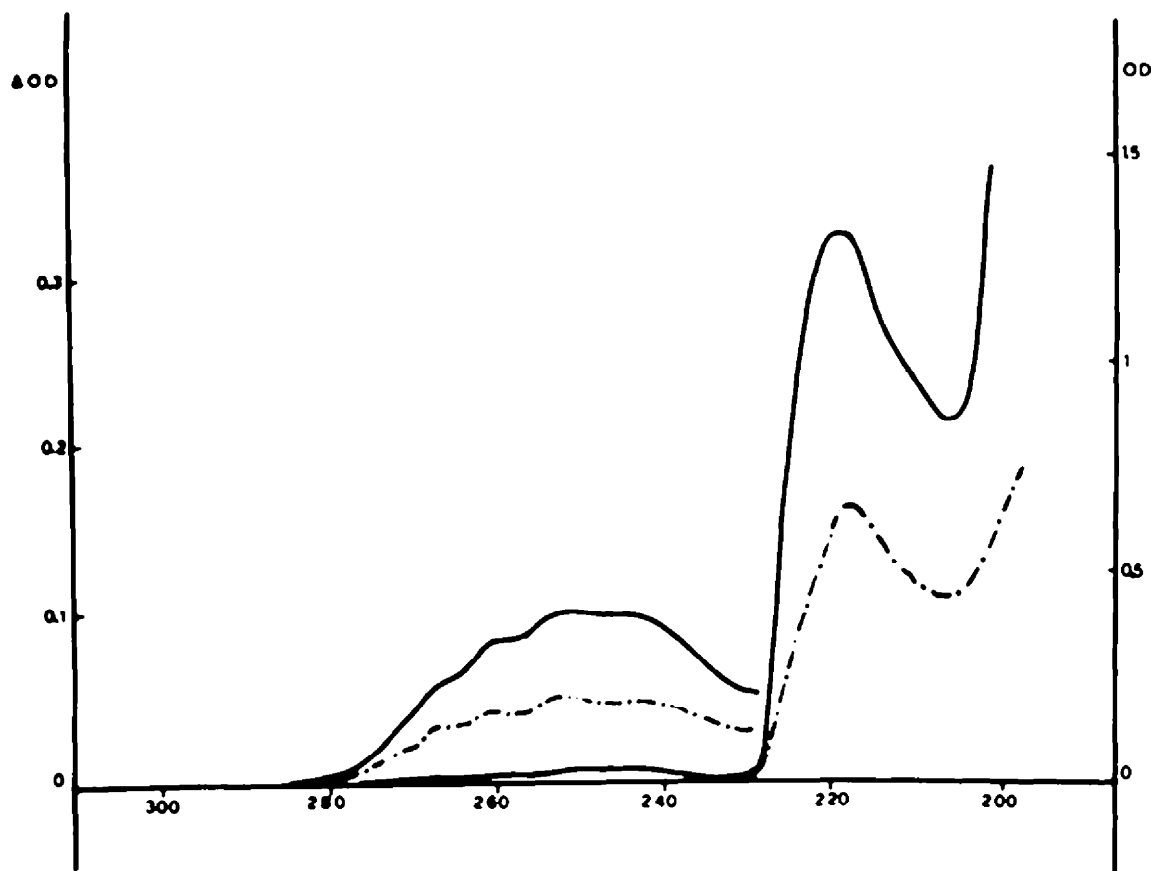


Fig. 2. The absorption (---) and LD (—) spectra of racemic 9 oriented in 71.1 1167 at 42° at two different concentrations

corresponding order parameters (+0.31 and -0.13) calculated from the spectra.¹⁷

The long and short axes of the phenyl chromophore responsible for the electronic transitions observed in the LD spectrum of 9 (Fig. 2) indicate the two molecular transition momentum (a') and (b') (see chart 1). Both transition moments have positive (+0.16 (a') and +0.09 (b')) computed values of the corresponding order parameters. This gives evidence for disk-like molecular orientation: the molecules of 9 are thus expected to assume a molecular packing in the nematic matrix which prevents orientations of their molecular planes perpendicular to the local director. Furthermore, a preferred alignment of the (a') direction along the nematic director is clearly shown by the corresponding higher value of the order parameter. By comparing the values of the order parameters of the (a) and (a') directions, it is evident that the mean orientation along the nematic director of the long axis (a) of 2 is higher than that of the (a') axis of 9.

By assuming a perfect rod-shaped orientation of 2 in the nematic solvent, the absorption components along the z long axis and the degenerate x and y short axes can also be calculated (i.e., be separated).^{17,18} Owing to the imperfect disk-shape of 9, separation in this case is not feasible.

Possible mechanism of induction

Summarizing the results from LD spectra, derivative 2 is aligned with the axis connecting the two aryl groups parallel to the nematic director; derivative 9 instead,

behaves approximately like a disk-shaped molecule with a slight preference of the mono-substituted phenyl group to lie with its long axis parallel to the director.

Although in different nematic solvents the S values of a given molecule might differ quantitatively, qualitatively the alignment is preserved in the absence of different specific interactions.¹⁸

The twisting power of 2 in different nematic solvents is reported in Table 2.

In all the solvents studied, the sign of β remains the same; the quantitative values are, however, very different.

Such variations cannot be understood solely on the basis of the different polarizabilities of the solvents, nor do the possible differences in K_{22} (the scalar twist elastic constant²⁰ of the LCs) justify the differences observed (rigorously $\beta_{\text{exp}} = \beta \cdot K_{22}$).²¹

It should be noted that in the first two solvents, MBBA and Phase IV which have aromatic rings separated by two atoms (as in the trans diaryl derivatives), the twisting power is high whereas it is drastically reduced in the biphenyl-type LCs and decreases even further in PCH and ZLI (mixture of bicyclohexyl nematics). The high values of β_M in the first two solvents can therefore be attributed to the strong structural similarity between the doping and nematic molecules.^{4,14}

Although in phenyloxiranes the rotation of the phenyl groups around the exocyclic carbon-carbon bond is relatively free,^{22,23} several reports show a preferred conformation for such a molecule. X-ray structure of 1-(p-

Table 2 Twisting power of (+)1R, 2R-2 in different nematic solvents

Solvent	Nature	γ_{λ}
MBBA ¹	Schiff base	-42
Phase IV ²	Azoxy derivatives	-39
ET	Mixture of diphenyl and terphenyl derivatives	-31
Phase 106 ³	Mixture of phenylcyclohexane derivatives	-17
211110 ⁴	Mixture of diacyclohexane derivatives	-25

¹ p-menthoxybenzyl tosyl propyltolyl ure

² p-menthoxy propyltolyl azoxybenzene

³ a mixture of 10₁ because of the unknown composition of the phase 106³ (see 51-52)

bromophenyl)-1,2-epoxycyclohexane demonstrate that the phenyl group adopts a quasi-bisected conformation in the crystal.¹⁶ MO calculations on phenyloxirane²² also indicate a quasi-bisected conformation, with the plane of the phenyl-group rotated towards the C-O bond of the oxirane ring. In this type of conformation the 2-aryl group of (+) R,R trans-stilbene oxide and analogous molecules are distorted and displayed a sort of left-handed (M) two-bladed propeller helicity.

A possible model to explain the induced solvent helicity is depicted in Fig. 3, where the dopant molecule is aligned with its long axis parallel to the rod-like molecules of the solvent, the three-membered ring disturbs the parallel alignment of other solvent molecules and imposes the correct twist.

This model is not in disagreement with the data of Table 1 since the derivatives having two aromatic group directly bonded to the three membered ring are likely to be better aligned along the director and should therefore display higher twisting power.

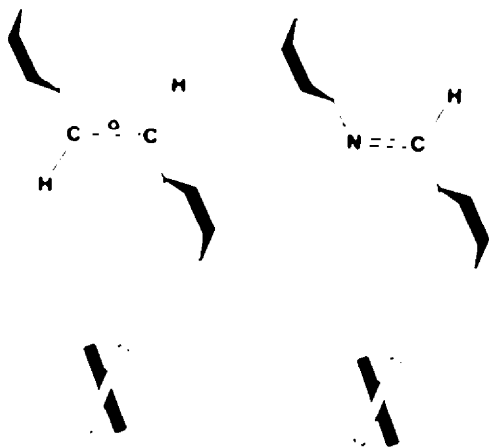


Fig. 4 Similarity between trans-diaryl epoxydes and the aromatic core of MBBA. The relative stereochemistry of the two distorted aryl groups resembles a left-handed two bladed propeller.

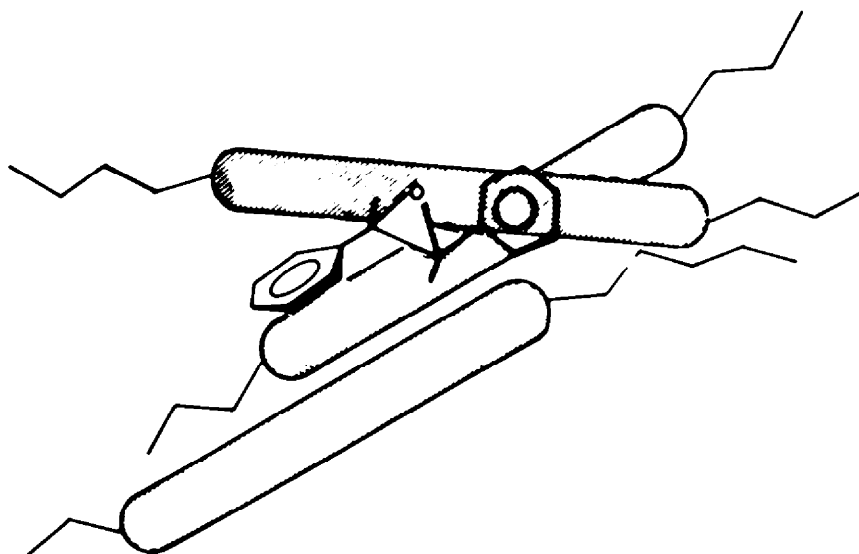


Fig. 3

On the other hand, this model, in which each molecule of LC is considered as an independently rotating rod, cannot explain the variations of β with the nature of the LC reported in Table 2. Nematics of the *p*-substituted benzaniline type, such as MBBA or EBBA, are known to be non planar;²³ the angle between the phenyl ring located on the Nitrogen atom and the plane containing the other phenyl ring and the imino double bond is between 41 and 55°. Such a conformation is stabilized by electronic interactions between the nitrogen lone-pair and the Π -electrons.

Recent work on EBBA in the crystal²⁶ and in the liquid crystalline state²⁷ confirms this conformation. Such a distorted conformation is chiral. However in the crystal or in the nematic phase the two enantiomerically distorted species are equally probable.

It is quite interesting to notice that the chirally distorted conformation (*M*-helicity) of substituted stilbene oxide fits very well into *M*-distorted conformations of MBBA (Fig. 4). This may explain the process of chirality transfer from the doping molecule to the solvent: the chiral conformation of the solute as well as its structural

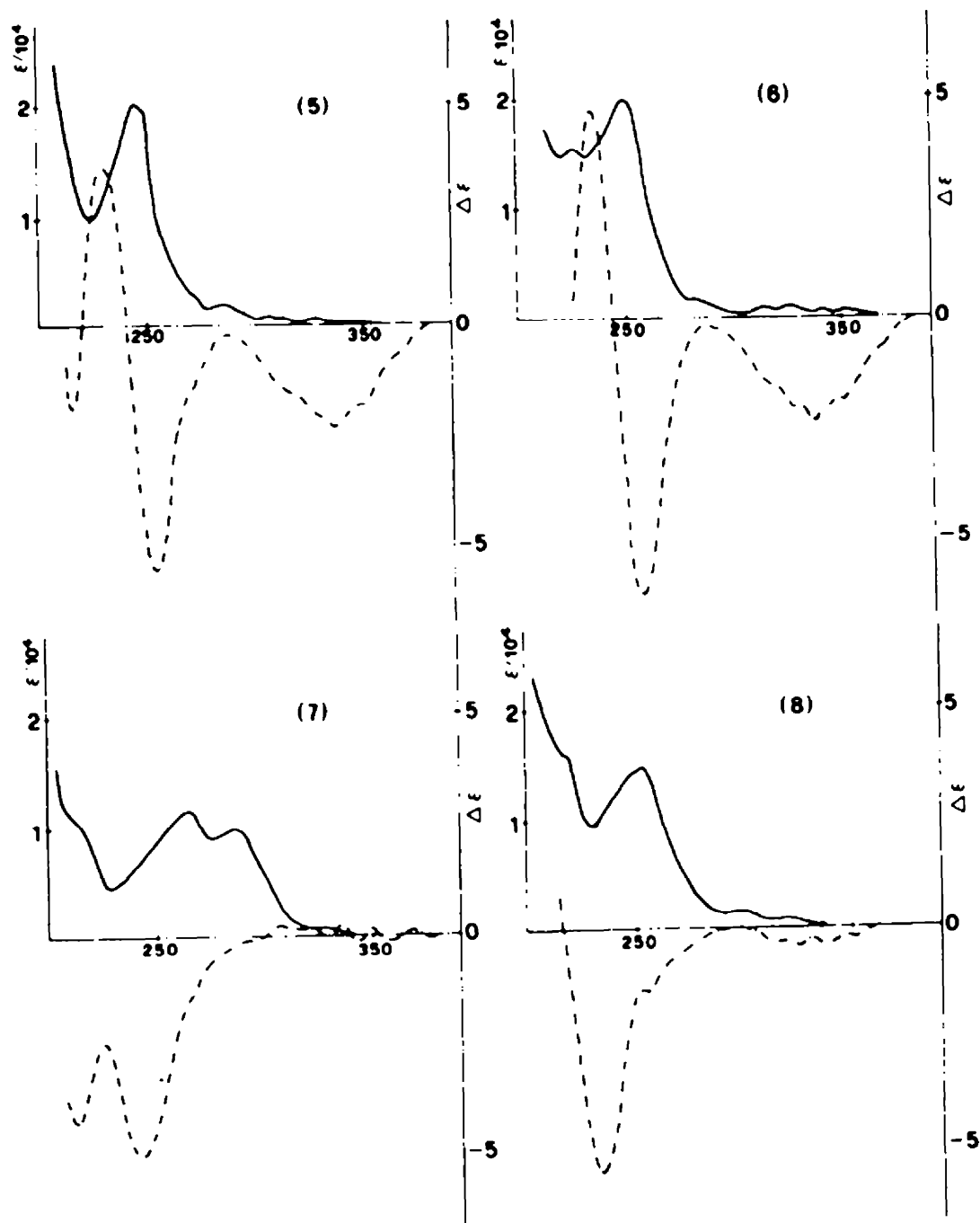


Fig. 5. The absorption (—) and circular dichroism (---) spectra of derivatives 5, 6, 7 and 8 in cyclohexane.

analogy with MBBA may induce a chiral conformation of the solvent which could be at the origin of the cholesteric helix.

A model of this type, which requires cooperative rotations of the molecules about their long axes, is in agreement with a recent investigation of nematic structure.²⁶

Modification of the structure of the inducing molecules from the "ideal" ones (1-3) would decrease their similarity to MBBA and, therefore, the dynamic asymmetric interactions with the solvent molecules; consequently the twisting power would decrease (see 11 and 12 which have a globular geometry leading to a low twisting power and the solvent effect reported in Table 2).

Circular dichroism and absolute configurations of derivatives 5-8

Circular Dichroism is a very useful technique for correlating absolute configurations in homogeneous series. However in some cases, the very complex nature of Cotton effects makes such a correlation difficult.

This is indeed the case with derivatives 5-8. The absolute configuration (1S,2R) of (-)-chalcone epoxide **5** was recently determined by Marsman and Wynberg²⁷ by chemical correlation.

Compounds 5-8 were all obtained by asymmetric epoxidation of the corresponding chalcones in the presence of poly-(S)-amino-acids²⁸ and there are no reasons to expect an inversion of configuration in this series.

The CD and adsorption spectra of 5-8 are reported in Fig. 5.

The CD of chalcone epoxide is in good agreement with that already described²⁴ and is practically superimposable on that of the p-chloro derivative **6**. In these spectra, the couplet centered at ca 240 nm can be interpreted as due to non-degenerate exciton coupling in a way similar to that reported for trans-stilbene oxide.²¹ The spectra of the thienyl compounds are instead very different and difficult to analyse. The lack of information about the thienyl-CO chromophore makes correlation of the absolute configurations with the spectra unsafe.

The handedness of the induced cholesterics as well as the similarity of the twisting powers of compounds 5-8 illustrate well the potentiality of the liquid crystal technique to correlate absolute configurations.

CONCLUSION

The presence of two chirally distorted aromatic groups is likely to be the principal factor determining the very high twisting power of trans-stilbene oxide and analogous molecules. The chirality is transferred from the dopant to molecules of MBBA which are consequently arranged to form a macrostructural helix.

It is possible to correlate the configuration of a series of oxiranes and thiranes by comparing the sign of their twisting powers in MBBA, even in the case where the correlation is impossible by CD spectroscopy.

EXPERIMENTAL

Microscopic measurements were carried out following the method described in Ref. 5, using a Zeiss polarizing microscope and Galileo plano-convex lenses of radius 20-40 mm. The concentric alignments were obtained by pressing the lens on a tissue paper attached to a rotating plate. In order to obtain the spirals more easily, both the lens and the glass plate were treated with N-methylamino-propyltrimethoxysilane or with polyvinyl alcohol.

The LD spectra were recorded by a modulated technique (JASCO LD attachment to the J-500 A spectropolarimeter) using a bicyclohexyl nematic liquid crystalline matrix transparent to the UV radiation (Merck ZLI 1167) and a surface coupling agent in order to get linearly anisotropic samples. The calibration and the experimental details of the technique will be discussed elsewhere.

Derivatives

(+)-(1R,2R)-trans-stilbene oxide, 1, $[\alpha]_D = -350^\circ$ (c = 0.5, benzene), 94% e.e. was prepared as described in Ref. 31 (-)-1S, 2S)-trans-1,2-di(4-pyridyl)oxirane, 2, $[\alpha]_D = -221^\circ$ (c = 0.5, H₂O) was prepared and described in Ref. 32. The optical purity based on the maximum rotation was ca 97% (-)-1S, 2S)-trans-stilbene episuiphate, 3, $[\alpha]_D = -313^\circ$ (c = 0.5, EtOH) was prepared as described in Ref. 33 (+)-(1R, 2R)-trans-1-phenyl-1,2-epoxypropane, 4²⁸, $[\alpha]_D = +115.7^\circ$ (neat), 98% e.e. (-)-1R)-styrene oxide, 9, $\alpha_D = -35.9^\circ$ (neat), 99% e.e., was prepared as described in Ref. 35 (-)-(1R, 2S)-cis-1-phenyl-1,2-epoxypropane²⁸, 10, $[\alpha]_D = +16.7^\circ$ (neat), 100% e.e. (+)-(1R, 2R)-trans-2,3-epoxybutane²⁸, 11, $[\alpha]_D = +56^\circ$ (neat), 95% e.e. (-)-1S, 2S)-trans-2,3-dimethylthirane,²⁸ 12, $[\alpha]_D = -95.5^\circ$ (neat), 100% e.e.

Chalcone epoxides were kindly provided by Prof. S. Colonna (Milan)²⁹ and had the following characteristics: 5, $[\alpha]_D = -179^\circ$ (CH₂Cl₂), 84% e.e.; 6, $[\alpha]_D = -148^\circ$ (CH₂Cl₂), 77% e.e.; 7, $[\alpha]_D = -183^\circ$ (CH₂Cl₂), 80% e.e.; 8, $[\alpha]_D = -118^\circ$ (CH₂Cl₂), 81% e.e.

Acknowledgments—We are indebted to NATO for the partial support of this research (Grant No. RG 081-81). We thank also Prof. S. Colonna (Milan) for the generous gift of compounds 5, 6, 7 and 8. G. G. and B. S. thank CNR (Rome) for financial support. Finally we gratefully acknowledge Prof. R. Weiss from Georgetown University, Washington D.C. (on sabbatical leave in Strasbourg) and Dr. A. Solladié-Cavallo for helpful discussions.

REFERENCES

- G. Friedel, *Ann. Phys. (Paris)* **10**, 273 (1922).
- H. Stegemeyer and K. J. Mainusch, *Naturwissenschaften* **58**, 599 (1971).
- E. H. Korte, B. Schrader and S. Bualek, *J. Chem. Res. (S)*, 236 (1978).
- J. M. Ruxer, G. Solladié and S. Candau, *Mol. Cryst. Liq. Cryst. (Letters)* **41**, 109 (1978).
- G. Gottarelli, B. Samori, C. Siremmeno and G. Torre, *Tetra. hedron* **37**, 395 (1981).
- G. Gottarelli, B. Samori, C. Fuganti and C. Grasselli, *J. Am. Chem. Soc.* **103**, 471 (1981).
- R. Grandjean, *C. R. Acad. Sci.* 172 (1921).
- F. Cano, *Bull. Soc. Fr. Mineral. Cristallogr.* **91**, 20 (1968).
- G. Heppke and F. Oestreicher, *Mol. Cryst. Liq. Cryst. (Letters)* **41**, 245 (1978).
- J. P. Berhaut, J. Billard and J. Jacques, *C. R. Acad. Sci. Paris* **C155**, 284 (1977).
- J. P. Berhaut, *These de Doctorat*, Paris, (1977).
- H. J. Krabbe, H. Heggemeier, B. Schrader and F. H. Korte, *J. Chem. Res. (M)* 3020 (1978).
- E. H. Korte, P. Chingduang and W. J. Richter, *Ber. Bunsenges. Phys. Chem.* **84**, 45 (1980).
- M. Hilbert and G. Solladié, *Mol. Cryst. Liq. Cryst. (Letters)* **64**, 211 (1981).
- H. P. Jensen, J. A. Shellman and T. Truxell, *Appl. Spectrosc.* **32**, 192 (1978).
- P. Palmieri and B. Samori, *J. Am. Chem. Soc.* **103**, 6818 (1981) and refs. therein.
- B. Samori, P. Mariani and G. P. Spada, *J. Chem. Soc. Perkin II* 447 (1982).
- G. Gottarelli, B. Samori and R. D. Peacock, *J. Chem. Soc. Perkin II*, 1208 (1977).
- E. W. Thulstrup and J. Michl, *J. Phys. Chem.* **84**, 82 (1980).
- F. Leenhouys and A. J. Dekker, *J. Chem. Phys.* **74**, 1936 (1981).
- G. Gottarelli, G. F. Pedulli and C. Zannoni, *Chem. Phys.* **64**, 143 (1982).

- ²²S. Sorriso, F. Stefani, E. Semprini and A. Flamini, *J. Chem. Soc. Perkin II* 374 (1976).
- ²³G. Gottarelli, S. F. Mason and G. Torre, *J. Chem. Soc. (B)* 1349 (1970).
- ²⁴S. Merlino, G. Lami, F. Macchia and L. Monti, *J. Org. Chem.* **37**, 703 (1972).
- ²⁵J. M. Ruxer, A. Solladie-Cavallo, G. Solladie and D. Ollhero, *Org. Magn. Res.* **10**, 105 (1977).
- ²⁶J. Howard, A. J. Leadbetter and M. Sherwood, *Mol. Cryst. Liq. Cryst. (Letters)* **56**, 271 (1980).
- ²⁷M. Yasuniwa, S. Taki and T. Takemura, *Mol. Cryst. Liq. Cryst.* **60**, 111 (1980).
- ²⁸R. F. Brian and P. Hartley, *Mol. Cryst. Liq. Cryst.* **62**, 259 (1980).
- ²⁹B. Marsman and H. Winberg, *J. Org. Chem.* **44**, 2312 (1979).
- ³⁰S. Julia, J. Guixer, J. Masana, J. Roca, S. Colonna and H. Molinari, *J. Chem. Soc. Perkin I* 1317 (1982).
- ³¹J. Read and L. G. M. Campbell, *J. Chem. Soc.* 2377 (1930).
- ³²G. Gottarelli and B. Samorì, *J. Chem. Soc. Perkin II* 1998 (1972).
- ³³R. Ketcham and V. P. Shah, *J. Org. Chem.* **28**, 229 (1963).
- ³⁴B. Wittkop and C. M. Foltz, *J. Am. Chem. Soc.* **79**, 197 (1957).
- ³⁵D. J. Pasto, C. C. Cumbo and J. Fraser, *J. Am. Chem. Soc.* **88**, 2194 (1966).
- ³⁶G. K. Helmkamp and N. Schnantz, *Tetrahedron* **2**, 304 (1958).