Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Solute-Solvent Chiral Interactions: Non-Symmetrical Effects of Enantiomers and Conformers on Right- and Left-Handed Cholesterics

Y. K. Yarovoy [a] & M. M. Labes [a]
[a] Department of Chemistry, Temple University, Philadelphia, PA, 19122

Version of record first published: 24 Sep 2006.

To cite this article: Y. K. Yarovoy & M. M. Labes (1995): Solute-Solvent Chiral Interactions: Non-Symmetrical Effects of Enantiomers and Conformers on Right- and Left-Handed Cholesterics, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 270:1, 101-112

To link to this article: http://dx.doi.org/10.1080/10587259508031020

Mol. Cryst. Liq. Cryst., 1995, Vol. 270, pp. 101–112
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Solute-Solvent Chiral Interactions: Non-Symmetrical Effects of Enantiomers and Conformers on Right- and Left-Handed Cholesterics

Y. K. YAROVOY and M. M. LABES

Department of Chemistry, Temple University, Philadelphia, PA 19122

(Received January 9, 1995; in final form March 10, 1995)

Effective helical twisting powers of a number of enantiomers and achiral conformers were measured in highly twisted cholesteric phases varying in both chemical composition and macroscopic chirality. In certain solute-solvent combinations, and particularly in steroidal solvents, pronounced non-symmetric effects of enantiomers and conformers were observed on right- and left-handed cholesterics. Achiral rod-like solutes, which can exist in different conformations, were found to behave as though they have a left-handed helical twisting power in both right- and left-handed short pitch steroidal cholesterics. All effects can be interpreted as being due to specific short range molecule-molecule interactions. No evidence was found that the macroscopic chirality of a cholesteric medium can influence the conformation of an achiral solute.

Keywords: Cholesteric, chiral, conformer, enantiomers, helix, pitch

INTRODUCTION

In the limit of low concentration, the pitch P of a cholesteric helix is inversely proportional to the concentration C of a chiral solute ($P^{-1} = \beta C$). The proportionality constant β is referred to as the "helical twisting power" (HTP) of the solute. There are two somewhat different models for this effect.[1–4] In the first, a chiral guest molecule perturbs the parallel stacking of the host nematic achiral species by virtue of intermolecular interactions with its nearest neighbors. In the second, the chiral guest induces chiral non-planar conformations of the adjacent nematic solvent molecules, which in turn induce chiral conformations in its nearest neighbors; that is, there is a longer range cooperativity than implied in the first model. Although there are experimental studies which support both models, an important aspect of the second, for which there is no experimental evidence, is the implicit assumption that there should be an inverse influence of a chiral medium on solute molecules; that is, the macroscopic chirality of a cholesteric medium should induce chiral conformations in appropriate achiral solutes. There is, however, no convincing evidence for such chiral induction. Experimentally, the most recent studies of this type from this laboratory first presented some evidence for chiral induction in rigid rod achiral solutes,[5,6] but subsequently it

was found that these effects could not be reproduced.[7] A recent theoretical study interprets the nonlinearity of reciprocal pitch-concentration dependence of cholesteric-nematic mxtures in terms of "induced deracemization" of flexible conformers;[8,9] however, the non-linearity could be equally well interpreted in terms of the first model discussed above.[10-14]

It occurred to us that further assessment of the models and testing of the hypothesis of chiral medium induced preferred conformation might come from measurements of effective HTP of conformers and enantiomers in tightly twisted cholesteric phases varying in both chemical composition and macroscopic chirality (pitch and handedness of the helix). Although it is generally assumed that equal amounts of enantiomeric guests of equal optical purity induce helical structures with identical pitch and opposite handedness, the reported studies employed only nematics consisting of optically inactive molecules. Studying diastereomers and conformers in both cholesterics and "compensated" nematics (compensated mixtures of optically active molecules with infinite pitch) may be useful in developing a deeper understanding of the nature of these intermolecular interactions.

EXPERIMENTAL

The liquid crystals, enantiomers and conformers employed were commercially available from E. Merck, Hallcrest, Eastman Kodak and Aldrich. The structures are shown in Figures 1 and 2.

Mixtures of liquid crystals were sandwiched between two quartz disks separated by a Teflon spacer and the sample was placed in a sample holder, the temperature of which could be controlled to ± 0.1°C. Helical pitch values P were determined by measuring the wavelength of maximum selective light reflection. For normal incidence a cholesteric film reflects, selectively, one sense of circular polarization. The wavelength $\lambda_0 = nP$ where n is the mean refractive index of the liquid crystal; n varies only slightly with temperature and addition of small amounts of dopants, so the observed variation of λ_0 with temperature and doping is solely due to the helical pitch. All spectra were recorded using a Perkin Elmer 330 UV-VIS spectrophotometer. Phase transition temperatures T_{is} were determined by observing the change of textures under a Nikon polarizing microscope using a Mettler FP 82 hot stage.

Since the employed cholesteric matrices exhibited linear temperature dependences of pitch, and addition of chiral and achiral dopants usually changed the clearing point of the compositions by several degrees, the pitch-dopant concentration dependence for determination of the effective HTP was plotted at an adjusted temperature $T = T_{is} - 20$ °C. Figures 3 and 4 present examples of the typical temperature dependences observed for the wavelengths of maximum reflection plotted versus temperature (Figures 3a and 4a) and versus reduced temperature (Figures 3b and 4b). The calculated HTP for benzene is equal to zero despite the drastic change of the color of the cholesteric composition upon doping it with this solvent. For benzene, the effect is solely due to the substantial depression of the clearing point of the cholesteric matrix.

Preparation of cholesteric mixtures and compositions with added enantiomers and conformers was accomplished by mixing components at a temperature above the

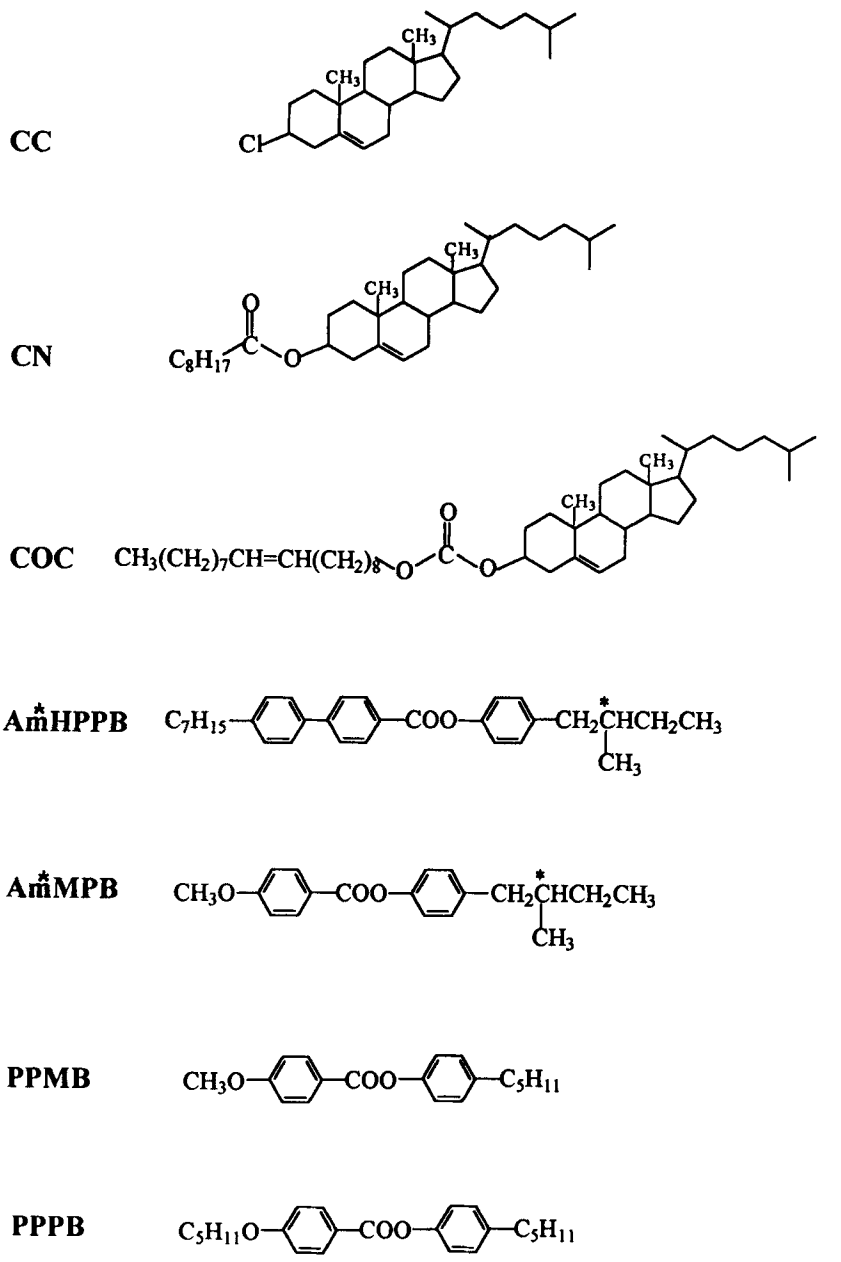
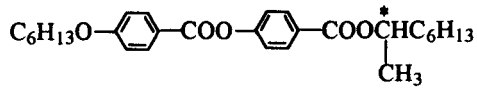


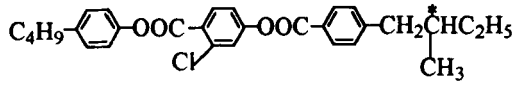
FIGURE 1 Structures of the compounds used in preparation of the cholesteric matrices.

clearing point until there were no visible traces of undissolved compounds. The solubility of these additives was then verified by the absence of observed crystallites under the polarizing microscope.

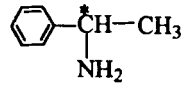
R811(S811)



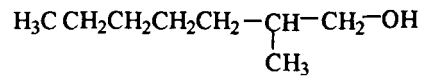
AmBEPH



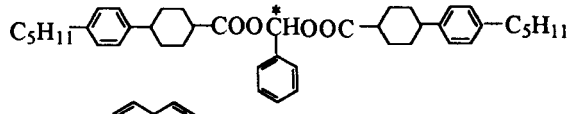
S-(-) / R-(+)-PEA



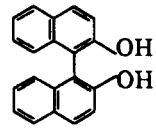
d/l -2-Octanol



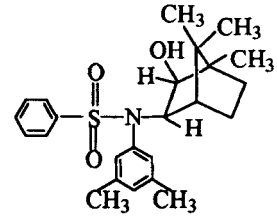
R1011 (S1011)



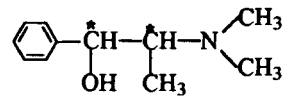
R-(+) / S-(-) -
1,1'-Bi-2-naphthol



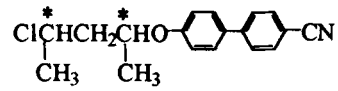
(1R,2S,3R)-(+)- or (1R,2R,3S)-(-) -
3-[Benzensulfonyl-N-(3,5-
dimethylphenyl)amino]-2-bornanol
((+)- / (-) BSDAB)



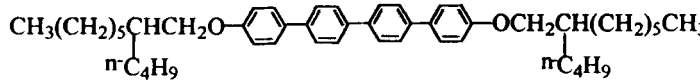
(1R,2S)-(-) / (1S,2R)-(+) -
(+)/(-)-Methylephedrine



(-)-(R,R)/ (+)-(S,S)-
1-Me,3-Cl-4OCB



BOQP



4PP$_1$P5

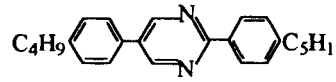


FIGURE 2 Structures of the enantiomers and anhiral conformers.

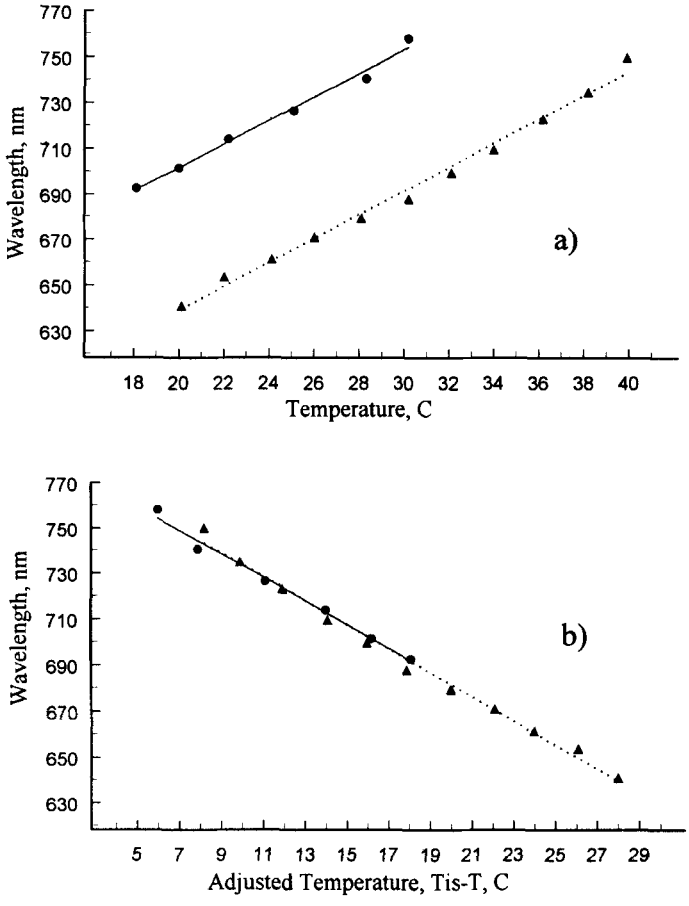


FIGURE 3 Temperature dependence of the wavelength of maximum reflection of matrix A (▲) and matrix A doped with 2.5 wt.% of benzene (●), plotted versus a) temperature and b) adjusted temperature $T = T_{is} - T$.

RESULTS

Two types of chiral matrices were employed: the first, based on steroidal cholesterics (A, A1, A2, AB1–AB3), and the second, based on chiral nematics (B) or nematics doped with chiral additives (PBS and PBR). The composition, handedness and temperatures of transitions to the isotropic phase of the matrices are shown in Table I. By changing component proportions in ternary (A, A1, A2) and binary (AB1–AB3) cholesteric mixtures, cholesteric matrices were obtained with opposite handedness and a wide range of pitch values, including a compensated nematic matrix ($P = \infty$).

Eight enantiomers varying in the position and nature of their chiral center, and two conformers (mesogenic $4PP_1P5$ and nonmesogenic BOQP), as well as a few small solute molecules were employed. The values of their effective HTP are shown in Table II. With the exception of enantiomers (+)-R/(−)-S-1,1′-bi-2-naphthols and

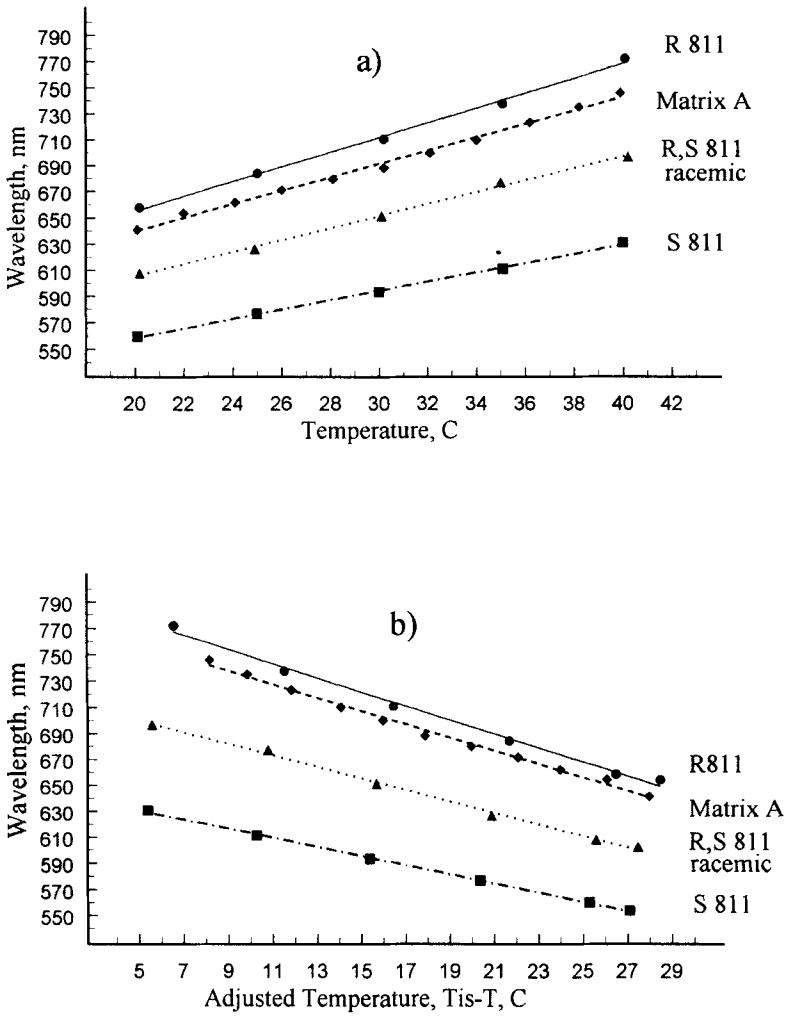


FIGURE 4 Temperature dependence of the wavelength of maximum reflection of matrix A and matrix A doped with enantiomers R811 (1.97 wt.%), S811 (1.95 wt.%) and a racemic mixture of R811 and S811 (2.01 wt.%), plotted versus a) temperature and b) adjusted temperature $T = T_{is} - T$.

R1011/S1011, which cause symmetrical changes of helicity in all matrices, the other enantiomeric pairs were found to produce either asymmetrical or symmetrical effects depending on the molecular structures of both solutes and solvents. These effects are summarized below.

(1) The enantiomeric pair R811/S811, when added to chiral nematics (B, PBS, PBR) produce symmetrical, opposite effects on the macroscopic chirality. But when added to a steroidal cholesteric mesophase, S811 produces a much larger effect on the pitch than does R811.

TABLE 1

Composition and Properties of the Cholesteric Matrices

Matrix	Composition	wt.%	Handedness	T_{is}°C	$d\lambda/dT$	$\lambda^{(a)}_{max}$
	CC	33				
A	COC	38	lEFT	48.1	+ 5.3	644
	CN	29				
	AmHPPB	17				
B	AmMPB	28	Right	49.2	− 1.1	671
	PPMB	55				
	PPMB	56.5				
PBS	PPPB	37.6	Left	43.1	− 5.3	880
	R1011	5.9				
	PPMB	56.5				
PBR	PPPB	37.6	Right	43.2	− 5.3	870
	S1011	5.9				
	CC	11.0				
A1	COC	61.4	Left	41.1	+ 2.1	525
	CN	27.6				
	CC	37.0				
A2	COC	43.4	Left	43.6	+ 36.4	1643
	CN	19.6				
AB1	CC	32.0	Left			723
	CN	68.0				
AB2	CC	80.0	Right			704
	CN	20.0				
AB3	CC	58.0	Compensated			∞
	CN	42.0				

[a] λ_{max} is given at 20°C, except for matrices AB1, AB2 and AB3, where the value is measured at 60°C.

(2) The optical antipodes d- and l-2-octanol produce opposite sign effects on the phase chirality of chiral nematics (B, PBS, PBR). But they behave identically in the steroidal matrix (A).

(3) There is no difference in sign of the chirality induced by enantiomers (+)-PEA and (−)-PEA in both steroidal (A) and chiral nematic (B) matrices.

(4) The achiral rod-like solutes BOQP and $4PP_1P5$, which can exist in different conformations, both behave as though they are left handed chiral compounds, producing pitch enlargement in a short pitch right handed chiral nematic (B) and significant pitch contraction in the left handed steroidal matrix (A). Another achiral solute which can also be envisioned as existing in several conformations-biphenyl, causes pitch contraction in both right handed (B) and left handed (A) matrices.

(5) In the cholesteric steroidal matrices, in which marked non-symmetric responses occur, the macroscopic chirality was varied both in terms of helix sign and pitch utilizing matrices A1, A2, AB1–AB3 (Table 1). The results are summarized in Table 3. It is clear that there is no correlation between the macroscopic chirality

TABLE 2

Effective helical twisting power (μm^{-1}/wt. fraction) of some chiral and achiral solutes in cholesteric media of different chemical composition

Solutes	Cholesteric medium			
	A	B	PBS	PBR
S811	−13.2	−8.2	−8.0	−8.4
R811	+1.5	+7.3	+9.0	+7.6
S811/R811	−5.7	−0.5	+0.4	−0.3
(+)-PEA	−2.7	−0.8	+0.5	+0.8
(−)-PEA	−1.9	−1.4	−0.7	−0.5
(±)-PEA	−2.3	−0.9	–	–
(+)-AmBEPH	0	+1.8	+3.5	+2.0
(±)-AmBEPH	−1.6	−0.9	+0.5	−0.6
d-2-octanol	−2.2	−2.7	−2.1	−0.8
l-2-octanol	−2.1	+1.1	+0.8	+1.9
S1011	−27.8	−16.7	−15.2	−14.8
R1011	+27.2	+17.2	+14.6	+14.5
S1011/R1011	0	0	0	0
R-(+)-Binaphthol	–	−12.8	−11.2	−9.8
S-(−)-Binaphthol	–	+11.9	+10.0	+11.1
BOQP	−6.0	−1.8	+0.4	−0.8
$4PP_1P5$	−3.3	−1.5	+2.1	−1.9
Benzene	0	0	0	0
Biphenyl	−3.8	+1.3	+0.9	−1.0
Naphthalene	0	−1.9	+0.5	−0.7
Anthracene	+6.3	−4.2	+0.6	−0.4
(+)-BSDAB	+5.7	+13.9	+13.5	+13.7
(−)-BSDAB	−4.2	+6.3	−6.2	−5.2
(+)-Methylephedrine	+3.3	+3.6	+4.3	–
(−)-Methylephedrine	−0.3	−5.4	−5.5	–
(−)11-Me,3-Cl-4OCB	−11.5	–	–	–
(+)-1-Me,3-Cl-4OCB	+14.0	–	–	–

of the media and the chirality induced by addition of enantiomers R811 and S811 or conformer BOQP. The changes in both sign and pitch have no impact on the effective HTP of both chiral and achiral additives.

DISCUSSION

1. S811/R811 in steroidal matrix A. It is known that the steroid ring system including the side chain at carbon 17 is effectively right-handed, and that increasing the chain length at the 3β carbon atom reduces the right-handedness by a factor proportional to the 3β side chain length.[15] When the 3β chain length is long enough, the compounds become left handed cholesterics. Thus, cholesteryl chloride (CC) is right handed whereas cholesteryl nonanoate (CN) and cholesteryl oleyl carbonate (COC) are both left handed.

It is also known that in binary steroidal cholesteric-nematic mixtures, the nematic component always behaves as though it were effectively left handed.[11] This phenom-

TABLE 3

Effective Helical Twisting Power of the Enantiomeric Pair R/S811 and of Achiral BOQP in Steroidal Cholesteric Matrices

Additive	Matrix	Chirality	Pitch, nm	HTP, (μm. × wt. fraction)$^{-1}$
R811	A	Left	644	+1.5
S811	A			−12.8
R811	A1	Left	525	+1.5
S811	A1			−12.8
R811	A2	Left	1643	+1.0
S811	A2			−12.2
R811	AB1	Left	723	+1.3
S811	AB1			−10.8
R811	AB2	Right	704	+1.5
S811	AB2			−12.4
S811	AB3	Compensated		−10.2
BOQP	AB1	Left	723	−5.2
BOQP	AB2	Right	704	−4.0

enon is attributed to the peculiarities of nematic-cholesteric orientational interactions; namely, molecules of nematics arrange parallel to the 3β aliphatic side chains of the steroidal derivatives, forming a "chiral associate". This results in an increase of the left-handedness of the associate as compared to the steroid derivative.[16] The same effect occurs when non-mesogenic long chain *n*-alkanes or *n*-alkyl alcohols are added.[17]

It seems reasonable to suggest that when an enantiomer is added to a cholesteric, one factor influencing the chirality of the medium is purely geometric-that is, **there is a component of the effective HTP in such structures which behaves in a left-handed manner irrespective of the optical sign of the enantiomer.**

Assume that the effective HTP of chiral rod-like flexible molecules in steroidal media might be represented as a sum of two terms: β_{chir}, denoting HTP originating from intrinsic molecular chirality, and β_{geom}, denoting effective HTP originating from a purely geometric factor. Then, for both members of the enantiomeric pair R811/S811 one can write the total HTP as follows:

$$\beta = \beta_{chir} + \beta_{geom}$$

Assuming further that the geometric factor is the same for both optical antipodes ($\beta_{geom}(R811) = \beta_{geom}(S811)$) and that the intrinsic chirality is of the same value but of opposite sign ($\beta_{chir}(R811) = -\beta_{chir}(S811)$) one can derive values for both terms from the measured effective HTPs in Table 2:

$$|\beta_{chir}| = 7.35 \qquad \beta_{geom} = -5.85$$

In non-steroidal matrices, the behavior of this enantiomeric pair was quite ordinary, revealing no effects of specific intermolecular interactions. It is worthy of note that the values of HTP for both optical antipodes in matrices B, PBS, PBR (absolute values ranging from 7.3 to 9.0 with average value ca. 8.1) are consistent with the calculated absolute value (7.35) of the intrinsic HTP in the steroidal matrix.

As to the effect of varying the macroscopic chirality with respect to *both* sign and pitch, it can be seen in Table 3 that the HTP asymmetry associated with R811/S811 is essentially invariant. There appears to be no coupling of the macroscopic chirality to those factors involved in the term β_{geom}.

2. (+)/(+)-AmBEPH. The R-(+) form of this chiral compound did not effect the cholesteric spiral in matrix A, whereas its racemic form produced a notable pitch contraction. In this case only the R-(+) enantiomer and a racemic mixture of R-(+)- and S-(−)-forms were available. Assume that the effective HTP of the racemic mixture should be equal to the arithmetic average of the effective HTP for both enantiomers. Using the same equations, one can calculate β_{chir} and β_{geom} as:

$$|\beta_{chir}| = 1.6 \qquad \beta_{geom} = -1.6$$

The calculated value of β_{chir} in matrix A is in reasonable agreement with the effective HTP of R-(+)-AmBEPH in matrices B and PBR, but is not consistent with data in matrix PBS.

3. (+)-PEA/(−)-PEA. In matrices PBS and PBR, which consist of a eutectic mixture of 4,4′-alkylalkyloxysubstituted phenylbenzoates (PPMB and PPPB), doped with ~ 6 wt.% of S1011 and R1011 respectively, enantiomers (+)-PEA and (−)-PEA cause a symmetrical effect on the helix, which undoubtedly originates from interaction of the enantiomers with the achiral nematics PPMB and PPPB, since the concentration of the third chiral component in these mixtures is rather small. However, in the right handed chiral nematic B, both (+) and (−)-PEA show a negative HTP. Matrix B consists of ~ 55 wt.% of nematic PPMB (the same compound employed in matrices PBR and PBS), but also contains ~ 45 wt.% of derivatives of chiral 4-isoamylphenols (AmMPP and AmMPPB) (see Fig. 1 and Table 1). One can attribute the observed nonsymmetrical effect to specific diastereomeric interactions between molecules of (+)-PEA or (−)-PEA and the chiral components of matrix B.

In steroidal matrix A an increase is observed in the absolute value of HTP as well as a negative sign of chiral induction for both optical antipodes. Although the relatively small molecular size of these enantiomers does not lend itself to applying the previously described model for interpretation of lefthandedness of both optical antipodes, one can nevertheless apply the analysis to this system. The effective HTP of these enantiomers in matrix A yields the following values for β_{chir} and β_{geom}

$$|\beta_{chir}| = 0.4 \qquad \beta_{geom} = -2.3$$

The absolute value of β_{chir} is in better agreement with those determined in matrices PBS and PBR where the members of the enantiomeric pair interacted primarily with

molecules of nonchiral nematics PPMB and PPPB. In this case, however, it is possible that the two terms contributing to the effective HTP might reflect the small solute molecule interacting with different chiral centers in the steroidal matrix rather than primarily side chain interactions.

4. d-2-Octanol/1-2-Octanol. Non-mesogenic long chain *n*-alkanes and *n*-alkylalcohols are known to shift the wavelength of maximum reflection of steroidal cholesterics to the blue, i.e. to contract the pitch of the lefthanded macromolecular helix. Therefore, the negative sign of the HTPs of both 2-octanol enantiomers in matrix A was more or less expected, but it is surprising that their magnitude is the same.

In the chiral nematics B, PBS, and PBR, these enantiomers consistently show opposite signs of HTPs (minus for d-2-octanol and plus for 1-2-octanol) and strong asymmetry in their absolute values. HTP of d-2-octanol is 3 times higher than that of 1-2-octanol in matrices B and PBS. But in matrix PBR the value of the HTP for d-2-octanol is 3 times less than that for 1-2-octanol. These results require further experimental confirmation.

5. R1011/S1011 and R-(+)-1, 1'-bi-2-naphthol/S-(−)-1, 1'-bi-2-naphthol. These two pairs of enantiomers produced quite symmetrical responses in all matrices. Unfortunately, due to the insolubility of 1, 1'-bi-2-naphthols in steroidal cholesteric media, it was impossible to measure their HTP in matrix A. As to the enantiomeric pair R1011/S1011, in view of the strong asymmetric behavior of all other optical antipodes in matrix A, their symmetric effects in fact is rather unusual and probably can be accounted for by the different position of their chiral center, namely close to the center of the molecule.

6. (+)-/(−)-BSDAB, (+)-/(−)-Methylephedrine and (+)-/(−) 1-Me, CB3-Cl-40 CB. These pairs, having more than one chiral center (two in (+)-/(−)-methylephedrine, three in (+)-/(−)-BSDAB and two in (+)-/(−)-1-Me, 3-Cl-4OCB), require a different analysis of their behavior.

The specific optical rotations of (+)-/(−)-BSDAB are, of course, not equal: $\alpha_{(+)\text{-BSDAB}} = +65°$; $\alpha_{(-)\text{-BSDAB}} = -26°$. Approximately the same ratio is observed between the absolute values of the effective HTP of these species in chiral nematic matrices (B, PBS, PBR) (see Table 2). But in the steroidal matrix A, the ratio of the values of HTP between (+)-BSDAB and (−)-BSDAB is much smaller; that is, there is a profound decrease in the HTP of (+)-BSDAB in the steroidal matrix.

In the case of (+)-/(−)-methylephedrine, the pair shows almost equal but opposite effects in chiral nematics (B, PBS, PBR), but in the steroidal matrix there is a much lower HTP for (−)-methylephedrine. On the other hand, the pair (+)-/(−)-1-Me, 3-Cl-4OCB produces almost symmetrical effects in steroidal matrix A. These examples further indicate the specific geometric effects which occur in the steroidal matrix with a wide variety of solutes.

CONCLUSION

The non-symmetric effects of enantiomeric pairs of solutes on the chirality of cholesteric phases reported in this work can be explained as being due to a combination of two factors, one arising from the intrinsic chirality of the enantiomer, and the other associated with steric factors arising from localized solute-solvent molecular interactions. These same short-range solute-solvent couplings are, of course, the primary factor responsible for the influence of a chiral solute on an achiral solvent, whether it be liquid crystalline or even an appropriate isotropic medium. Gottarelli, Osipov, and Spada[4] have shown that isotropic biphenyl type solvents show evidence of preferred conformations in the presence of axially chiral biaryl solutes.

There is, however, no evidence that the macroscopic chirality of a cholesteric can influence the microscopic chirality of either an achiral or chiral solute. In the solid state, there are cases where the existence of a chiral space group influences the reactivity of molecules within that structure, resulting in so-called topochemically controlled reactions with chiral consequences. Such cases could also, in principle, exist in liquid crystal phases, but as yet there is no clear-cut example.

Acknowledgments

This work was supported by the National Science Foundation under Grant No. DMR-93-12634. We wish to thank Dr. T. Shibata for providing samples of some of the chiral solutes. Discussions with Prof. H. -G. Kuball and Prof. G. Gottarelli are also gratefully acknowledged.

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