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INDUCTION OF CHOLESTERIC MESOPHASES IN NEMATIC LIQUID CRYSTALS BY SOME CHIRAL ARYL ALKYL CARBINOLS

A QUANTITATIVE INVESTIGATION

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Abstract—A series of chiral aryl alkyl carbinols, dissolved in MBBA and other nematic solvents, induce cholesteric structures. The handedness of the induced mesophases and the twisting power of the dopant alcohols are studied by means of CD and Grandjean-Cano microscopic techniques. The investigation points out the possibility of obtaining information on the stereochemistry of the dopant by studying the characteristics of the induced helices.

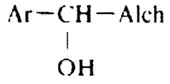
Two different types of H-bonds between alcohols and MBBA are discussed in connection with a possible model of induction.

When a chiral "guest substance" is dissolved in a nematic mesophase, the longitudinal axes of the "host" molecules become twisted to form a helical structure.[1] The cholesteric mesophase so obtained is characterized by handedness (P or M-helix) and pitch. Equal amounts of enantiomeric guest substances of equal optical purity induce helical structures with opposite chirality and identical pitch.[2] Different substances show a different ability to twist the nematic phases.

These facts point out the possibility of obtaining stereochemical information by studying the characteristics of the helices induced by different "guest substances".

The usefulness of comparing the chirality of the induced cholesteric mesophases, in order to correlate the absolute configurations of the inducing molecules, relies on the expectation that molecules with similar chemical structures and having the same configuration interact in a similar way with the nematic liquid crystal used as a solvent. It is fundamental for the competitivity of the method that the variations of the interactions between "host" and "guest" according to the molecular structure of the guest are less dramatic than the variations observed in the chiroptical properties of the guest itself.

The first successful application of this idea was the correlation of the absolute configurations of a series of chiral secondary alcohols containing an aromatic ring and having a single asymmetric centre, using a qualitative comparison of the helices induced in MBBA.[3]



$$\underset{\displaystyle OH}{Ar-\underset{|}{C}H-Alch}$$

After the first experimental observations a tentative explanation of the results was given in which the alcohols interact by means of a H-bond with the nitrogen of the Schiff-base (MBBA) and the aromatic group (Ar) is aligned parallel to the nematic director. The steric bulk of the third substituent of the chiral carbon atom (Alch) prevents a nearby molecule of MBBA from lying parallel to the hydrogen bonded one and imposes a definite twist.[4]

A different approach to the determination of the absolute configuration was recently attempted and is based on measurements of the pitch and handedness of a large number of organic molecules by means of IR ORD.[5a,b] As the results obtained did not show a correlation between the *R-S* Cahn-Ingold-Prelog configuration symbols (based on the atomic numbers) and the induced handedness, a different empirical system of priorities was proposed which allows the correlation of a large number of derivatives. However, this scheme of priorities does not seem to be general and exceptions were found by the authors themselves[5] and other workers.[6] Generally speaking, it seems difficult to assign to a set of chemical groups a sequence of priorities which applies also to molecules having a very different structure"[a] [7]; moreover, the specific chemical structure of the liquid crystalline solvent cannot be ignored.

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[a] A striking example which shows how delicate the situation is which determines the handedness of cholesteric mesophases is the even and odd alternating effect described for pure mesogens by Gray and McDonnell.[8]

More recently, Pirkle and Rinaldi[9] studied qualitatively the cholesteric mesophases induced by alcohols and proposed an alternative induction mechanism based on specific interactions between MBBA and the inducing alcohols.

In this paper we complete and extend our investigations to the quantitative determination of the "twisting power" of a series of alcohols where the aromatic system, the polarity and the bulk of the alkyl groups are varied.

Determination of pitch and handedness of cholesteric mesophases

Both the pitch and handedness of the cholesteric helices can be detected by chiroptical techniques, optical rotatory dispersion (ORD) and CD, by characterizing the selective reflection band. A right-handed helix (P-helix) originates a negative reflection Cotton-effect and vice versa[10] (λ_0 = np where λ_0 is the wavelength of the reflection band, n the main refractive index and p the pitch). However cholesteric mesophases induced by the addition of optically active non nematogenic substances to nematic liquid crystals are in most cases characterized by such long pitches that the corresponding reflection bands lie in the IR region[11,12] which is outside the range of commercial dichrographs.

With standard dichrographs, it is possible to detect only the chirality of the helices working at the absorption band of the liquid crystal chromophore.

The pitches were determined by means of the Grandjean–Cano method which is based on the observation of the discontinuity lines appearing when a cholesteric liquid crystal is inserted in a cell of variable thickness.[13,14] A drop of the cholesteric solution was put between a plano convex lens and a glass plate both rubbed previously with tissue paper: the rubbing directions of the lens and plate were kept parallel to each other.[15] The preparation was observed with the polarizing microscope using monochromatic light, and showed both Grandjean–Cano disclinations (concentric circles) and extinction rings which are connected to the variation of the rotatory power with the sample thickness.[16,17] The separation of the disclination lines gives the pitch value:[15]

$$\frac{r^2}{2R} = (n - \tfrac{1}{2})|p|/2 \qquad n = 1, 2, 3$$

Where R is the radius of the lens and r is the radius of the Grandjean–Cano circles.

Rotation of the analyzer displaces the extinction lines due to the rotatory power. In particular, if a clockwise rotation of the analyzer displaces the circles towards increasing thickness of the sample, the rotatory power is right-handed, as is the cholesteric helix (if the wavelength of the light used is shorter than the wavelength of the selective reflection band).[16,17]

The handedness of the helices was further investigated by means of the elegant method recently described by Heppke and Oestreicher[18] 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 double spiral disclination line appears: a right-handed helix gives a left-handed double spiral and vice versa. In all cases the independent methods, CD, sign of the rotatory power (some preparations however did not show a clear displacement of the extinction lines) and spiral, gave concording results.

The pitch is inversely proportional to the concentration of the solute and it is convenient to define a quantity β, the "twisting power", which represents the ability of the "guest" to twist the nematic phase.[19] Here we shall use the definition given by Korte *et al.*[19]

$$\beta = (pcr)^{-1}$$

where c is the concentration (in mol. of solute/mol. of solution) and r the enantiomeric purity of the "guest".

A rigorous comparison of the twisting powers of different optically active compounds should be based on measurements of pitches performed at the same reduced temperature (T/T_c) and possibly at a temperature (T) at least 20° lower than the clearing point (T_c).

In fact the temperature dependence of the long range orientational correlation of the mesomorphic solvent and the occurrence of pretransitional effects could produce scattered results of twisting powers[a].

RESULTS AND DISCUSSION

The characteristics of the cholesteric mesophases induced in a 50:50 mixture of MBBA and EBBA by the compounds investigated together with the handedness of the helices induced in nematic phase IV are reported in Table 1. In Table 2 the data for phenylethanol in different nematic solvents are reported.

With the exception of 1-phenyl-2,2,2-trifluoroethanol which shows a very small twisting power of opposite handedness, and will be discussed later, all aromatic derivatives show a correlation between their absolute chirality (the *R*, *S* nomenclature is misleading owing to the different priority of the CF_3 and the alkyl groups with respect to the aromatic moiety) and the handedness of the induced helices. As has previously been reported, the configuration corresponding to *R*-phenylethanol induce negative helices and vice versa the configuration corresponding to *S*-1-phenylethanol induce positive helices.

The values of the twisting power greatly increase by increasing the size of the aromatic moiety, and are less markedly but clearly influenced by increasing the bulk of the alkyl group when the aromatic moiety is the same. In derivatives **2**–**5** one observes a nice increase of β in passing from Me to Et, i-Pr and t-Bu. In derivatives **8** and **9** the substitution of Me with CF_3 causes a comparable relative increase of the twisting power.

The series of derivatives **2**–**9** seems to fulfill the requirement that the dominant "host-guest" interactions are of the same type in all members.

The variations of β with the structure are not unexpected in the light of the model hypothesized.

It is worth noting that the methyl ether of derivative **2** induces in the mixture MBBA/EBBA helix of opposite handedness[5b] and that also a solution of **2** in Merck phase 1008 (a mixture of benzoates esters) gives an opposite helix with respect to MBBA/EBBA. In other

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[a] In our case the clearing points of the solutions do not differ more than 6° and are more than 30° higher than the temperature of the experience.

Table 1. Dependence of the twisting power of the chiral aryl-alkhyl carbinols on R and R′ substituents and handedness of cholesteric induced helices relative to the same absolute chirality (I) of the alcohols

	Alcohol		Absolute	Helix	Twisting power[a]	Helix
n	R	R′	Configuration	(MBBA)	(MBBA)	(Phase IV)
1	CF_3	Phenyl	S[b]	P	0.2[c]	P
2	Me	Phenyl	R	M	1.0[d]	M
3	Et	Phenyl	R	M	1.3	M
4	Pr^i	Phenyl	R	M	1.4	M
5	Bu^t	Phenyl	R	M	1.5	M
6	Me	3-Pyridyl	R	M	1.0	M
7	Me	Mesityl	R	M	3.4	M
8	Me	1-Naphthyl	R	M	7.7	M
9	CF_3	1-Naphthyl	S[b]	M	8.5	M
10	CF_3	2-Naphthyl	S[b]	M	8.1	M

[a]Values corrected tp 100% optical purity of chiral alcohol. [b](S)-trifluoromethylcarbinols are configurationally related to the corresponding (R)-methyl alcohols. [c]lit.[5b] < 0.5. [d]Lit.[5b] 0.99.

Table 2. Chiralities of the induced helices and twisting power (β) of R-(+)-1-phenylethanol in different nematic solvents

MBBA	"Phase IV"	"Phase 1008"
M β =1.0	M β =1.1	P β =2.5

words, suppression or variation of the hydrogen bond seem to cause dramatic effects.

The qualitative data in "Phase IV" are instead for all derivatives the same as for mixture MBBA/EBBA and similarly the quantitative value for derivative **2**.

A possible model of induction

In a previous research we showed[4] that alcohols are selectively H-bonded to the nitrogen of the Schiff base and that the O–H stretching direction is perpendicular to the local nematic director (long axes of the MBBA molecules). These data, considerations of the property of aromatic groups to align in the liquid crystalline matrices and standard conformational analysis arguments concerning the preference of the O–H group, H-bonded, to be *anti* to the alkyl group, led to the tentative model depicted in Fig. 1: the two principal interactions between the chiral guest molecule and an MBBA molecule are the H-bond and the tendency to align of the aromatic moiety. The steric bulk of the alkyl group prevents a nearby molecule of MBBA from lying parallel to the H-bonded one and imposes a definite local twist: the overall effect will be a macroscopical chirality dependent on the concentration of the dopant.

Obviously this will not be the only possible interacting arrangement in the solution and alternative configurations could be expected such as a doubly H-bonded one, the first H-bond being identical to the one described, the second one being formed between the carbinyl hydrogen of the dopant and one aromatic ring of MBBA[†]. In this configuration, however, the aromatic ring of the alcohol is quasi perpendicular to the nematic director, leading to a conformation which is certainly not favoured and

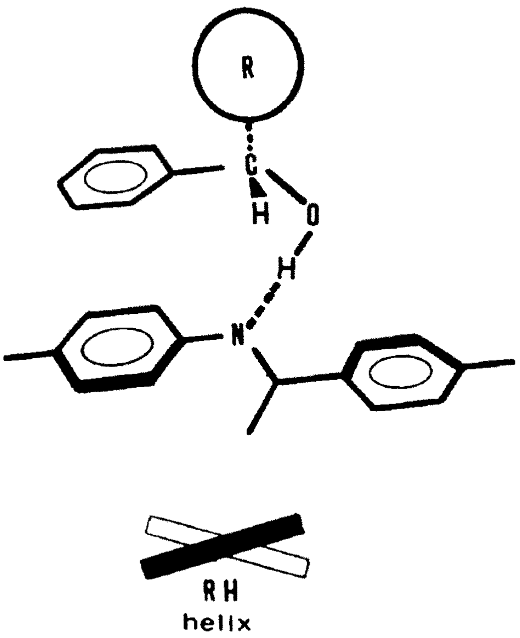
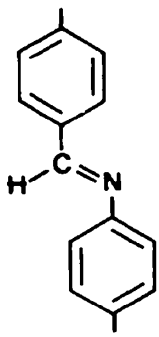
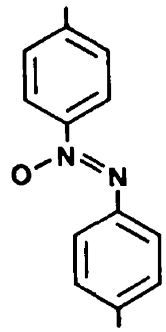
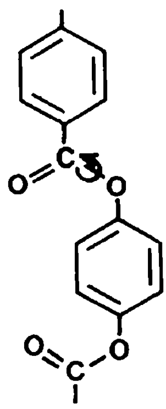


Fig. 1. Principal interaction between a chiral alcohol and a MBBA molecule. The steric bulk of the *R* group prevents nearby molecules of MBBA from lying parallel to the H-bonded one and imposes a definite twist. The (*S*)-alcohol induces a right-handed helix (P).

This type of interacting configuration is the base of the model of induction proposed by Pirkle and Rinaldi. Both the aromatic and the alkyl carbinyl substituents are quasi perpendicular to the long axis of MBBA. The adjacent MBBA molecules will align on the side of the less repellent of the two protruding carbinyl substituents; Me is less repellent than phenyl, CF_3 more more repellent than phenyl,[9] *R*-phenylethanol gives a M-helix and the corresponding *S*-trifluoro derivative a P-helix.







therefore less populated and important in a fairly rigid mesomorphic matrix[d].

According to our model, the twisting power should increase when the tendency to align of the aromatic group is greater and when the bulk of the alkyl group is augmented. This is in fact what is observed.

The effects of solvent variation are not unexpected: "Phase IV" is a mixture of azoxy derivates of structure and rotational freedom analogous to the Schiff bases (Fig. 2).

In this case, there is probably an H-bond with the oxygen and sterically the situation does not change with respect to MBBA.

In the mixture of esthers constituting the nematic "Phase 1008", there are several equivalent sites available for hydrogen bonding; the possibility of sign inversion is therefore not surprising.

The deviating case of 1-phenyl-2,2,2-trifluoroethanol can be understood if one considers that the carbinyl hydrogen must be more acidic than in 1-phenylethanol and therefore its ability to give an H-bond with one aromatic ring of MBBA will probably compete favourably with the contrasting tendency of the substituted phenyl group to avoid perpendicular orientations and to align its long axis parallel to the director; this will not be the case when a naphthyl group is present which is much better aligned and is very unlikely to be found in a perpendicular position. As a result of the two opposite effects (in the trifluoro derivate the doubly H-bonded configuration should give opposite chirality to the cholesteric structure[9]) a very small twisting power is expected. Possibly alcohols not containing aromatic groups will also adopt a perpendicular configuration in MBBA/EBBA mixture.

CONCLUSION

With the exception of derivative 1 it is possible to correlate the configurations of the alcohols containing an aromatic group directly bonded to the asymmetric centre by comparing the handedness of the cholesteric mesophases induced in the MBBA/EBBA mixture and in "Phase IV". A similar correlation by comparing the CD spectra is impossible owing to the different nature of the aromatic chromophores.

The method is rapid and requires only a few milligrams of one single enantiomer.

The quantitative values of the twisting power are a useful guide for monitoring possible abnormal or deviating behaviour of one member during the study of a series and are fundamental in the attempt to understand a possible induction mechanism.

Even if the situation in general is probably more complex (e.g. twisted MBBA, several conformations of the hydrogen-bonded species, etc.) the model proposed does not seem to be weakened by the quantitative investigation, but rather to gain strength.

EXPERIMENTAL

CD spectra were measured using a Jouan II dichrograph. In order to check artefacts due to linear dichroism, the measurements were carried out with the cell in two positions rotated of 90 degrees.

Microscopic measurements were carried out using a Zeiss polarising microscope and "Galileo" plano convex lenses of radius from 20 to 40 mm.

The concentric alignments were obtained by pressing the lens on a tissue paper attached to a rotating plate. In order to obtain more easily the spirals, both the lens and the glass plate were treated with N-methylaminopropyltriethyoxysilane (MAP by Dow-Corning).[28]

For sake of simplicity in Table 1 are reported data for chiralities related to *R*-1-phenylethanol.

Derivatives

-(S)-(+)-1-*Phenyl-2,2,2-trifluoroethanol* (1) was obtained by fractional of the esters of the racemate with (−)-*ω*-camphanic acid,[21] b.p. 83–85° at 14 mmHg, $[\alpha]_D^{20}$ + 40.1° (neat) {lit.,[21] b.p. 100–110° at 0.6 mmHg, $[\alpha]_D^{20}$ + 41.3° (neat)}.

(R)-(−)-1-(1-*Naphthyl*)-2,2,2-*trifluoroethanol*,[10] b.p. 160° at 2 mmHg, $[\alpha]_D^{25}$ − 19.5° (*c* 3.0 in EtOH) {lit.,[21] m.p. 51.6 − 53.2°, $[\alpha]_D^{25}$ − 25.7° (EtOH)} and (R)-(−)-1-(2-*naphthyl*)-2,2,2-*trifluoroethanol*,[11] m.p. 84–86°, $[\alpha]_D^{25}$ − 18.8° (*c* 9.2 in

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[d] This configuration can instead be possible in an isotropic solvent when the alcohol-imine systems are characterized by a more pronounced conformational freedom. For instance, specific carbinol-imine solvation model, based on doubly H-bonded interactions, seem to rationalize asymmetric reaction results obtained by oxidation of prochiral Schiff bases with *m*-chloroperoxybenzoic acid in the presence of chiral methyl or trifluoromethyl-carbinols[20] better than the model of the present work.

$CHCl_3$) {lit.,[23] $[\alpha]_D$ − 3.7° ($CHCl_3$), optical purity 11.5%} were obtained by reduction of the corresponding ketones by actively fermenting yeast.[24]

(S)-(−)-1-(3-*Pyridyl*)-*ethanol* (**6**),[25] was obtained by fractional crystallization of the acid tartrate from MeOH, $[\alpha]_D^{20}$ − 33.5 (10%, HCl) {lit.[25] $[\alpha]_D^{20}$ − 33.4 100% optical purity}.

Derivatives, *R*-(+)-**3**, $[\alpha]_D$ + 7.59, optical purity 26.4%, *R*-(+)-**4**, $[\alpha]_D$ + 20.3 optical purity 42.6% and *S*-(−)-**5**, $[\alpha]_D$ − 7.98, optical purity 22.0% were kindly provided by Prof. L. Lardicci.[27]

Methyl-carbinols (**7** and **9**) were resolved by fractional crystallization of the brucine salts of the respective phthalic mono-esters, prepared by conventional methods.[27]

(R)-(+)-1-(2,4,6-*Trimethylphenyl*)-*ethanol* (**7**) had m.p. 49–51°, $[\alpha]_D^{20}$ + 47.0 (*c* 1.0 in EtOH) {lit.,[28] m.p. 52°, $[\alpha]_D^{20}$ + 52.0 (EtOH)}

(R)-(+)-1-(1-*Naphthyl*)-*ethanol* (**9**) had b.p. 165° at 11 mmHg, $[\alpha]_D^{20}$ − 71.4 (*c* 4.0 in EtOH) {lit.,[25] b.p. 166° at 11 mmHg, $[\alpha]_D^{20}$ + 78.9 (EtOH)}.

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