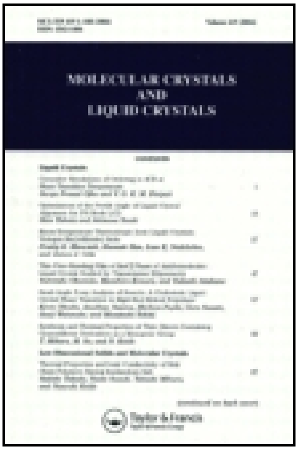

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Helical Twisting Powers of Steroidal Molecules in Aromatic Nematic Liquid Crystals

Marcel Hibert [a] & Guy Solladie [a]

[a] Laboratoire de Stéréoohimie de l'Ecole Nationale Supérieure de Chimie, ERA DU CNRS n° 687, Université Louis Pasteur - B.P. 296/R8 - 67008, STRASBOURG, France

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HELICAL TWISTING POWERS OF STEROIDAL MOLECULES IN AROMATIC NEMATIC LIQUID CRYSTALS

by Marcel HIBERT and Guy SOLLADIE

Laboratoire de Stéréochimie de l'Ecole Nationale Supérieure de Chimie, ERA DU CNRS n° 687, Université Louis Pasteur - B.P. 296/R8 - 67008 STRASBOURG - France.

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Abstract

Twisting powers of steroidal molecules were shown to be a property strongly dependent of the nematic structure. The twist handedness of 4-cyano 4'-n-pentyl biphenyl by cholesteryl derivatives appears to be controlled by the steric environment of steroid carbon-3.

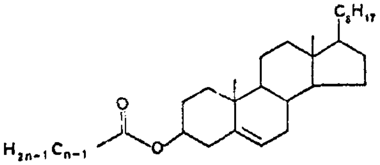
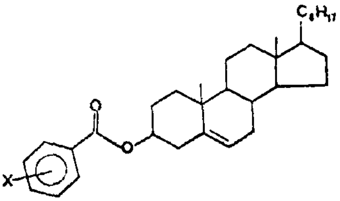
In spite of numerous publications on the twisting powers of optically active molecules in nematic liquid crystals (1-13), there is still a lack of a general relationship between molecular structure and helical twist. The recent works of Korte (14) and Gottarelli (15,16) showed that there is indeed no simple general relationship between the absolute configuration of the doping molecule and the handedness of the twist.

In this paper, we report a study of the twisting powers of cholesteryl alkanoates as well as some other steroïd derivatives in an aromatic nematic liquid crystal : 4-cyano 4'-n-pentylbiphenyl (PCB).

The helical pitches p of the cholesteric phase obtained by doping PCB with these steroïdal molecules as well as the handedness of the macrostructure were determined either by the droplets method or by the Grandjean-Cano Wedges method (13, 17, 18).

TABLE I

Twisting Powers of Cholesterol esters in PCB

 			 		
n	β^a	β^b_M	X	β^a	β^b_M
2	-6.5	-11.3	H	-5.0	-9.9
3	-5.4	- 9.7	p-F	-4.4	-9.0
4	-5.1	- 9.4	p-Cl	-4.3	-9.1
5	-5.1	- 9.5	p-Br	-4.0	-9.2
6	-4.8	- 9.4	p-NO_2	-4.5	-9.7
7	-4.7	- 9.4	p-CN	-3.6	-7.5
8	-4.5	- 9.2	p-Me	-4.5	-9.1
9	-4.5	- 9.6	m-OMe	-4.7	-9.9
10	-4.4	- 9.5	p-OMe	-4.5	-9.3
14	-3.9	- 9.3	p-tBu	-4.0	-8.8
16	-3.7	- 9.1	p-NH_2	-1.9	-4.0

a) $\beta = 1/p.c$, determined from the slopes of the experimental curves $1/p = f\ (c)$, p expressed in microns and c in g/g - A negative sign indicates a left handed helix.

c) $\beta_M = \beta . |M_D/M_N|$, molecular twisting power, M_D and M_N being the molecular weights of the doping molecule and the nematic (13)

The comparison of our results, listed in Table I, to those obtained by Baessler and Labes (8) from the same cholesteryl alkanoates but dissolved in a compensated nematic (cholesteryl myristate and chloride in the ratio : 1.00/1.75), lead to several comments :

- a weak variation of the β_M values in our case (from 9 to 11) in sharp contrast with the results in the compensated nematic (from +2 to -7.5). These twisting powers are in both cases considerably smaller than in other nematics : cholesteryl myristate (n = 14) showed a β_M = -25.2 in MBBA and -16.7 in MBAB (18). Therefore the strong dependence of the twisting power of a given molecule on the nematic structure is once again fully demonstrated (13,18).

- in the compensated nematic, Baessler and Labes observed that the twisting power increased with the ester chain length till n = 6. In our case, we observed the reverse : β_M decreased from n = 2 to n = 3 with no significant variation with a further lengthening of the chain.

Therefore, the ester chain length does not contribute to the twist of PCB, result ruling out, at least in our case, the model proposed by Baessler and Labes in which the handedness of the twist was supposed to be the result of the lever arm made by this side chain in a peculiar conformation.

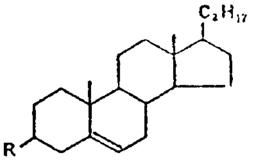
The second set of results listed in Table I showed in addition that in the case of substituted cholesteryl benzoates, the aromatic part of the molecule appears to have no significant contribution to the twist, whatever was the substituant on the aromatic ring, with however two exceptions : a p-cyano group and a p-amino group, the latter giving quite similar results to cholesterol itself and cholesteryl chloride (Table II).

We observed also that β_M decreased sharply and linearly in going from an acetate group to a trichloroacetate one (Table II) as probably the result of the strong negative dipole moment introduced by the chlorine atoms.

We also noticed that an iodine atom increased significantly β_M with respect to a chlorine atom.

TABLE II

Twisting Powers of cholesteryl derivatives in PCB



R	β	$β_M$	R	β	$β_M$
OH	-3.6	- 5.6	OH	-3.6	- 5.6
$OCOCH_3$	-6.5	-11.3	Cl	-2.1	- 3.5
$OCOCH_2Cl$	-4.4	- 8.1	I	-4.4	- 9.5
$OCOCHCl_2$	-3.9	- 7.8	$OCOCH_3$	-6.5	-11.3
$OCOCCl_3$	-3.2	- 6.9	OTHP[a]	-9.0	-17.0

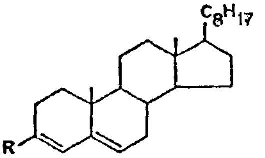
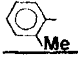
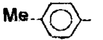
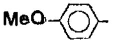
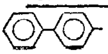
a) OTHP = O-tetrahydropyranyl.

Finally the aromatic nature of PCB and its ability to give charge transfer complexe interactions prompted us to investigate substituted aryl-3 cholestadienes as doping molecules (Table III)

If the induced helicity is still left-handed in the case of 3-(O-tolyl)-cholestadiene, it changes drastically to a right-handed in the other cases, behavior already noticed in MBBA and MBAB. Therefore, the coplanarity of the aromatic ring and the double bonds seems to be an important factor.

TABLE III

Twisting Powers of aryl-3 cholestadienes in aromatic nematics

	R	β_M in PCB	β_M in MBBA[a]	β_M in MBAB[b]
		-3.2	-1.7	-2.7
		+6.8	+12	+5.1
		+8.1	+15.6	+2.7
		+8.2	+ 0.7	+3.1

a) results from (18), MBBA = p-méthoxybenzylidène p-n-butylaniline

b) results from (18), MBBA = p-méthoxy p-n-butyl azoxybenzene.

In conclusion to this study, we can refute the concluding remarks of Baessler and Labes claiming that the twisting power was a molecular property independent of the matrix. It is indeed the results of solute-solvent interactions and as so strongly dependent of the liquid crystalline matrix.

In the case of PCB and steroidal solutes, the molecular packing appears to be controlled, at least in part, by the steric environment of carbon-3 : a 3 β substituent as well as an aromatic ring non-coplanar with the double bonds of cholestadiene gives a left handed helix. The polarity of the substituent is probably one of the factors controling the twist amplitude.

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