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HELICAL TWISTING POWER OF CHIRAL SUBSTITUTED DIBENZO |b,f|1,4-DIAZOCINES IN NEMATIC LIQUID CRYSTALS.

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*Abstract.*Twisting powers of some chiral substituted dibenzo|b,f|1,4-diazocines were determined in nematic liquid crystal MBBA.

Since the pioneering work of Friedel(1) in 1923, it is well known that on dissolving a small amount of optically active material in a nematic mesophase one gets a cholesteric structure.Such long pitch cholesteric liquid crystals suitable for the cholesteric-nematic phase-change of electro optical display devices are usually obtained by doping nematics with cholesterol derivatives mainly because of the low cost and high twisting power of these molecules.However till now,only few studies have attempted a systematic study of the factors controlling the helical twisting power of molecules (2,3).

Our approach to this problem was to assume that

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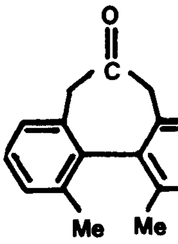
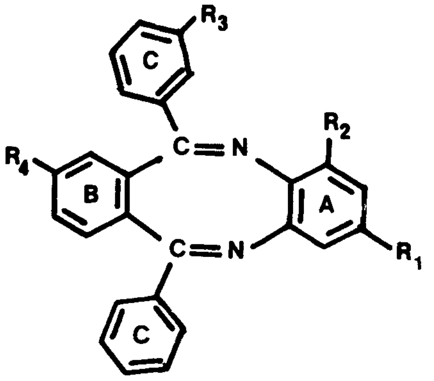
dissymetric chiral compounds,where the chirality origin is conformational,should have high helical twisting powers.

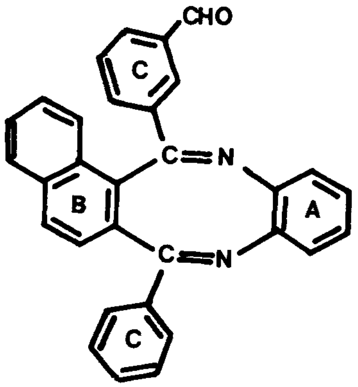
Recently,we have shown (4) that the chiral ketone 1 has a high twisting power in MBBA.We are reporting now the results concerning a series of chiral substituted dibenzo|b,f| 1,4-diazocines 2 to 6.These molecules possess a three dimensional tub-like conformation (the eight-membered ring being a diazacyclooctatetraene system) and as such are resolvable into optically active forms because of their high inversion barriers (5).



1

$|\alpha|^{D}_{20} = + 617°$





	R_1	R_2	R_3	R_4	$\|\alpha\|_D$
2	CHO	H	H	H	+ 277°
3	H	CHO	H	H	+ 242°
4	H	H	CHO	H	- 43°
5	H	H	H	CHO	- 33°

6

$|\alpha|_D = + 154°$

Molecules 2 to 5 differ only by the position of the carboxaldehyde group (6).

The twisting powers β of these molecules have been determined in MBBA; the half-pitches were measured from the optical pattern displayed by droplets of the cholesteric phase floating in an isotropic liquid (7), (fig. 1).

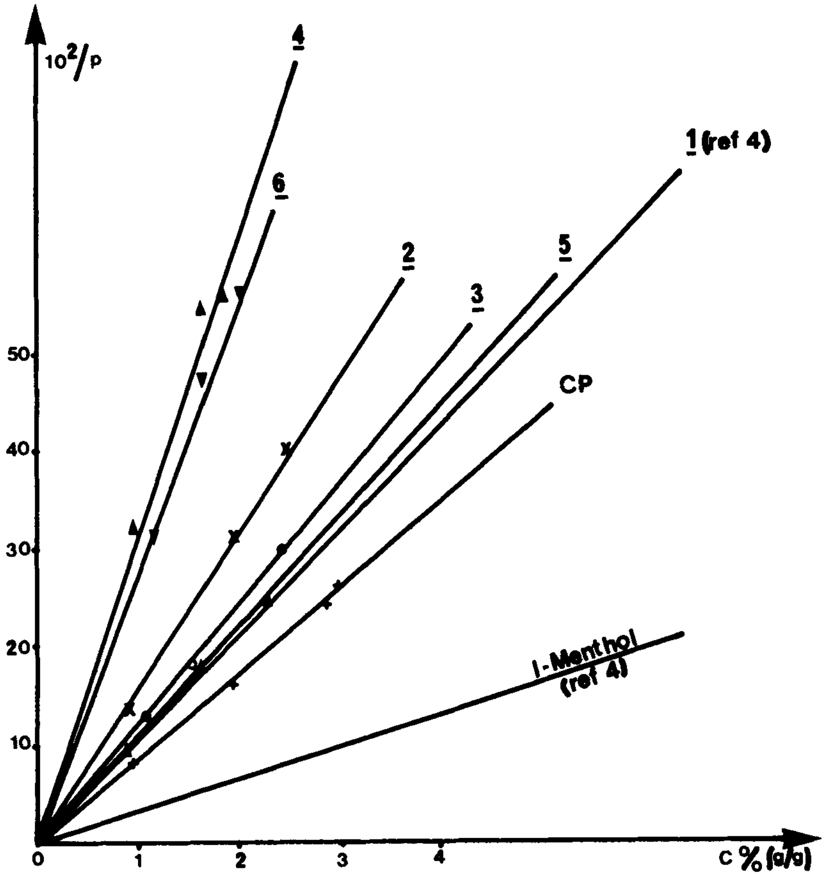


Figure 1
Concentration dependance of the helical pitch for different MBBA-optically active compounds mixtures.

We have also determined by the same method the β value for cholesteryl propionate (CP) in MBBA : $\beta = 8.4 \mu m^{-1}$ which is in good agreement with the litterature value (8) : $\beta = 9 \ \mu m^{-1}$ by the Cano-Wedge method.

We have also introduced (Table 1) molecular twisting powers $|\beta|_M$ which ,in our opinion,are more suitable because the resulting twist is produced by an asymmetric molecular arrangement localy created by one (or a full number) of doping molecules.These $|\beta|_M$ values emphasizes particularly that diazocines 2 to 6 have higher twisting powers than CP and 1-menthol (1-M).We shall notice also that CP has a $|\beta|_M$ value higher than molecule 1.

Table 1
Twisting powers of some optically active molecules in MBBA.

molecule	1	2	3	4	5	6	1-M	C.P.
$\beta = \frac{1}{p.c}$ a	10.2	16	12	30	11	27	3	8.4
$\lvert\beta\rvert_M = \beta.\frac{M_D}{M_N}$ b	8.8	23.1	17.3	43.4	15.9	44	1.7	13.9

a) determined from the slopes of the experimental curves $1/p = f(c)$,p expressed in microns and c in g/g.

b) molecular twisting powers,M_D and M_N being the molecular weights of the doping molecule and the nematic.

These results and the results obtained (4) with compound 1 : $|\beta|_M = 13.5$ in K15 (p-n-hexyl p-cyanobiphenyl) and $|\beta|_M = 8.8$ in MBBA,suggest that there is a close relationship between the nematic and optically active molecule structures.The twisting powers are higher when the chiral molecule has a structure similar to the nematic structure,allowing a better intermolecular arrangement and a better transmission of the chirality.That's indeed the case with diazocines and MBBA (fig.2).

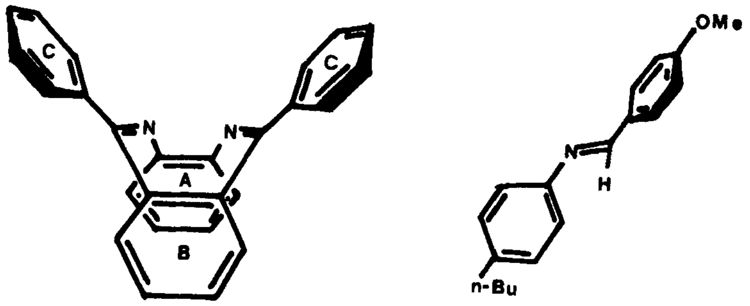


Figure 2

Comparison of the results of table 1 shows a marked difference in β values according the aldehyde location : the twisting power is about two times higher when the aldehyde is on ring C.

Finally we can remark that,as expected,there is no relationship between the β value and the amplitude of the optical rotation of the chiral doping molecule.

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