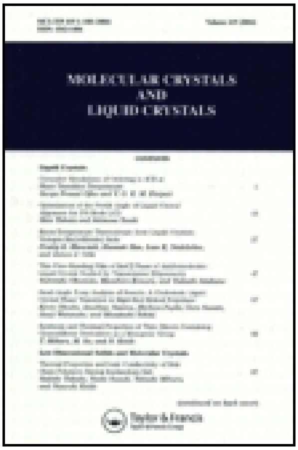

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The Relationship Between Helical Twist Sense, Absolute Configuration and Molecular Structure for Non-Sterol Cholesteric Liquid Crystals

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THE RELATIONSHIP BETWEEN HELICAL TWIST SENSE, ABSOLUTE CONFIGURATION AND MOLECULAR STRUCTURE FOR NON-STEROL CHOLESTERIC LIQUID CRYSTALS

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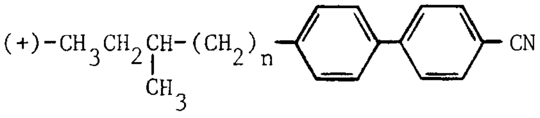
Abstract The helical rotary senses for a number of non-sterol cholesteric liquid crystals have been determined and from the results, a simple rule relating molecular structure, absolute configuration and twist sense is proposed. The rule has been used to predict correctly the helical twist senses for some new cholesterogens.

Many non-sterol cholesterogens are now known[1,2,3] in which the optical activity is provided by terminal chiral alkyl or alkoxy groups, and the influence of molecular structure, particularly the proximity of the chiral centre to the ring system, on twisting power, i.e., on the pitch of cholesteric liquid crystal, has been mentioned.[1,2]

Recently we reported the synthesis and properties of a number of new cholesterogens[4] of general structures I-VII and briefly referred to the cholesteric helical twist senses of these materials on the basis of some preliminary measurements and experimental observations.

I



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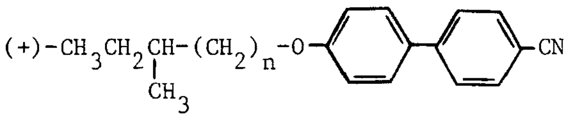

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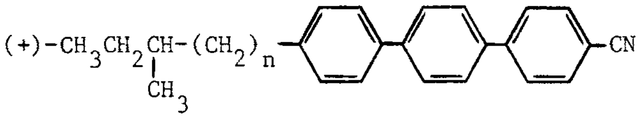

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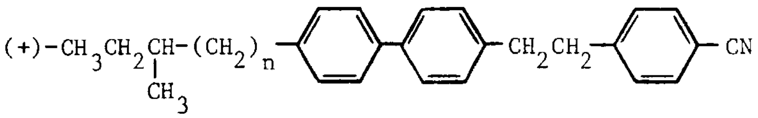

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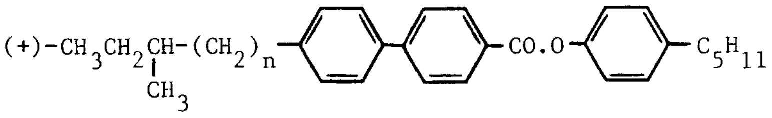

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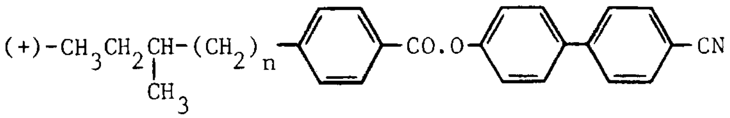

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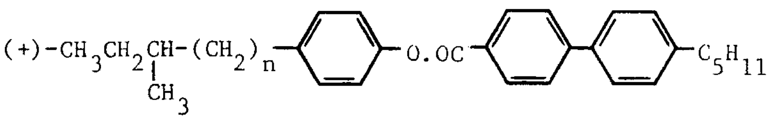


In the above structures, n has a small integral value, e.g., 1, 2, 3.

All the above compounds have now been studied using the contact method[5] and their cholesteric helical twist senses have been established. As standards for the experiments, cholesteryl chloride, which is known[6] to give a cholesteric phase with a right handed helical rotation (type:dextro), and cholesteryl myristate (type:laevo) were used.

When the interface of two cholesteric phases with the same helical senses was observed microscopically, no discontinuity in the texture was visible, i.e., a continuous cholesteric texture was observed (Fig. 1a) from left to right across the field of view. However, when the helical twist senses were opposite, a narrow band of nematic texture was observed (Fig. 1b) separating two cholesteric regions.

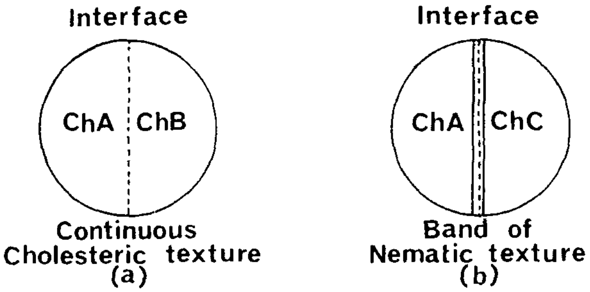


FIGURE 1 Field of view in the contact method in the neighbourhood of the interface between (a) two cholesteric phases (ChA and ChB) of identical helical senses and (b) two cholesteric phases (ChA and ChC) of opposite helical senses.

The results obtained in this way for 15 compounds with structures I-VII indicated that when the point of chirality was at an <u>even</u> number of atoms* from the ring system, then the cholesteric phases were <u>dextro</u> in type, and conversely, when the chiral centre was at an <u>odd</u> number of atoms* from

---

* These atoms may be entirely carbons, or in the case of compound II, carbons and oxygen, etc.

the ring system, the cholesteric phases were laevo in type. Since all of the materials examined were synthesised from (−)-2-methylbutan-1-ol, via (+)-2-methylbutyl bromide, both of which have the absolute configuration S,[7] by reactions which would not invert the configuration at the chiral centre, then all the cholesterogens can also be assigned the S configuration. Since enantiomers give cholesteric phases with opposite helical twist senses,[8] we can therefore propose the following rule expressed as permissible combinations of three letters defined below.

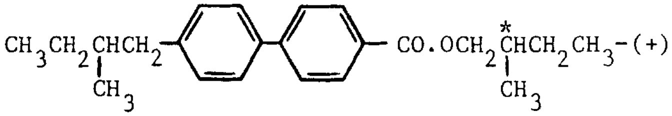
Right-handed cholesteric helices	Left-handed cholesteric helices
S E D	S O L
R O D	R E L

where:

S and R	refer to the absolute configuration at the chiral centre and not to the sign of the optical rotation measured using a polarimeter.
D and L	refer to the senses of helical rotation, dextro and laevo respectively, of the cholesteric phases.
E and O	refer to the point of asymmetry being at an even or odd number of atoms from the ring system.

If we consider the compound with structure VIII below, we can now test the applicability of the rule when the chiral centre has an environment with respect to the ring system which is different from that in compounds I-VII.

VIII



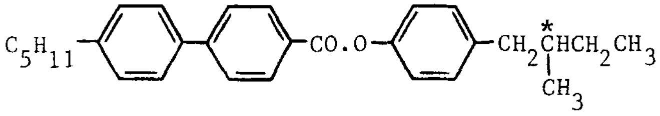
* Denotes the single asymmetric centre in the molecule; the ester was made from the racemic modification of 4'-(2"-methylbutyl)biphenyl-4-carboxylic acid.

C-I, -4°; Virtual Ch-I, -70°
Pitch for a 30 % (w/w) solution in a mixture of
MBBA/TBBA = 3.1 μm.

We know that the absolute configuration of the molecule is S, since (−)-2-methylbutan-1-ol was used to prepare the ester, and that the chiral centre is at an even number of atoms (four) from the ring system. Therefore the cholesteric helical sense must be dextro. This is in fact what is found experimentally.

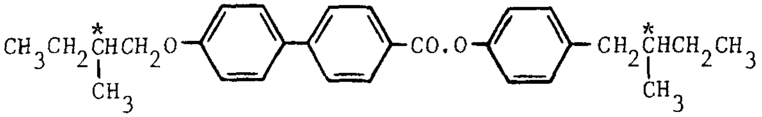
Thus the rule can be used to predict one unknown value if any two of the above three quantities are known. The rule can also explain apparent discrepancies in cholesteric pitch lengths when a second chiral centre is introduced into a cholesterogen - see compounds IX and X below.

IX



C-S_B, 66°; S_B-S_A, 77.3°; S_A-Ch, 133.9°; Ch-I, 156°
Pitch = 2.6 μm for a 10% (w/w) solution in
4-n-pentyl-4'-cyanobiphenyl (5CB)

X



C-S_A, 87.8°; (S_C-S_A, 85.3°); S_A-Ch, 123.4°; Ch-I, 144.5°
Pitch for a 10% (w/w) solution in 5CB = 4.6 μm

Compound IX, which has only one chiral centre, has a smaller cholesteric pitch length than the cholesteric phase of compound X, which contains two chiral centres.

However, this result is understandable when one considers that the (+)-2-methylbutyloxy group is S O L, while the (+)-2-methylbutyl group is S E D. There is therefore a cancelling-out effect. Since the (+)-2-methylbutyl group

(S E D) has the greater twisting power, the net helical twisting sense is right-handed (type:dextro) for the cholesteric phase. This agrees with the experimental observations.

Our results for compounds I-III have also been confirmed[9] for their low concentration solutions in wide range, nematic liquid crystal eutectics[10] such as E_7, used in twisted nematic display devices. It is of course important that the helical twist sense of cholesteric additives used for the prevention of areas of reverse twist should be the same as the preferred sense of the quarter helix of the device; the sense of this quarter helix is determined by surface forces originating from molecules adhering to the glass surfaces at a low tilt angle. Therefore we hope that the empirical rule we have developed will serve as a useful guide to the choice of non-sterol cholesterogens for display device application.

Acknowledgement The authors thank the U.K. Ministry of Defence for a research grant.

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Note: Since this manuscript was completed, discussions with Professor J Billard have revealed three further instances in which the empirical rule applies (including an example of REL). However, one exception to the rule has arisen and will require experimental checking. Despite this, we feel that it is worthwhile to state the empirical rule in print, as this may encourage the publication of further results which will accumulate more information concerning the general validity of the rule, or its limitations.