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INDUCTION OF A CHOLESTERIC MESOPHASE IN A NEMATIC LIQUID CRYSTAL BY SOME OPTICALLY ACTIVE ALCOHOLS: A POSSIBLE METHOD FOR THE CORRELATION OF CONFIGURATIONS

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It is well known that cholesteric mesophase can be produced by addition of chiral molecules to nematic liquid crystals (1); in particular it has recently been shown by using chiroptical techniques that enantiomeric cholesteric mesophases are formed by the addition of enantiomeric optically active compounds (2). Despite these observations, no systematic attempts have been made to correlate the configuration of the inducing optically active molecule to the chirality of the helix induced in the nematic mesophase. The only paper which has appeared on the subject deals with very few examples and does not afford any applicable results(3). This approach seems interesting to us as it is often impossible using C.D. spectra to correlate absolute configurations of molecules possessing a similar chemical structure, but with small differences, particularly in the chromophoric groups (for example benzenes and substituted benzenes) (4). If the chirality of the induced cholesteric mesophase depends principally on the chirality of the inducing molecule, it is in principle possible, by measuring the C.D.(*) of the liquid crystal chromophoric group, to obtain information on the configurations of the inducing molecule, despite the different nature of the chromophores of the latter. We have measured the C.D. spectra of solutions of a series of alcohols having known absolute configuration in p-Methoxy benzylidene-p'n-butilaniline (MBBA) (2 mol per cent) using an optical pathlength of 50μm (Mylar spacers). The measurements were performed at the band edge of the MBBA absorption at ca. 410 nm at temperatures ranging from 18 to 22°C; no reflection colours were observed in the solutions and no "reflection bands" (6) were detected in the Jouan II dichrograph range. However, the very strong C.D. measurement at the band edge warrants the formation of the cholesteric mesophase. A small C.D. absorption can sometimes be detected in samples of pure MBBA, caused by an undesired twist of the quartz walls composing the "sandwich" cell; this phenomenum is, however, in the

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(*)The C.D. measured is a function of the linear dichroism of the MBBA chromophore (5).

worst cases, one order of magnitude smaller than that induced by the optically active compound, and has a sign which can vary from one preparation to another. Measurements performed an several different preparations rule out such possible artefacts. In other induced cholesteric mesophases, recently described (5), no reflection colours and "reflection band" were observed. In these cases the "reflection band" probably lies in the I.R. region; in our case it was impossible to shift it to the 400-600 nm region by temperature variations. No dichroic absorption was detected by heating the sample above 40°C (isotropic). The results are summarized in the Table. For the first nine members of the series, e.g. the alcohols containing an aromatic moiety, there is indeed a correlation between the chirality of the induced cholesteric mesophase and that of the inducing optically active molecule, despite the different nature of the chromophores and chemical substitution around the asymmetric centres. Derivatives V and VI have S and R absolute configuration on account of the precedence of the $CH_2-N<$ over the phenyl group, but the sequence around the asymmetric centre is the same as in R and S phenyl ethanol respectively. For the aliphatic derivatives instead, the chirality of the cholesteric mesophase depends heavily on the chemical constitution; however, the two derivatives substituted with similar groups (X,XI) and (XII and XIII) give homogeneous results. A model which is not disagreement with current theoretical knowledge (9) could be one where the optically active molecule orient themselves in MBBA and form a sandwich-type complex causing, by means of the chiral centre, a rotation of the superimposed MBBA molecule with respect to the molecule lying below. The good correlation obtained in the aromatic series is probably connected with the ability of the aromatic groups to orient themselves in the liquid crystalline mesophase (10). This is not the case for the aliphatic series where the orientation is small and therefore influenced by different substitution. From these first results, the applicability of this method for correlating absolute configurations seems to be at least in the same range as the "quasi-racemate" techniques with the advantages of requiring only a few milligrams of active substance and of being a very quick experimental procedure.

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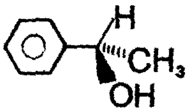
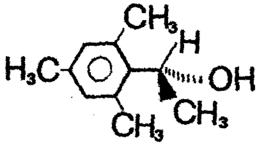
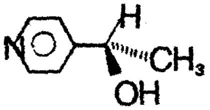
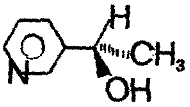
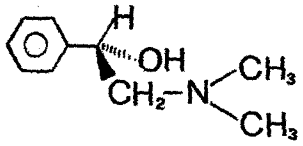
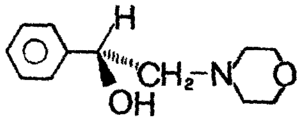
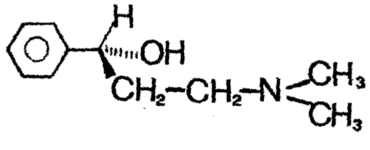
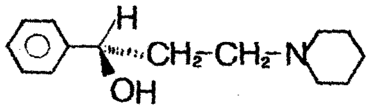
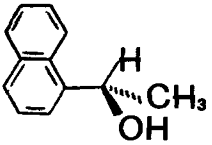
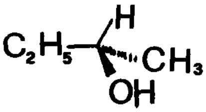
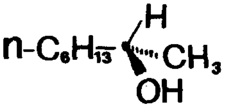
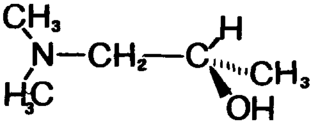
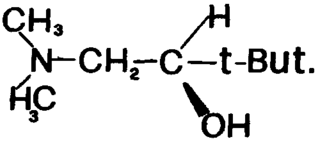
TABLE

Configuration	Compound	Reference	Sign of the C.D. at the band edge of the MBBA absorption
I° S (-)			+
II° R (+)		7	-
III° S (-)		8	+
IV° S (-)		8	+
V° S (+)		9	-
VI° R (-)		9	+
VII° R (+)		10	-
VIII° S (-)		10	+

IX°	S(-)		7	+
X°	S(+)			-
XI°	S(+)			-
XII°	S(-)		9	+
XIII°	S(-)		9	+

REFERENCES

(1) H.Stegemeyer and K.J.Mainush, Chem.Phys. Letters 6, 5,(1970) and references therein

(2) H.Stegemeyer and K.J.Mainush, Naturwiss., 58, 599 (1971).

(3) F.D.Saeva, Mol. Cryst. and liq. Cryst. 23, 171 (1973).

(4) P.Biscarini, G.Gottarelli, B.Samori' and G.D.Nivellini, Tetrahedron, 28, 4139 (1972).

(5) R.J.Dudley, S.F.Mason and R.D. Peacock, J.C.S. Chem.Comm., 1084 (1972).

(6) L. De Vries, Acta Cryst. 4, 219 (1951).

(7) V.Prelog, E.Philibin, E.Watanabe and M.Wilhelm, Helv. Chim. Acta, 39, 1086 (1956).

(8) G.Gottarelli and B. Samori', J.C.S. Perkin II, 1974, 1462.

(9) S.Marzocchi, unpublished results.

(10) R.Andrisano, A.S.Angeloni and S.Marzocchi, Tetrahedron, 29, 913 (1973)

(11) W.J.A.Goossens, Mol.Cryst. and Liq. Cryst., 12,237 (1971).

(12) A.Saupe, Mol. Cryst. and Liq. Cryst., 16, 87 (1972).