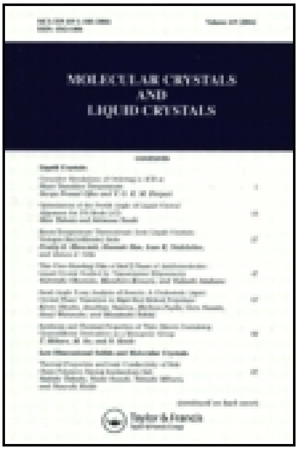

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DIPOLE MOMENTS AND THE SMECTIC C PHASE

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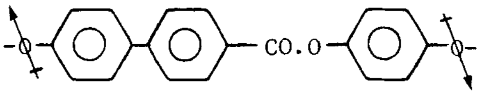
Abstract Current theories of the smectic C phase depend primarily on the presence of dipole moments. However, certain mesogens have now been prepared which suggest that an alternative view relating to the origin of these tilted lamellar phases will have to be considered.

Introduction Until recently, the McMillan Theory[1] of the smectic C phase had been widely accepted, although there were some anomalies[2]; furthermore, over the past two years, the preparation of new mesogens[3] has cast further doubt over the theory. The McMillan model is dependent on the molecules having two large, oppositely directed, 'outboard' dipoles associated with oxygen or nitrogen atoms. If the molecule possesses an additional dipole moment positioned at the molecular centre and directed across the molecular axis, it is proposed that the outboard dipoles should be equidistant from this dipole. Thus, for a molecule containing a 'central core' of the type

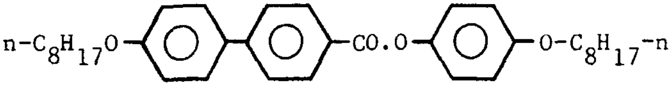


the outboard dipole moments would occur at the terminal oxygens. The ester function constitutes the central dipole.

We have now synthesised compounds that contain the above 'central core' structure except for the oxygens at each end of the core. These have been eliminated at one end or both ends by having either branched or n-alkyl chains directly attached to the ring system. Using these new systems, we have still succeeded in obtaining mesogens which exhibit smectic C phases. The following mesogens (2)-(4), involving partial or complete replacement of the terminal oxygens of the 'central core' shown above, are of particular interest. Compound (1) containing two terminal alkoxy groups provides the reference system for comparison.

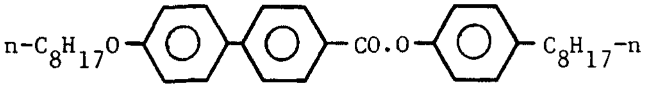
In the data below, C = crystal; S_A, S_B, S_C = smectic of the A, B, C types; Ch = cholesteric; I = isotropic liquid. Transition temperatures in °C are given below the arrows representing the transitions. The asterisks indicate any chiral centres in the molecules.

(1)



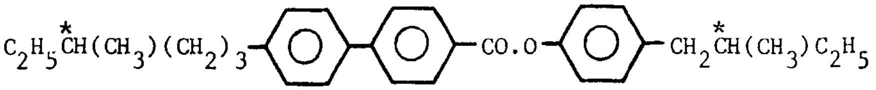
$$C \xrightarrow[110^\circ]{} S_B \xrightarrow[116^\circ]{} S_C \xrightarrow[165^\circ]{} S_A \xrightarrow[200^\circ]{} I$$

(2)



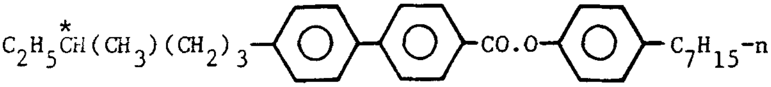
$$C \xrightarrow[110^\circ]{} S_B \xrightarrow[110.5^\circ]{} S_C \xrightarrow[132.5^\circ]{} S_A \xrightarrow[184^\circ]{} I$$

(3)



$$C \xrightarrow[83.4^\circ]{} Ch \xrightarrow[114^\circ]{} I \qquad (Ch \xrightarrow[81.0^\circ]{} S_A \xrightarrow[74.3^\circ]{} S_C) \text{ monotropic}$$

(4)



$$C \xrightarrow[91.5^\circ]{} S_C \xrightarrow[93^\circ]{} S_A \xrightarrow[112^\circ]{} Ch \xrightarrow[131^\circ]{} I$$

A smectic C phase was observed for all the above mesogens which range from type (1) with two outboard dipoles and one central dipole, to types (3) and (4) with only one dipole associated with the ester function, through the intermediate case for type (2).

Experimental evidence for the S_C phases The microscopic textures of the S_A phases of compounds (1) and (2) showed both focal-conic and homeotropic areas which, on cooling, gave the broken fans and the schlieren texture, respectively, which are typical of the S_C phase. On further cooling, the S_C phases gave rise to the clear unbroken fan texture and homeotropic areas of the S_B phase.[3b] Since this third phase is positive uniaxial and of lower thermal stability than the S_A phase, it must therefore be an orthogonal S_B phase, i.e., S_{B_A}. Thus, the preceding tilted phase cannot be a tilted S_B phase. The chiral S_C phases of the compounds (3) and (4) had the 'petal' texture[3c] typical of these S_C phases when they are in the planar texture. Moreover, when the S_A phases were cooled to give focal-conic S_C phases, an iridescent[4] planar texture was obtained by mechanical displacement of the cover slip. A colour change in the reflected light was then obtained by further cooling the slide in air.

The S_A and S_C phases of compound (1) were shown to be separately miscible with the S_A and S_C phases respectively of the standard ester n-butyl 4'-n-octyloxybiphenyl-4-carboxylate. In turn, compound (1) was shown to be completely miscible with compound (2) for each of their three phases (S_A, S_C, S_{B_A}). Furthermore, these three phases of compound (1) were shown to be separately miscible with the S_A, S_C, and S_{B_C} phases of TBBA. Similarly, the S_A, S_C, and Ch(N) phases of compounds (3) and (4) were shown to be separately miscible with the corresponding S_A, S_C, or N phases of TBBA.

Finally, the enthalpy peak associated with the S_A to S_C transition for compound (1) was shown to be almost undetectable by D.T.A., and the enthalpy value is considered too small to quote a meaningful value. This suggests a second order or a very weak first order transition in agreement with other thermodynamic data for S_A to S_C transitions.

Discussion Consider now what consequences the properties of these four compounds have for the McMillan Theory of the S_C phase. McMillan's Theory was based firmly on the belief held at that time that all the known compounds exhibiting the S_C phase contained terminal outboard dipole moments. For example, evidence in support of the theory was drawn from the fact that the 4,4'-di-n-alkoxyazoxybenzenes exhibit S_C phases, whereas the corresponding 4,4'-di-n-alkylazoxybenzenes exhibit S_A phases. However the new compounds (2), (3), and (4) contradict the idea that two such dipoles are necessary to provide the driving force to tilt the overall structure, and thus we believe that this puts McMillan's Theory seriously in doubt. We would add however, that such dipolar properties do appear to stabilize the S_C phase, i.e., give higher S_C-S_A transition temperatures.

The Wulf Theory[5] on the other hand, depends on the molecule being of a zig-zag shape. The branched alkyl compounds now prepared are in fact moving away from such a zig-zag conformation, and yet they exhibit the S_C phase, whilst their non-branched anologues exhibit S_A and S_B phases; this is the opposite of what Wulf predicts. The latest theory, by Priest,[6] does not really consider changes in molecular architecture as small as these shown by compounds (1) to (4). However, since such small changes as those involved on moving from n-alkyl terminal to branched terminal chains are of paramount importance in deciding whether the S_C phase is formed at all, we feel that Priest's Theory is not detailed enough in concept to be regarded as an absolute theory.

Finally, we would note that, because the branched molecules (3) and (4) are chiral,[4] this does not preclude the possibility that the ferroelectric dipole, proposed by Meyer et al.[7] for the chiral S_C phase, provides the driving force for tilt to occur for such mesogens. To show that chirality and symmetry considerations are not important factors in relation to tilt, we prepared the racemic modification of compound (3); this showed an ordinary S_C phase which was miscible with that of TBBA. This shows that the tilt in these S_C phases is not an outcome of symmetry and the induced ferroelectric dipole. Hence the ferroelectric properties of chiral S_C phases are a consequence of tilting and not the cause of tilting.

The transition temperatures for the racemic modification of ester (3) were different from those of the chiral ester: C-S_A, 86°; S_A-N, 96.1°; N-I, 118.5° (S_A-S_C-monotropic, 78.1°). This must reflect the fact that the ester molecules contain two chiral centres, and that the racemic modification is a physical mixture of two diastereoisomeric pairs of compounds.

No existing theory of the S_C phase therefore appears to offer an explanation of these results which we now report briefly because of their general significance. Further studies in this area are in progress and it is hoped that from this work a clearer understanding of the relationships between molecular structure and the incidence of S_C phases will finally emerge.

A detailed version of this work will be presented elsewhere. However, it is relevant to state that each of the esters described was purified by column chromatography and recrystallisation until constant transition temperatures were obtained. The products were each shown to give a single spot on thin layer chromatography, and mass spectrometry and infra-red spectroscopy confirmed their structures. Transition temperatures were determined using a Mettler FP 52 hot stage and control unit. A 7% w/w solution of the racemic modification of ester (3) gave a zero rotation, within experimental error, when examined using a Bendix-NPL Automatic polarimeter (Type 143A). As a consequence, the highest temperature phase of the racemic modification was a nematic phase of infinite pitch.

References

1 W.L. McMillan, Phys. Rev., A8, 1921 (1973).

2 H. Schubert, R. Hacker, and K. Kindermann, J. prakt. Chem., (4) 37, 12 (1968). R. Steinsträsser, Z. Naturforsch., 27b, 774 (1972). G.W. Smith,

Z.G. Gardlund and R.J. Curtis, Mol. Cryst. Liq. Cryst., 19, 327 (1973).

3 a J.W. Goodby and G.W. Gray, J. Phys. (Paris), 37, 17 (1976).

b J.W. Goodby and G.W. Gray, Mol. Cryst. Liq. Cryst., 37, 157 (1976).

c G.W. Gray and D.G. McDonnell, Mol. Cryst. Liq. Cryst., 37, 189 (1976).

4 G.W. Gray and D.G. McDonnell, to be published.

5 A. Wulf, Phys. Rev., A11, 365 (1975).

6 R.G. Priest, J. Chem. Phys., 65(1), 408 (1976).

7 R.B. Meyer, L. Liébert, L. Strzelecki and P. Keller, J. Phys. Lett. (Paris), 36, L69 (1975).