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# Some New Smectic F Materials

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# SOME NEW SMECTIC F MATERIALS

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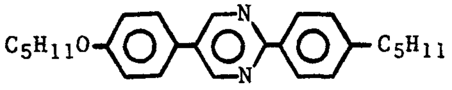
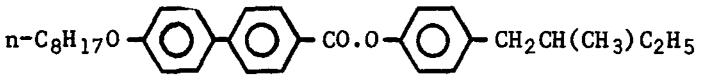
*Abstract* In the course of studies on the smectic C phase, we have succeeded in preparing three new compounds each of which exhibits a well defined smectic F phase. In all of these materials, the F phase gives a smectic C phase on heating and a smectic H phase on cooling. Moreover, these three compounds are members of two related homologous series of esters; therefore it seems probable that many more of the other homologues will exhibit smectic F properties.

*Introduction* Until this present work, only one material[1] was known to exhibit a smectic F phase. This compound has the structure



and is very difficult to synthesise. Recently,[2] however, we have been studying the effect of 'terminal outboard dipole moments' on the formation of the smectic C phase, and as a consequence of this, we have succeeded in preparing (by general methods) three new esters which exhibit smectic F phases. The structures and transition temperatures (°C) of these three compounds are:

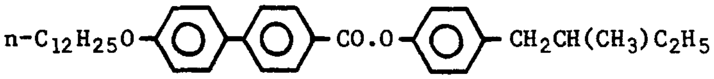
(1)



$$C \xrightarrow[76]{} S_F \xrightarrow[79]{} S_C \xrightarrow[132]{} S_A \xrightarrow[170]{} N \xrightarrow[174]{} I$$

$$(S_F \xrightarrow[72]{} S_H \xrightarrow[61]{} S_G \xrightarrow[46]{} C_1 \xrightarrow[37]{} C_2)$$

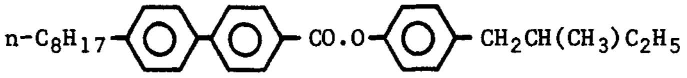
(2)



$$C \xrightarrow[72]{} S_F \xrightarrow[78]{} S_C \xrightarrow[131]{} S_A \xrightarrow[164]{} I$$

$$(S_F \xrightarrow[68]{} S_H \xrightarrow[64]{} C)$$

(3)



$$C \xrightarrow[67]{} S_F \xrightarrow[69]{} S_C \xrightarrow[84.5]{} S_A \xrightarrow[136]{} N \xrightarrow[141]{} I$$

$$(S_F \xrightarrow[64]{} S_H \xrightarrow[40]{} C)$$

( ) monotropic sequences of transition

It is interesting to note that ester (1) (4-(2'-methylbutyl)phenyl 4'-n-octyloxybiphenyl-4-carboxylate) is pentapolymorphic, so establishing the thermodynamic sequence of five smectic phases. Since it has also been shown that the D phase is more thermally stable than the C phase,[3] and that the B phase is more thermally stable than the H phase[4] (tilted B phase), the thermodynamic ordering of the known smectic polymorphic forms appears to be as follows:

A, D, C, F, B, H, E, G

| most thermally stable | least thermally stable |
|---|---|

The G phase is placed below the E phase, simply because tilted smectic phases appear to lie below their orthogonal analogues.

Note: all three esters were racemates

*Discussion* The proof that these three esters exhibit smectic F phases was obtained by rigorous methods. These are discussed in the four sections given below:

(a) Microscopic Textures: 4-(2'-Methylbutyl)phenyl 4'-n-octyloxybiphenyl-4-carboxylate, compound (1), on cooling from the isotropic liquid, gave a nematic phase. On further cooling, this phase gave a smectic phase with either the homeotropic or the clear focal-conic fan texture. The phase separated from the nematic phase as bâtonnets, indicating that it was of the A type. On cooling, this phase gave a tilted smectic phase which exhibited two textures, the broken fan and schlieren textures. In the fan texture, the fans were exceptionally broken, and their backs were sanded and mottled. The schlieren texture was highly birefringent, and changed colour with temperature decrease. The phase was shown to be mobile by the flow properties on mechanical displacement of the coverslip. Thus, this evidence indicates that the phase is of the C type.

On further cooling, this phase gave another tilted smectic phase which also exhibited two types of texture, namely the schlieren texture and the broken fan texture. The phase was highly birefringent and exceptionally mobile, thus indicating that the phase was not smectic H in type. The broken fans exhibited a chequerboard pattern across their backs. The schlieren texture was characterised by the lack of real 'brushes', and it was impossible to bring the texture into sharp microscopic focus. The schlieren texture was also highly coloured.

On cooling this phase, there was a transition to another tilted phase. This again exhibited two textures, the broken fan and mosaic textures. The broken fans had a patchwork pattern across their backs. The mosaic texture resulted on cooling the schlieren texture of the preceding phase, and was characteristic of the $S_H$ phase. Thus, if this phase is of the $S_H$ type, then the preceding phase must be either a $S_F$ phase or a completely new type of phase.

On further cooling, the $S_H$ phase gave rise to yet another tilted phase. The transition was characterised by the mosaic areas becoming crossed with a number of lines, creating the impression of a corrugated surface; these lines disappeared on further slight cooling. The phase therefore exhibited either the broken focal-conic texture or the mosaic texture. The mosaic texture was distinctly different from that of the preceding phase. Thus, if the preceding phase is $S_H$ in type, then, as this phase is biaxial and exhibits a mosaic texture, it is reasonable to assume that it is G in type.

Although compounds (2) and (3) do not exhibit $S_G$ phases, they otherwise exhibit the same smectic sequences as that of compound (1). The microscopic textures of the $S_F$ phase of (2) and (3) are not quite the same as those exhibited by the $S_F$ phase of compound (1). The $S_F$ phase of (2) exhibits a texture which is less highly coloured than the corresponding texture of (1). The texture has a wizened appearance and there are less schlieren ' brushes' compared with (1). Compound (3) exhibits a $S_F$ phase which has a mosaic type of texture which is distinctly different from that of the $S_H$ phase formed on further cooling. The 'mosaic' texture of the $S_F$ phase of (3) is not therefore a true mosaic; it has certain schlieren characteristics, and therefore has a texture of an intermediate nature.

(b) Differential Thermal Analysis: Differential thermal analysis showed that the enthalpy values associated with each of the $S_A$ to $S_C$ transitions were extremely small. This is typical of a weak first order or second order change, and is in keeping with the transition being of the $S_A$ to $S_C$ type. All the $S_C$ to $S_F$ transitions gave relatively large enthalpy values. The enthalpies for all the transitions are given below; where the values are in k cal mol$^{-1}$.

| Ester | ΔH N-I | ΔH $S_A$-N or I | ΔH $S_C$-$S_A$ | ΔH $S_F$-$S_C$ | ΔH $S_F$-$S_H$ | ΔH $S_H$-$S_G$ | ΔH C-S |
|---|---|---|---|---|---|---|---|
| 1 | 0.23 | 0.61 | * | 0.44 | 0.095 | * | 1.94 |
| 2 | - | 0.77 | * | 0.32 | * | - | 4.24 |
| 3 | 0.25 | 0.41 | * | 0.34 | * | - | 3.76 |

* too small to be evaluated

(c) Miscibility Studies: Compound (1) was shown to have N, $S_A$, $S_C$, $S_H$, and $S_G$ phases by their separate co-miscibility with the corresponding known phases of the standard material TBBA (N, $S_A$, $S_C$, $S_H$, and $S_G$). The smectic F phase of compound (1) was also shown to be miscible with the F phase of the pyrimidine compound.[1] Moreover, the F phases of (2) and (3) were shown to be miscible with that of (1).

(d) X-ray Studies: Measurements of the lamellar spacings in all the smectic phases mentioned have been obtained[5] by X-ray methods. For example, for ester (1) the lamellar spacings were: $S_A$, 30.9Å; $S_C$, 30.8Å to 27.7Å as the temperature falls; $S_F$, 28Å; $S_H$, 28.4Å; $S_G$, 28.4Å (fully extended molecular length, 31.8Å). The diffraction pattern for each $S_F$ phase showed a sharp inner ring and an outer ring which was less diffuse than that of a $S_C$ phase.

*Experimental* The three esters were prepared by standard methods. All were purified by column chromatography and recrystallised 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 analysis confirmed their structures. Transition temperatures were determined using a Mettler FP 52 hot stage and control unit. Checks on the transition temperatures and the measurement of enthalpies of transition were made using a Stanton-Redcroft low temperature differential thermal analyser (Model 671 B).

*Conclusion* The preparation of these $S_F$ esters confirms that the $S_F$ phase does exist and has a structure intermediate between the structures of the $S_C$ and the $S_H$ phases.

A more detailed account of this work giving photomicrographs, miscibility diagrams, and differential thermal analysis traces, together with results on other homologues of the series in which these esters occur, will be presented at a later date.

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