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Liquid-crystalline cyclic trimers derived from benzene-1,3,5-tricarboxylic acid

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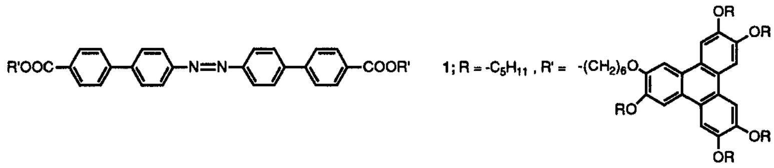
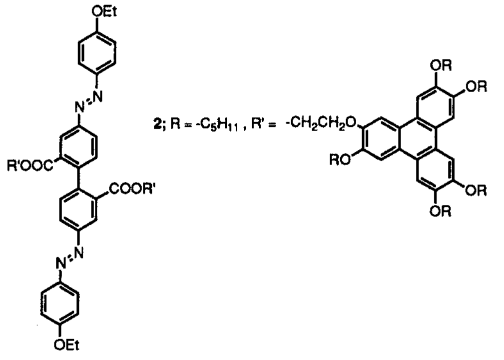
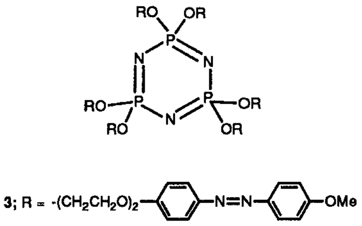
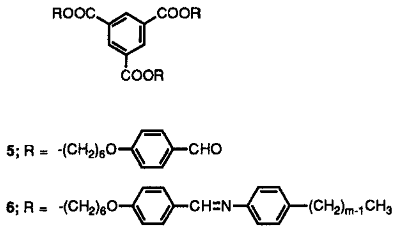
A new class of structurally complex materials whose constituent molecules are composed of three rod-like units, each attached to a central disc-like unit via a flexible spacer have been synthesized and their phase behaviour investigated. They are found to exhibit a rich and unusual liquid-crystalline polymorphism.

Mesogenic molecules with complex architectures (for example, phasmidic, linear and dimeric, cross-shaped, and swallow-tailed molecules) [1] are of great fundamental interest since they provide a challenge to our understanding of the molecular factors which lead to the stabilization of liquid-crystalline phases. Among the many complex


1; R = $-C_5H_{11}$, R' = $-(CH_2)_6O-$


2; R = $-C_5H_{11}$, R' = $-CH_2CH_2O-$


3; R = $-(CH_2CH_2O)_2-C_6H_4-N{=}N-C_6H_4-OMe$


5; R = $-(CH_2)_6O-C_6H_4-CHO$

6; R = $-(CH_2)_6O-C_6H_4-CH{=}N-C_6H_4-(CH_2)_{m-1}CH_3$

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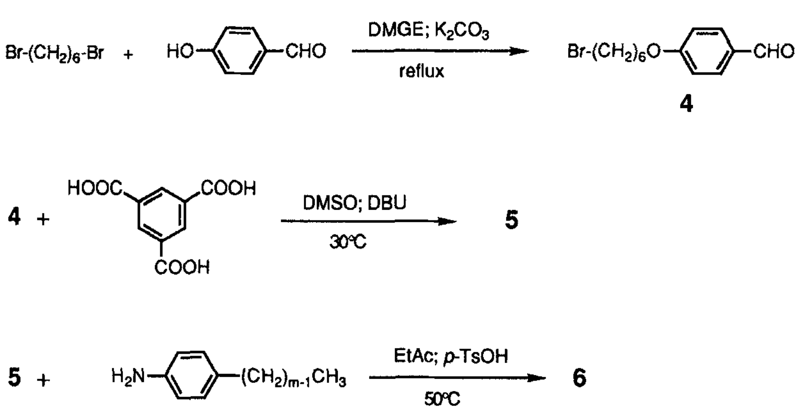
molecular architectures which have been found to lead to thermotropic mesomorphism, systems which combine disc-like units with rod-like units are particularly intriguing. To date, three classes of systems of this type have been reported [2–6] (structures **1**, **2**, and **3**); only **2** and **3** exhibit liquid-crystalline behaviour. Compound **2** forms a columnar phase and compound **3** forms a nematic phase, although it is not stated whether this is calamitic or discotic in nature. In this preliminary communication we describe the unusual phase behaviour of a new class of liquid crystal (**6**). Materials such as **1**, **2**, and **6** can be regarded as liquid-crystalline chimeras [7] in that they have disc-like units with the high substitution symmetry that is required for the formation of discotic mesophases, but also have structural elements (i.e. rod-like units) that promote calamitic mesomorphism. It is possible, at least in principle, that chimerical molecules of this type could exhibit a cross-over from calamitic to discotic behaviour either as a function of temperature or as a function of subtle structural changes which alter the relative importance of rod–rod and disc–disc interactions. In view of the unusual geometry of these systems it might be expected that the cross-over regime could involve the formation of biaxial mesophases.

The homologues **6** are denoted as [6; *m*], where *m* represents the number of carbon atoms in the *n*-alkyl chain attached to the aniline ring. They were obtained by the sequence of reactions shown in the scheme. The transition properties of the series [6; *m*] were investigated by polarized light microscopy, differential scanning calorimetry, and X-ray diffraction. Their phase behaviour is shown in figure 1. All members of the homologous series exhibited liquid-crystalline behaviour. The homologous series shows a crossover from nematic to purely smectic behaviour when the number of carbon atoms in the terminal chain exceeds the number of carbon atoms in the central methylene chain (i.e. when $m > 6$). Thus, whereas the homologue with $m = 6$ has an N–I transition, the homologue with $m = 7$ exhibits an S_C–I transition. A particularly interesting and unusual feature of the crossover regime is that the S_C phase becomes progressively less stable than the S_A phase as the length of the terminal chain increases, such that when $m \geqslant 8$ the S_C–I transition is replaced by an S_A–I transition. The N, S_C, and S_A phases were identified on the basis of their textures and of X-ray diffraction data. It should be noted that the optical textures of these mesophases correspond to the textures observed in conventional calamitic systems. Homologues with $m = 7$, 8, and 9 exhibit transitions from the S_C phase into a tilted mesophase. A further, low-lying smectic phase was observed for homologues with $m \geqslant 6$. The optical textures of these



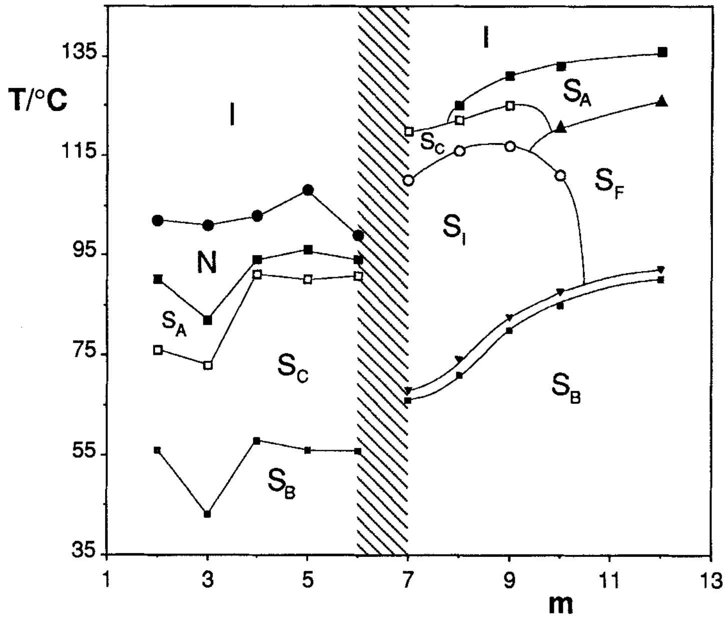


Figure 1. Transition temperatures for series **6**. Note that the solid lines are intended only as a guide to the eye. The identification of the low lying smectic phases as S_I, S_F, and S_B is purely speculative.

two smectic phases, which are mobile though highly viscous, could not be related to the textures observed in conventional calamitic materials. If it is assumed that all of the mesophases formed by series **6** are calamitic in nature, then these two smectic phases could be S_I and S_B type phases, respectively. Note that for homologues with $m \geqslant 7$ the transition into the putative S_B phase appears to be preceded by an unidentified mesophase with a temperature range of $\sim$2°C. The temperature range of the S_B phase increases as *m* increases. By contrast, the phase provisionally identified as S_I initially increases in stability, peaking when $m=9$, then its temperature range decreases dramatically for $m=10$, being progressively replaced by another smectic phase, which may be an S_F phase. It is emphasized that these phase assignments are highly speculative, and in particular, it should be noted that the X-ray diffraction patterns of the phases identified as S_I and S_F do not exhibit the sharpened wide angle reflections normally associated with such calamitic mesophases.

The transition entropies of compounds **6** are listed in the table. The entropy change associated with the N–I transition is small ($\Delta S/R \approx 0{\cdot}8$ to $1{\cdot}3$ as *m* increases), though somewhat larger than the values for the N–I transitions in monomeric calamitic mesogens. The S_A–N entropies are small ($\Delta S/R \approx 0{\cdot}3$–$1{\cdot}9$) but not unlike the case of low molar mass materials. The S_C–S_A transitions for homologues with $m \leqslant n$ are weakly first order ($\Delta S/R \approx 0{\cdot}2$) becoming second order as *m* increases. The entropy changes associated with the S_C–I and S_A–I transitions span the range 6·9 to 8·9 as a function of increasing *m*. These values are much larger than those reported for monomeric or most dimeric calamitic mesogens. It should be noted that the entropy change at the S_A–I transition for compound [6; 8] is 7·55 while $\Delta S/R$ for the S_C–I transition of compound [6; 7] is 6·94. This appears to be anomalous since S_C phases are generally more ordered than S_A phases. However, the unusually highly ordered nature of these S_A phases is

Entropy changes at the transition for series **6**, expressed as the dimensionless quantities $\Delta S/R$.

m	N–I	S_A–N S_A–I*	S_C–I S_C–S_A* S_F–S_A**	S_I–S_C S_I–S_F*	S_B–S_C S_B–S_I* S_B–S_F**
2	0·80	1·86	0·17*		1·13
3	0·87	0·25	0·20*		0·40
4	0·85	†	†*		1·18
5	1·27	0·68	(0·00)*		0·92
6	†	†	(0·00)*		0·33
7			6·94	0·09	1·16*
8		7·55*	(0·00)*	0·15	1·41*
9		8·13*	(0·00)*	0·13	1·67*
10		8·48*	0·22**	0·12*	1·95*
12		8·86*	0·37**		3·14**

† Denotes overlapping peaks while (0·00) denotes second order transitions.

evident from the X-ray diffraction data which exhibit three orders of reflection from the lamellar periodicity.

A further and most unusual aspect of the thermal behaviour of the homologous series **6** is the dramatic change in the relative magnitude of $\Delta S/R$ for the mesophase–isotropic transition on crossing from the nematic regime to the smectic regime ($6<m<7$). As has already been remarked the entropy changes of the smectic to isotropic transitions are much larger than those observed for analogous monomeric and dimeric materials. This could be a direct consequence of the high molar mass of

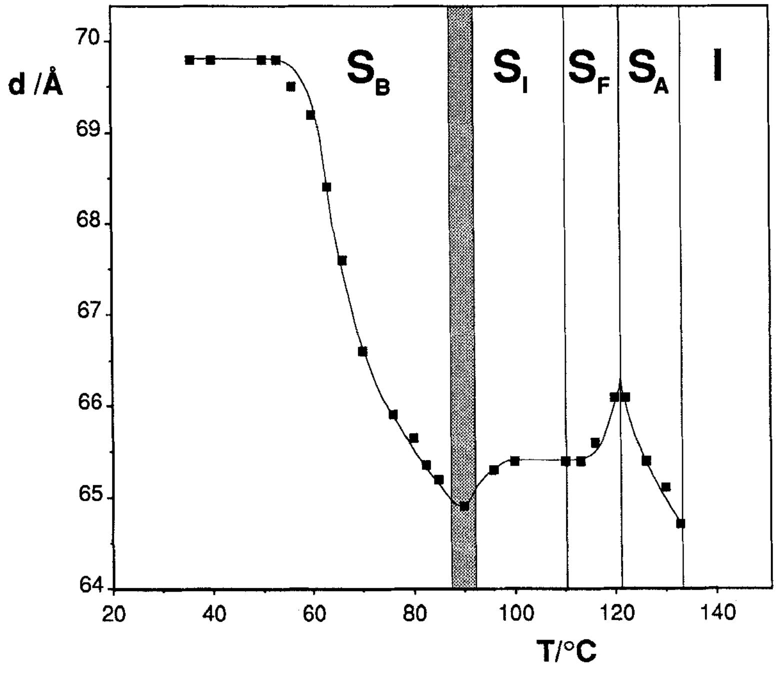


Figure 2. Plot of the layer spacing (d) as a function of temperature for homologue [6; 10]. Note that the solid line is intended only as a guide to the eye.

compounds **6**. However, the $\Delta S/R$ values for the N–I transition are comparable with those of monomeric materials or of dimeric systems with odd-parity central chains. This behaviour could be rationalized in two ways. It could be argued that homologues with $m < 7$ have a higher molecular biaxiality than homologues with $m > 7$, resulting in a reduction of $\Delta S/R$. Alternatively, it could be argued that the smectic phases are stabilised by specific interactions between neighbouring molecules. This would lead to aggregation, and hence a higher degree of order in the phase.

The changes in smectic layer spacings for compound [6; 10] are shown in figure 2. In the S_A phase the layer spacing (d) increases from 64·7 Å to 66·3 Å as the temperature decreases. In the putative S_I and S_F phases d decreases to ~65·4 Å suggesting that the maximum tilt angle in these phases is ~10°. In the S_B phase the layer spacing increases rapidly as a function of decreasing temperature, then stabilizes at a value of 69·8 Å. From calculations on space filling molecular models the length of the side chain is found to be ~32 Å. This suggests that the spatial structure in the S_A, S_I, and S_F phases corresponds to roughly twice the length of the side chain whose alkyl segments are, on average, in the all-*trans* conformation. In order that compounds of type **6** exhibit calamitic behaviour they need to adopt a linear geometry. This implies that the interactions between the rod-like units are sufficiently strong to bias the conformational distribution of one or more of the central alkyl chains in favour of conformations with a number of *gauche* linkages. A similar argument has been used to rationalize the behaviour of a tetramer in which four rod-like units are attached to the same carbon atom via flexible spacers [8]. However, even if we allow one of the side

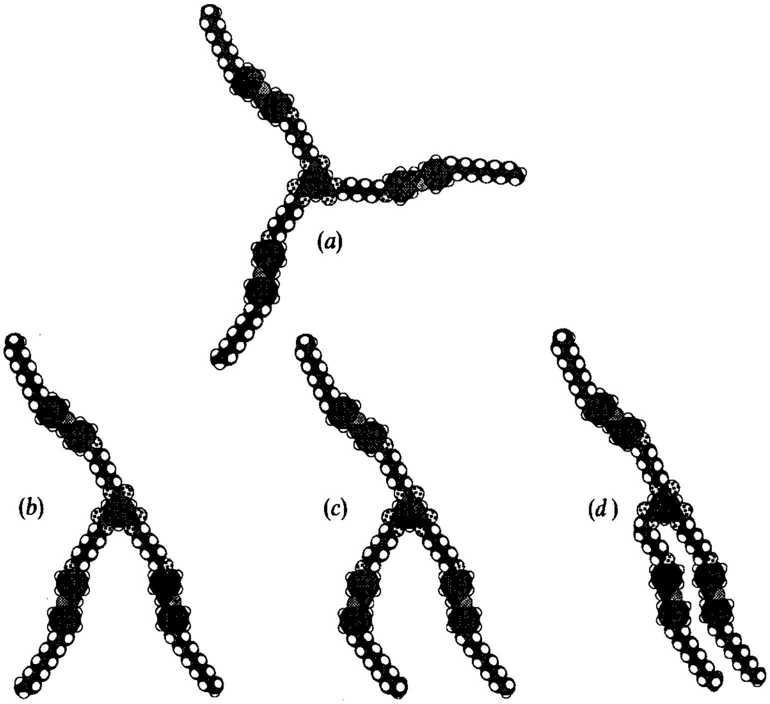


Figure 3. Schematic view of four possible conformers of homologue [6; 4]. Note that in structure (d) one of the side chains has the C–C bond nearest the ester linkage in the *cis* conformation.

chains to bend back so as to lie parallel with the other two side chains (for example see figure 3), it is difficult to envisage what type of molecular packing would give rise to the periodicities we have observed.

It is clear from these experimental observations that the cyclic trimers **6** exhibit an unusual and ambiguous phase behaviour. Thus, while on the basis of the optical textures of the N, S_A, and S_C phases it would appear that these compounds do form calamitic mesophases, we cannot exclude the possibility that some of these mesophases are biaxial, and the possibility that the more highly ordered mesophases involve some columnar (i.e. discotic) arrangement of the molecules. A more detailed assignment of the molecular organisation in the mesophases formed by these complex materials must await detailed X-ray diffraction studies of aligned samples.

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[7] Chimera is defined as: (i) (in Greek mythology) a fire-breathing female monster with a lion's head, a goat's body, and a serpent's tail; (ii) any fabulous beast with parts taken from other animals. 1990, *The Concise Oxford Dictionary*, 8th Edn (Clarendon Press).
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