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TILTED LAYERED PHASES: THE INFLUENCE OF THE INCLUSION OF A NON-LINEAR MACROCYCLE IN CALAMITIC LIQUID CRYSTALS - SYNTHESIS AND PHASE BEHAVIOUR

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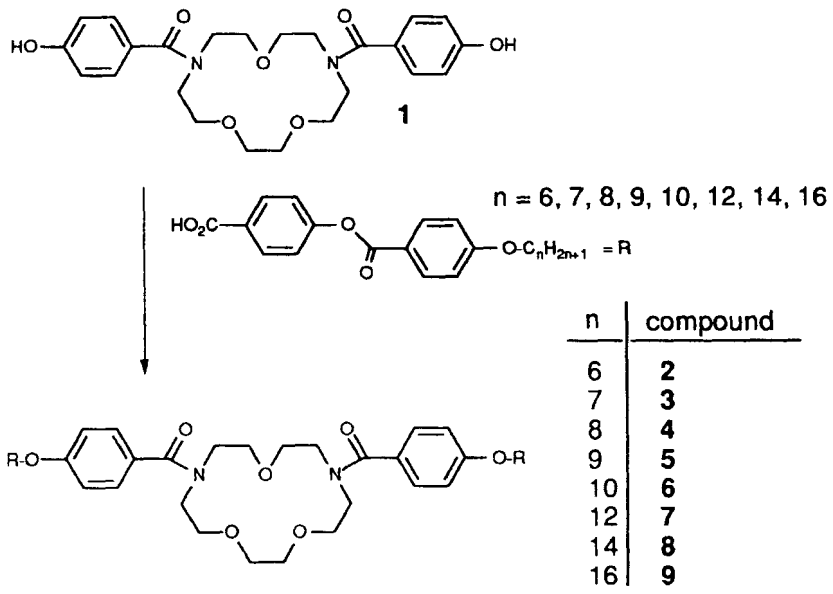
Abstract This paper describes the synthesis and the characterisation of the phase behaviour of a homologous series based on the macrocycle 1,7-diaza-4,10,13-trioxa-cyclopentadecane. The mesogenic units attached to the two aza-groups consist of three aromatic rings and the length of the terminal chain is varied between six and sixteen methylene groups. Three different types of tilted smectic phases were observed which are believed to differ in their layer packing in that one may have aligned tilt (normal smectic C) and the other two may have alternating tilt.

INTRODUCTION

The existence of several types of the smectic C phase has been observed in numerous materials and these different forms arise from variations in the tilt direction between adjacent layers. If the tilt direction is the same in adjacent layers then the smectic C phase has archetypical ordering, but if the tilt angle is rotated through 180° in the plane of the layer then a herringbone (S_O)[1] or alternating tilt ordering which is often described as anticlinic smectic C (S_{CAlt}) is formed. It has been observed that the formation of the anticlinic phase is favoured in some dimeric systems or swallow-tailed materials[2,3]. The formation of a zig-zag layering in the smectic C phase in low molar mass materials can be explained *via* the formation of bent dimeric pairs, either through chiral, polar or steric associations of single molecules or through covalently bound dimers where the geometry of the molecule is bent[4]. In the case of the diaza-15-crown-5 systems reported here, bent mesogenic dimers are formed as a result of the molecular geometry, and unlike the bent dimers described above they do not appear to be restricted to one particular geometry and hence show normal and alternating ordering.

EXPERIMENTAL

The general synthetic route to the final products is illustrated in Scheme 1. 4-(4-Alkoxybenzoyloxy)benzoic acids are prepared from the corresponding alkoxybenzoic acids by esterification with benzyl 4-hydroxybenzoate followed by hydrogenolysis (Pd/C) to remove the protecting benzyl group. *N,N* -[Bis-(4'-hydroxybenzoyl)]-1,7-diaza-4,10,13 tri-oxacyclopentadecane, **1**, was prepared and subsequently esterified with the appropriate 4-(4-alkoxybenzoyloxy)benzoic acid as described previously[5].



n	compound
6	**2**
7	**3**
8	**4**
9	**5**
10	**6**
12	**7**
14	**8**
16	**9**

SCHEME 1 Synthetic route to compounds **2-9**.

The final products were purified by flash chromatography over silica gel (40-60 μm) using methanol (1-3%) in dichloromethane as eluent and were subsequently recrystallised from isopropyl alcohol or acetone until the transition temperatures were found to be constant. The chemical characterisation of the materials will be described elsewhere[6]. The solid state properties of the final products were investigated by thermal microscopic studies using a Zeiss Universal polarising microscope in conjunction with a Mettler FP52 microfurnace and a FP5 control unit. Calorimetric experiments, relative to an indium standard, were carried out using a Perkin-Elmer DSC 7 calorimeter. Phase transition temperatures were given as the exothermic onset in the cooling curves (10 °C min^{-1}).

mol^{-1}) is associated with the transition to the lower temperature phase. Compounds with terminal methylene chains containing less than twelve carbon atoms show, on cooling, a glass transition before crystallisation occurs and they tend to recrystallise on heating.

TABLE 1. Phase transitions temperatures (°C) and enthalpies (kJ mol^{-1}) as determined by DSC (2°C min^{-1}), [a] Cpd = compound, [b] melting point.

Cpd [a]	n	cr[b]-S_{C3}/ S_{C2}	S_{C3}-S_A/N	S_{C2}-S_{C1}/N	S_{C1}-Iso	S_A-N	N-Iso
2	6	152	150.0 [3.3]	-	-	150.2 [-]	179.9 [1.61]
3	7	154	144.0 [3.47]	-	-	-	178.9 [1.47]
4	8	151	139.9 [4.11]	-	-	-	171.8 [1.57]
5	9	149	135.1 [4.10]	-	-	-	166.1 [1.47]
6	10	148	-	136.8 [7.29]	-	-	162.9 [1.84]
7	12	126	-	162.0 [-]	164.1 [16.65]	-	-
8	14	122	-	168.7 [0.17]	173.8 [17.85]	-	-
9	16	118	-	170.4 [0.21]	180.1 [19.77]	-	-

For materials **7-9** with longer terminal alkyl chains (>12), the first-formed mesophase, which emerges from the isotropic liquid was found to show focal-conic bâtonnets which rapidly coalesce and reorient with respect to the surface to form a typical smectic C *schlieren* texture characterised by the formation of 4-brush singularities (s=1); a typical example of such a texture is shown in Plate 2. On cooling further a phase transition to another *schlieren* texture which is more birefringent than the previous one was observed. An additional feature of this phase (of which a typical photomicrograph is shown in Plate 3) is the occurrence of both two- (s=1/2) and four-brush (s=1) singularities; for this phase the change of the structure can be observed more easily on heating. For members of the dodecyloxy to hexadecyloxy series, the

RESULTS AND DISCUSSION

The nematic phase formed by compounds **2-6** of the series is characterised by a typical *schlieren* texture. On cooling material **2**, the occurrence of a very short range smectic A phase, characterised by homeotropic and focal-conic regions was observed. On lowering the temperature further a phase change occurs to a mesophase denoted as a smectic C_3 phase. For materials **3-5** a direct transition from the nematic to the smectic C_3 phase was observed. The phase is characterised by a *schlieren* texture which is much less birefringent than that observed for the nematic phase and a typical photomicrograph of a texture of this phase is shown in Plate 1.

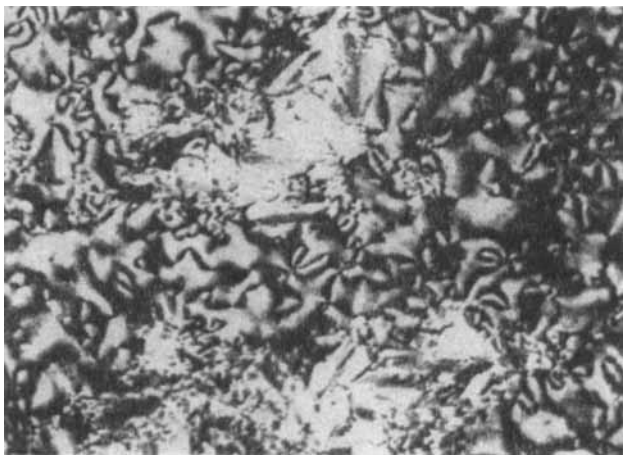


PLATE 1 Texture of the smectic C_3 phase. (See Color Plate VII).

The texture of the smectic C_3 phase is more distinct than that of the nematic phase and shows two-, four- and six-brush defects. Fan-shaped domains are also present and appear to be focal-conic in nature, although the typical elliptical and hyperbolic optical discontinuities were not seen.

The phase behaviour of the materials as determined by DSC is shown in Table 1. The enthalpy changes for the hexyloxy to nonyloxy homologues at the isotropisation transitions are comparatively small and a slightly larger enthalpy change (approx. 5 kJ

enthalpy change associated with the isotropic to smectic C transition are observed to be larger than those of the combined enthalpy changes of the Iso-N and N-smectic C_3 phase of the lower homologues. The transition from the smectic C_1 phase to the smectic C_2 phase, detected by DSC was found to be associated with a very small transition enthalpy of about 0.1-0.2 kJ mol^{-1}. For the homologues with longer alkyl chains no glass transitions could be observed.

In order to confirm that the smectic C_3 phase of the hexyloxy to nonylyloxy homologues and the two smectic C phases of the longer chain materials were not of the same type, contact and miscibility studies were performed. It was found that the smectic C_3 phase was immiscible with both the smectic C_1 and the smectic C_2 phase of the long chain members of the series.

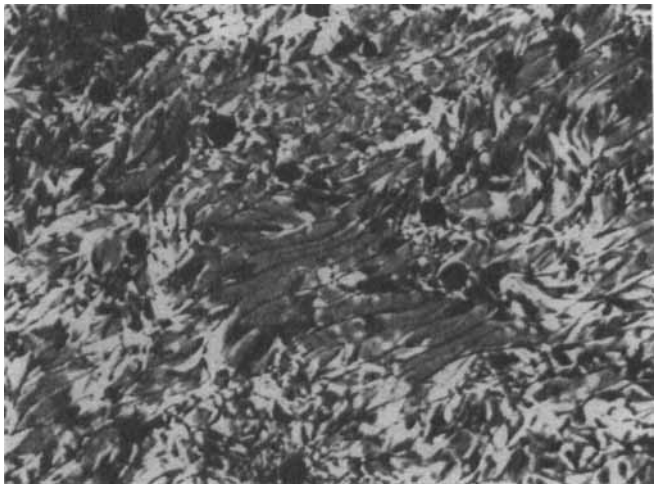


PLATE 2 Texture of the smectic C_1 phase. (See Color Plate VIII).

The phase identified as smectic C_1 was found to be completely miscible with the smectic C phase of the hexadecyloxy homologue of the diaza-18-crown-6 series of materials which were characterised previously[5]. The smectic C_1 can therefore be identified as a "normal " smectic C phase where no zig-zag ordering in adjacent layer occurs.

In order to investigate the structure of the observed smectic C phases further, switching studies with mixtures containing a chiral dopant were performed. To avoid difficulties related to mixtures of compounds of dissimilar chemical structures, a chiral dopant was synthesised containing the core unit **1**, to which the 4'-*(S)*-2-methylbutylbiphenyl-4-carboxyl moiety was attached. The resulting material was used

for the preparation of phase diagrams and electro-optical experiments. A detailed description of these experiments will be subject of a separate report[6].

For the hexadecyloxy derivative **9,** it was found that mixtures containing up to 50% of the chiral dopant showed the formation of the smectic C_1 and C_2 phases. For a mixture containing 30% dopant, the transition from the smectic C_2 to smectic C_1 phase was found to be at 136 °C, and the clearing temperature to be at 160 °C. For a 2.4 μm buffed polyimide coated cell filled with this mixture it was observed that at 146 °C employing an ac field (60Hz, 15V), a single hysteresis loop was obtained which is expected for a "normal" smectic C phase; at 114 °C (60Hz, 15V and 15Hz, 15V), a double hysteresis loop was observed. Several cells were prepared of mixtures exhibiting the smectic C_2 phase in order to find optimum alignment and switching behaviour. For a 15% mixture in a 6.9 μm buffed polyimide cell fast tristable switching proceeding *via* a grey state could be detected and this observation supports the hypothesis of the assignment of the smectic C_2 phase as containing adjacent layers of opposite tilt direction.

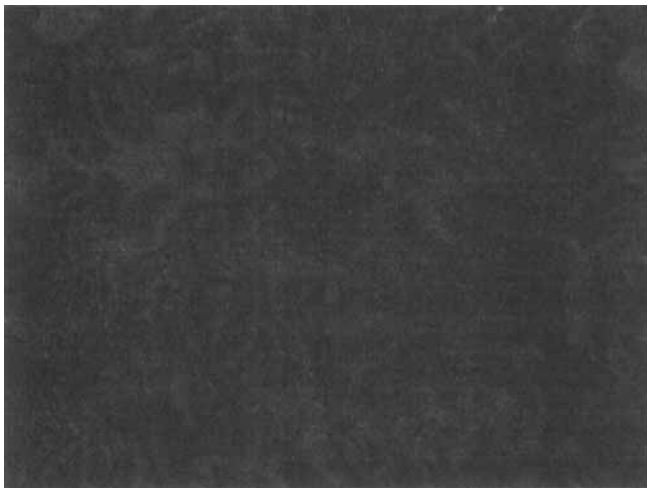


PLATE 3 Texture of the smectic C_2 phase. (See Color Plate IX).

Experiments of a similar nature were performed with the hexyloxy derivative **2** and because of the almost similar size of host and dopant no phase separation occurred in the region of nematic/cholesteric phase. The 10-20% mixtures were found to show a transition from a cholesteric to a smectic A *via* a short TGB A phase [7] and at lower temperatures to a smectic C phase. No switching behaviour of aligned mixtures in cells or realignment in the cholesteric phase could be achieved. Such behaviour might

be explained on the basis of an induced polarisation which was too weak to overcome the helical forces in the cholesteric phase, or by the tilt in the smectic phase being too large for switching to occur. Furthermore, it is possible that if this phase has an interdigitated layer structure it will not switch because the layers will have to break upon switching *i.e.*, if one layer were to switch, then this would affect the next layer which would also need to move in order to maintain the layer structure, but this would be opposed by the external field.

CONCLUSION

Qualitatively the phase behaviour of the materials is characterised by the formation of a nematic phase at high temperatures for compounds with terminal chains of up to ten methylene groups and by the formation of smectic C phases for materials with longer terminal chains. Compared to the diaza-18-crown-6 series[5] the clearing temperatures are reduced by about 20 °C. The current experimental evidence allows the assignment of the smectic C_1 and the smectic C_2 phase as having tilted and anticlinically tilted structures. The identification of the smectic C_3 is more difficult. As the materials are of relatively low viscosity and the enthalpy change from the preceding phase is small this does not favour the assignment as a smectic I phase and so the smectic C_3 phase appears also to be of anticlinic type. The current experimental data agrees with the proposition of a phase structure, where interdigitation occurs. The experimental observations seems to support the hypothesis that the unusual phase behaviour of these materials derives from a combination of the dimeric nature of the molecules and the additional constraints given by the two linking groups of the crown ether core compared to that of a single chain linkage.

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