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George S. Attard[a]; Corrie T. Imrie[a]
[a] Department of Chemistry, University of Southampton, Southampton, England

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Liquid-crystalline and glass-forming dimers derived from 1-aminopyrene

by GEORGE S. ATTARD* and CORRIE T. IMRIE
Department of Chemistry, University of Southampton,
Southampton SO9 5NH, England

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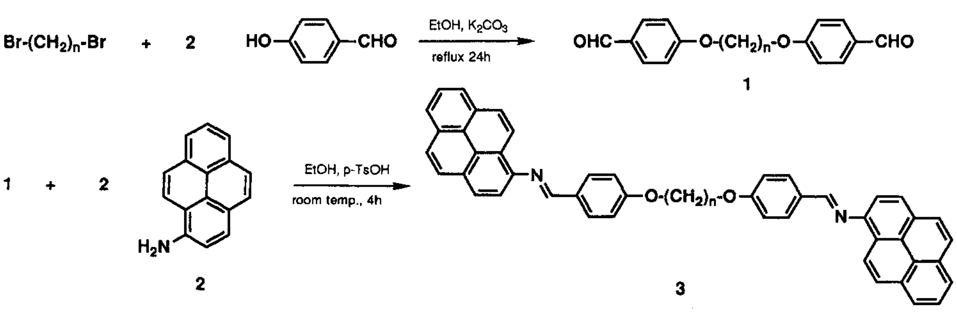
A homologous series of symmetric dimeric liquid crystals has been synthesized and its phase behaviour investigated. All members of the series were found to form glassy phases above room temperature.

The coupling of glass-forming behaviour with liquid-crystallinity is of central importance in new laser-addressed optical information storage media consisting of liquid-crystalline side chain polymers [1]. However, the high viscosities of these materials lead to slow electro-optic response times even at high switching voltages. By contrast monomeric liquid crystals exhibit rapid responses to applied electric fields and to surface forces. It is, therefore, of considerable technological interest to achieve materials which combine the advantageous properties of low molar mass liquid crystals with the glass-forming characteristics of polymeric systems.

It has been known for some time that the rapid cooling of a number of monomeric liquid crystals, either in pure form or mixtures, can lead to the formation of metastable glassy phases [2–4]. More recently it has been shown that dimeric molecules linked laterally to each other via sulphinyl or sulphonyl groups form glassy liquid-crystalline phases above room temperature [5]. The use of such materials as media for optical information storage has been reported [6]. In the present work we describe the synthesis and transtional properties of a new class of structurally simple dimeric liquid crystals which form stable glassy phases above room temperature. The materials synthisized are the α,ω-bis-(1-pyrenimine benzylidene-4′-oxy)alkanes **3**; their synthesis is outlined in the scheme. The α,ω-bis(4-formylphenyl-4′-oxy)alkanes (**1**) were obtained by refluxing the appropriate α,ω-dibromoalkane (0·025 mol), 6·5 g (0·053 mol) of 4-hydroxybenzaldehyde, and 8·7 g (0·063 mol) of anhydrous potassium carbonate, in absolute ethanol for 24 h. Yields were in excess of 65 per cent. The melting points of the homologues in series **1** were in agreement with those reported previously [7]. The



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* Author for correspondence.

symmetric pyrenimine benzylidene dimers **3** were obtained by reacting each of the α,ω-bis(4-formylphenyl-4′oxy)alkanes (0·001 mol) with 0·5 g (0·0023 mol) of 1-aminopyrene (Aldrich, 97 per cent recrystallized once from absolute ethanol) in absolute ethanol at room temperature for 4 h using catalytic quantities of 4-toluene sulphonic acid. The yellow/orange powders obtained were recrystallized twice from a mixture of dichloromethane and hexane (70:30) and their chemical constitutions verified by means of elemental analysis, together with IR and NMR spectroscopy. Overall yields for compounds **3** were in excess of 40 per cent.

The thermal transitions (determined by polarized light microscopy), and their associated entropy discontinuities (determined by differential scanning calorimetry), of the homologous series **3** are listed in the table and plotted in figure 1. With the exception of the propyl and pentyl homologues all members of the series exhibit mainly nematic behaviour. In addition, the compounds with $n=6$, 8 and 10, exhibit monotropic smectic A phases. A strong alternation in the N–I transition temperatures (T_{NI}) is observed as a function of the parity of the alkyl chain which links the pyreniminobenzylidine rigid units. Such behaviour is a common feature of dimeric liquid crystals [8]. An interesting feature of the data shown in figure 1 is that the clearing temperatures are considerably lower than for the analogous α,ω,-bis-(4-alkylaniline benzylidene-4′-oxy)alkanes [7]. The clearing temperatures of the even homologues in the series initally fall rapidly as a function of increasing *n*. The curve flattens off for the higher homologues. By contrast, the homologues with odd-membered alkyl chains show an initial rapid increase in T_{NI} which attenuates as the length of the chain increases. This type of behaviour has been reported in a number of dimeric mesogens [7, 8].

The hexyl, octyl, and decyl homologues exhibit a S_A–N transition at lower temperatures. The transition temperatures lie on a curve which has a maximum for the octyl homologue indicating that the stability of the smectic A phase is very sensitive to the length of the spacer chain. It should be noted that this is the first reported occurrence of smectic behaviour in dimeric materials whose mesogenic units do not have terminal groups.

The entropy changes associated with the N–I transitions also exhibit an odd–even effect as a function of the parity of the central alkyl chain as shown in figure 2. The magnitudes of $\Delta S/R$ are considerably smaller than is the case for most dimeric liquid crystals [7, 8]. It is likely that this phenomenon is due to the higher molecular biaxiality

Transition temperatures and entropy discontinuities for the homologues of series **3**.

n	T_C/°C	T_{NI}/°C	T_{S_AN}/°C	T_g/°C†	$\Delta S_{NI}/R$	$\Delta S_{S_AN}/R$
3	190	—	—	70·0	—	—
4	213	187·9	—	66·0	0·44	—
5	155	—	—	64·0	—	—
6	204	171·7	95·4	66·0	0·62	0·09
7	194	110·7	—	51·0	0·12	—
8	184	157·0	101·1	54·0	0·73	0·66
9	107	116·4	—	44·0	0·17	—
10	167	147·2	76·0	44·0	0·85	0·21
11	130	120·8	—	41·0	0·29	—
12	152	132·9	—	35·0	1·01	—

† The errors associated with the glass transition temperatures are of the order of ±3°C.

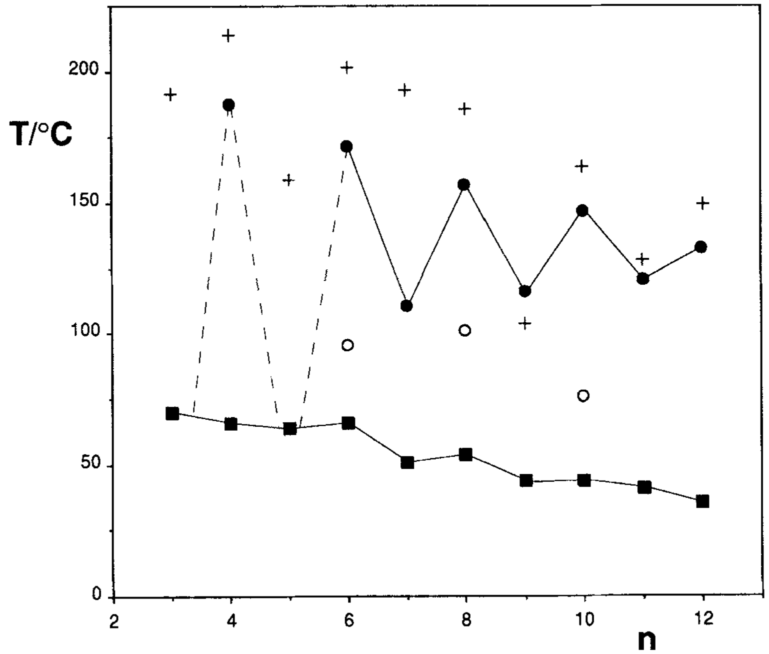

Figure 1. Transition temperatures for series 3. ●: nematic to isotropic transition; ○, smectic A to nematic transition; ■, glass transition; +, crystal to isotropic transition. Note that the glass transition temperatures were measured by DSC using heating/cooling rates of 10°C min^{-1}. The dashed lines are intended solely as a guide to the eye.

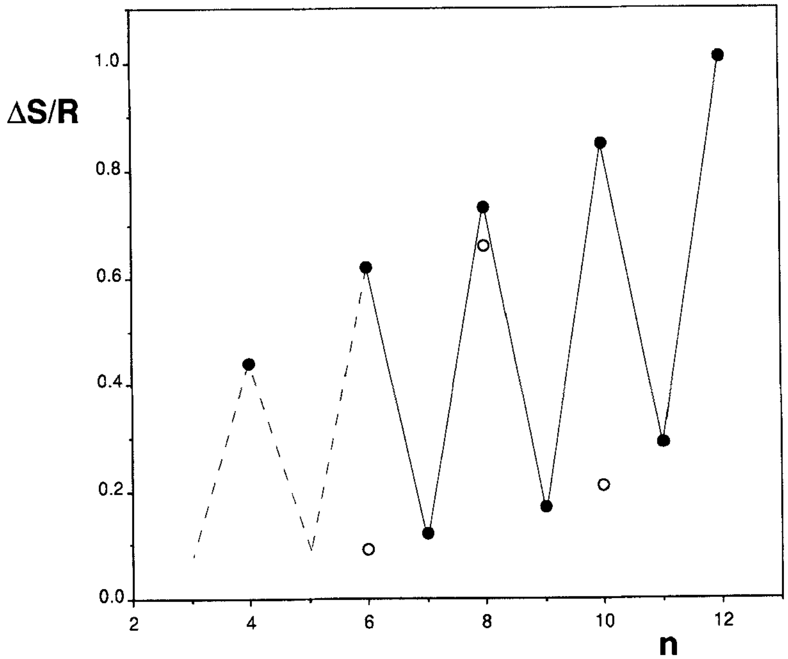

Figure 2. Entropy discontinuities for the nematic to isotropic (●) and smectic A to nematic transitions (○) of series 3. The dashed lines are intended solely as a guide to the eye.

of the pyrenimine benzylidene unit compared with more conventional rod-like mesogenic units (for example cyanobiphenyl). The magnitude of $\Delta S/R$ appears to increase as a function of increasing spacer chain length for both even- and odd-membered homologues. This behaviour is typical of symmetric dimeric mesogens. The entropy change associated with the S_A–N transition follows the same qualitative behaviour as a function of increasing n as does T_{S_AN} and is largest for the octyl homologue. In the case of hexyl homologue the S_A–N transition is very weakly first order ($\Delta S/R = 0{\cdot}09$). This partly reflects the fact that the smectic phase is preceded by a nematic range extending over 76°C. Note however that in the decyl homologue the S_A phase is preceded by a nematic range which extends over 71°C, and yet has a $\Delta S/R$ value of 0·21. In view of this it is likely that other factors are contributing to the observed entropy changes.

As is shown in figure 1, all of the members of the homologous series form glassy phases above room temperature. It should be noted that, in contrast to previous reports of glassification in low molar mass mesogens, rapid quenching is not necessary to observe the glassy state in the members of series **3**. Different types of glassy phase are formed by the homologues of series **3**, depending on the nature of the phase behaviour of the materials. For example, while the propyl and pentyl homologues form isotropic glasses, the hexyl, octyl and decyl homologues form smectic glasses, and the remaining members form nematic glasses. An interesting feature of the glassy phases is that once formed they appear to remain glassy indefinitely at room temperature (for example, at the date of submission of this communication, glassy samples of the pentyl and nonyl homologues have remained unaltered at room temperature for over 13 months).

A common observation in highly monotropic mesophases is their liability to crystallize. In this respect the homologues of series **3** differ markedly from other monotropic mesogens. For example, the mesophases of the homologues with odd-membered alkyl chains and of the decyl and dodecyl homologues can be heated or cooled at temperatures between T_g and T_c without crystallization occurring in any part of the sample.

The unusual phase behaviour and mesophase stability of these materials, and in particular their propensity for forming glassy phases can be attributed to intermolecular face-to-face association of the pyrene moieties. This type of association can be regarded as analogous to the ground singlet state, ^{1}(AA), produced from the excited singlet excimer state, ^{1}(AA)*, of pyrene according to: $^1(AA)^* \rightarrow {}^1(AA) + h\nu$ (excimer fluorescence) [9]. Face-to-face association of the pyrene moieties leads to the formation of virtual oligomeric or polymeric species. This accounts for the high viscosities of the fluid phases formed by series **3**. By analogy with the case of pyrene solutions, it would be expected that this type of aggregation would be strongly thermally activated. This means that the higher temperature phase behaviour of the homologous series *3* is dominated by the anisotropic interactions between the pyrenimine benzylidene groups, while the rapid increase in viscosity observable at lower temperatures is driven by the specific pyrene–pyrene interactions.

On the basis of the thermal data we report it would appear that the induction of glass-phase formation in low molar mass mesogens by the use of polycyclic aromatic hydrocarbon substituents is a promising route to new materials for optical technologies. Furthermore, the interplay between strongly thermally activated specific intermolecular interactions and anisotropic interactions has important implications for our understanding of the fundamental factors which affect liquid-crystalline behaviour.

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