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PRELIMINARY COMMUNICATIONS

Asymmetric dimeric liquid crystals

The preparation and properties of the α-(4-cyanobiphenyl-4′-oxy)-ω-(4-*n*-alkylanilinebenzylidene-4′-oxy)hexanes

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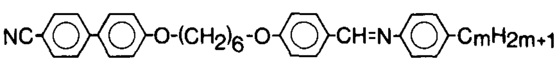
The first eleven members of the homologous series of α-(4-cyanobiphenyl-4′-oxy)-ω-(4-*n*-alkylanilinebenzylidene-4′-oxy)hexanes have been synthesized. The compounds are all enantiotropic nematogens and, with the exception of the heptyl, octyl and nonyl homologues, exhibit smectic phases. The thermal stability of the smectic A phase initially increases with the length of the terminal alkyl chain, passes through a maximum and then falls dramatically before disappearing. The smectic A phase subsequently reappears with the decyl homologue which has the highest smectic A–nematic transition temperature of the series. In order to understand this unusual behavior we have determined the entropies of transition for the compounds and we have measured the layer spacing of the smectic A phase for three of them.

The recent rediscovery of dimeric liquid crystals [1] over 50 years after the first synthesis of such compounds [2] has generated considerable interest in this class of material. The interest stems, in part, from the similarity of the dimers to main chain liquid crystal polymers and also from their quite different properties to conventional mesogens which contain a semi-rigid core. Many series of dimeric liquid crystals have been reported (see, for example, [3]) although all of these compounds may be termed symmetric because in each case identical semi-rigid mesogenic moieties are linked through the flexible alkyl spacer. As part of our continuing programme to investigate the properties of dimeric liquid crystals and their relationship to molecular structure we have synthesized a new class of dimer in which different mesogenic groups are joined by a flexible chain. Here we present our results for one such homologous series, namely the α-(4-cyanobiphenyl-4′-oxy)-ω-(4-*n*-alkylanilinebenzylidene-4′-oxy)hexanes:



the mnemonic used for this series is CB.O6O.*m* where *m* denotes the number of carbon atoms in the terminal alkyl chain. The two mesogenic groups were selected for a variety of reasons. First, the corresponding symmetric dimers, the α,ω-bis(4-cyanobiphenyl-4′-oxy)alkanes [3] and the α,ω-bis(4-*n*-alkylanilinebenzylidene-4′-oxy)alkanes [4] have been prepared and certain of their properties determined. Secondly, the analogous monomeric species, the 4-*n*-alkoxy-4′-cyanobiphenyls and *N*-(4-*n*-alkoxybenzylidene)-4′-*n*-alkylanilines, have also been thoroughly investigated.

Thirdly, the properties of these monomers are known to be qualitatively different [5] and their binary mixtures exhibit unusual phase behaviour [6]. Finally, it is easy to vary the length of both the flexible spacer and the terminal chain independently although here we are only concerned with compounds in which the spacer length is fixed. The phase behaviour of three other series with differing spacers will be published elsewhere.

The synthetic route taken for the preparation of the CB.O6O.*m*'s involves essentially three steps: the reaction of 4-cyano-4′-hydroxybiphenyl with 1-chloro-6-iodohexane to produce 1-chloro-6-(4-cyanobiphenyl-4′-oxy)hexane, the subsequent reaction of this with 4-hydroxybenzaldehyde to give 1-(4-cyanobiphenyl-4′-oxy)-6-(4-formylphenyl-4′-oxy)hexane and finally the condensation of this with a 4-*n*-alkylaniline to yield the asymmetric dimers. Details of the syntheses and the characterization of the products will be given with the description of the properties of the other series.

The thermal properties of the CB.O6O.*m*'s were determined using a Perkin–Elmer DSC-2C differential scanning calorimeter as well as a Nikon polarizing microscope equipped with a Linkam hot stage. This was also employed to investigate the optical texture of the liquid-crystalline phases. Certain of the smectic phases were studied further by X-ray diffraction with a Guinier camera fitted with a bent quartz monochromator (R. Huber, F.R. Germany) using $\mathrm{CuK}\alpha_1$ radiation (λ = 0·15405 nm).

All eleven members of the CB.O6O.*m* series with *m* equal 0 to 10 were found to be enantiotropic mesogens; their transitional properties are listed in the table. The nematic phases were assigned from their schlieren optical texture, combined with the high mobility of the phase which flashed when subjected to mechanical stress. With the exception of the heptyl, octyl and nonyl homologues the nematic schlieren texture changed, on cooling, to give regions of homeotropic and focal-conic fan texture. We therefore assign the lower temperature phase as a smectic A, a result which is confirmed for three members of the series by their X-ray diffraction patterns. On lowering the temperature of the smectic A phase of the decyl homologue the regions of focal-conic fan texture become somewhat broken and sanded while the homeotropic

The transition temperatures and entropies of transition for the CB.O6O.*m* homologous series.

	T/°C							
m	C–	S_C–S_A ‡S–S_A	S_A–N	N–I	$\Delta S_{C-}/R$	$\Delta S_{SN}/R$	$\Delta S_{NI}/R$	T_{S_AN}/T_{NI}
0	161	—	(133)	174	8·7	—	1·88	0·908
1	151	—	(147)	217	9·3	0·30	1·81	0·857
2	142	—	152	207	5·9	0·36	1·65	0·885
3†	106	‡(105)	140	210	9·4	0·15	1·89	0·855
4	111	—	142	202	9·7	0·30	1·70	0·873
5	113	‡(87)	(109)	199	10·4	—	1·96	0·809
6	116	—	(95)	192	11·2	—	1·84	0·791
7	116	—	—	189	11·3	—	2·00	—
8	119	—	—	184	9·9	—	1·80	—
9	118	—	—	181	10·8	—	2·10	—
10	119	(103)	155	177	12·8	0	1·95	0·951

( ) denotes monotropic transitions.
†$\Delta S_{SS}/R$ is 2·42.

regions produced a schlieren texture. In consequence this new phase is assigned as smectic C. The lower temperature phases of CB.O6O.3 and CB.O6O.5 have yet to be identified positively. However, on cooling the smectic A phase of CB.O6O.3 the focal-conic fans became crossed by permanent lines and large, poorly coloured platelets develop from the homeotropic regions; this suggests that the phase may be a smectic G. The low temperature smectic phase of CB.O6O.5 displays similar optical textures but it is harder to study because the sample crystallizes rapidly after the phase is formed.

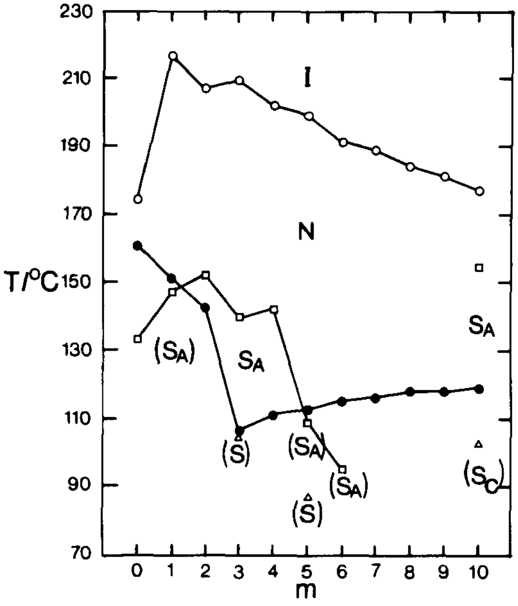


Figure 1. The dependence of the transition temperatures on the length of the terminal chain *m* in the CB.O6O.*m* homologous series of asymmetric dimers. The melting point is denoted by ●, ○ indicates the nematic–isotropic transition, □ the smectic A–nematic transition and △ the smectic–smectic A transition. Monotropic phases are marked in parentheses.

The dependence of the transition temperatures on the length of the terminal alkyl chain is shown in figure 1. The nematic–isotropic transition temperature increases markedly on going from CB.O6O.0 to CB.O6O.1 although it is not apparent why the addition of a single methyl group should have such a large relative effect on T_{NI}. Subsequent increases in the length of the alkyl chain cause the nematic–isotropic transition temperature to fall with a small alternation between odd and even members of the series, as observed for conventional nematics with high transition temperatures [7]. The entropy change at the nematic–isotropic transition also exhibits a small alternation (see the table) although the main feature is their large value in comparison with conventional nematogens with a semi-rigid core. This large value for $\Delta S_{NI}/R$ is in accord with the results obtained for symmetric dimers containing an even number of groups in the flexible spacer [3]. The melting points decrease with increasing length of the alkyl chain until the propyl homologue and then they show a gradual linear increase.

In contrast to such anticipated behaviour, the smectic A–nematic transition temperature shows a very unusual dependence on the length of the terminal chain.

For conventional mesogens with a semi-rigid core T_{S_AN} increases with the chain length [7]. This increase is observed for the first three members of the series but then the smectic A–nematic transition temperature is found to fall, quite rapidly, for the next four members. This rapid decrease presumably continues, for the heptyl, octyl and nonyl members do not possess smectic phases, at least not at temperatures of about 80°C which is the lowest to which the nematic phases can be supercooled. The smectic A phase then reappears dramatically with the decyl member of the series; indeed T_{S_AN} is higher for this than for any other homologue.

The entropy changes at the smectic A–nematic transitions, listed in the table, also reveal an interesting difference in behaviour between the early members of the series ($m = 1$–4) and the higher decyl homologue. Thus, for the lower homologues $\Delta S_{S_AN}/R$ is approximately 0·3 whereas for CB.O6O.10 it is essentially zero, to within the experimental error. However the interpretation of such entropies of transition is not straightforward because they are known to depend on the length of the nematic range. In fact, $\Delta S_{S_AN}/R$ is observed and predicted to decrease as the ratio, T_{S_AN}/T_{NI}, of the transition temperatures deviates from unity [8]. These ratios are given in the table where we can see that for CB.O6O.10 T_{S_AN}/T_{NI} is considerably closer to unity than for the early members of the series. In consequence, we expect that $\Delta S_{S_AN}/R$ for these lower members should be significantly smaller than for the decyl homologue whereas the reverse is the case. This unusual behaviour of the entropies of transition suggests that the structures of the smectic A phases for CB.O6O.*m* where $m = 1$–4 are similar but may well be different from the homologue with $m = 10$.

This suspicion was confirmed by our X-ray measurements of the layer spacing or periodicity in the smectic A phases of CB.O6O.2 ($T \approx 140$°C), CB.O6O.5 ($T \approx 105$°C) and CB.O6O.10 ($T \approx 140$°C). The layer spacings determined from the first order reflections are found to be 16·6 Å ($m = 2$), 18·5 Å ($m = 5$) and 78·4 Å ($m = 10$). The dramatic difference in the layer spacing between the two early members of the series and CB.O6O.10 remains when it is expressed as a fraction of the length of the molecule, estimated for their all-trans conformation. The ratios are about 0·5 for both CB.O6O.2 and CB.O6O.5 but 1·8 for CB.O6O.10. The large value of this ratio found for the decyl homologue is in accord with the interdigitation of the cyanobiphenyl groups observed for 4-*n*-octyl-4′-cyanobiphenyl where the antiparallel arrangement of these groups results in a layer spacing which is less than twice the molecular length [9]. The driving force for such dimerization appears to be an electrostatic interaction between the polar and polarizable cyanobiphenyl groups while the smectic phase results from the molecular inhomogeneity produced by the long terminal alkyl chain. The dramatically smaller ratio determined for the two early members of the series must also be produced by interpenetration of the molecular layers. Now however the two different mesogenic groups, of the asymmetric dimers, must be associated, as, for example, in the structure sketched in figure 2, where the periodicity is essentially half the molecular length. We describe this as an intercalated structure to distinguish it from an interdigitated arrangement where the same groups of different molecules are interleaved. An analogous structure has been proposed for the smectic A phase of compounds with a lateral chain terminated with a cyanophenyl group although for these the interpenetration of the layers is not so large [10]. This structure, like that suggested for the asymmetric dimers, would possess ferroelectric properties and we suppose that these are removed by such local molecular groupings being randomly arranged at the macroscopic level. The extensive interleaving of the molecular layers might be expected to have a profound influence

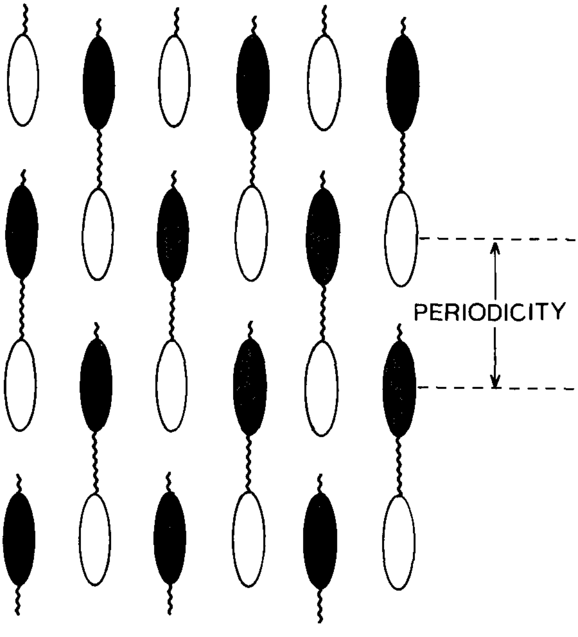


Figure 2. The intercalated structure proposed for the smectic A phase of the early members of the homologous series CB.O6O.*m*. The Schiff's base is shaded while the cyanobiphenyl group is not.

on the mechanical properties of the smectic A phase, although these have yet to be studied. It has been suggested that there is a favourable charge transfer interaction between a cyanobiphenyl and a Schiff's base which may be responsible for the formation of an injected smectic phase [6]. If this is the case then the driving force for the creation of the intercalated structure, proposed in figure 2, is easy to understand. This also explains why the smectic stability first increases and then decreases as the length of the terminal chain increases. Initially the short chains can pack with greater efficiency into the space between the layers, the size of which is dictated by the length of linking hexane group. However as the length of the terminal chain is further increased there is insufficient space and so the layers are pushed apart in a manner which reduces the overlap between the cyanobiphenyl group and the Schiff's base, thus reducing their interaction. Finally we note that such an ordered structure is consistent with the relatively high entropy change at the smectic A–nematic transition.

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