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Mesomorphic phase transitions of a series of D-phase compounds

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Mesomorphic phase transitions of 4′-*n*-alkoxy-3′-nitrobiphenyl-4-carboxylic acids (ANBC) with numbers of carbons (*n*) in the alkoxy group ranging from 11 to 22 have been studied by differential scanning calorimetry (DSC) and polarizing optical microscopy. The D phase, a mesophase of particular interest through its being optically isotropic, was observed for the $n=17$, 19, 20, 21, and 22 members of the ANBCs, as well as for the $n=16$ and 18 members, as reported previously. The S_C–D phase transition temperature decreased with increasing *n*, so that the temperature range of the D phase extended over 64° at $n=22$. In the $n=15$ member, the D phase was certainly observed on first heating, but was not seen on subsequent cooling and second heating processes.

The 'smectic' D (S_D) phase, which was discovered by Gray *et al.* [1], and defined by Demus *et al.* [2], is a mesophase having the particular feature of being optically isotropic. To elucidate why the S_D phase shows optical isotropy, several structural studies have been made for this phase, mainly by use of X-ray diffraction techniques [3], and have revealed that the optical isotropy of the S_D phase originates from cubic symmetry of the molecular arrangement [4–7]. Since the structure of the S_D phase is incompatible with the layer-structures seen in smectic phases, this phase is frequently named simply the D phase [6, 7], as adopted in this paper. Recently, other optically isotropic cubic mesophases have been found, but these are not miscible with the D phase [8–14]. The D phase, therefore, can be classified as one of the cubic mesophases. In spite of much research, the complete picture of the arrangement of the molecules in the D phase remains unclear. This is because the D phase has been so far found in only four compounds, the $n=16$ and 18 members of the 4′-*n*-alkoxy-3′-nitrobiphenyl-4-carboxylic acids (ANBC) synthesized by Gray *et al.* in 1957 [1] and the $n=16$ and 18 members of the analogous 3′-cyano compounds (ACBC) prepared by Goodby and Gray in 1980 [3, 15], where *n* is again the number of carbons in the alkoxy group. These four D-phase compounds have very similar chemical structures and nearly equal molecular sizes. Their temperature regions for the D phase are however too high for performing precise X-ray scattering analyses without decomposition of the samples. Therefore, new compounds exhibiting the D phase have been earnestly sought.

In this communication, we report the phase behaviour of a homologous series of ANBC compounds with alkoxy groups with lengths from $n=11$ to 22. One concern is

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whether the appearance of the D phase is limited to the $n=16$ and 18 members, but we have found that the D phase also appears in the $n=17$, 19, 20, 21, and 22 members, and that even for $n=15$, the D phase was observed on first heating. As n increases, the temperature at which the D phase appears becomes lower, resulting in widening of the D phase temperature range.

The ANBCs were prepared according to the method of Gray *et al.* [1, 16]. The samples were identified as ANBCs from IR, ^{1}H-NMR, and MS, and were confirmed to be fully pure by DSC and elemental analysis. The phase transitions were studied by DSC and polarizing microscopy. Textures observed for each mesophase were the same as those reported previously [1, 2, 17, 18]. The D phase of the $n=22$ member was completely miscible with that of the $n=16$ member.

Figure 1 shows DSC heating curves measured at a rate of $5\,\mathrm{K\,min^{-1}}$ for ANBC homologues with $11 \leqslant n \leqslant 22$. Phase transitions of ANBC homologues on cooling, which are not displayed here, depended upon the cooling rate, as Demus *et al.* pointed out [17]. Thermal parameters of all ANBC homologues are listed in the table. The transition temperatures for the $n=12$, 14, 16, and 18 members agree well with those reported by Gray *et al.* [1], and Demus *et al.* [2, 17]. As shown in figure 1, the $n=11$–14 members show S_C and S_A phases on heating. The $n=15$ and 16 members show S_C, D, and S_A phases on heating, and the longer alkoxy homologues with $n=17$–22 exhibit S_C and D phases. The $n=15$ compound also exhibited the D phase, but this was observed only on the first heating and not for subsequent cooling and second heating processes. This unusual behaviour, however, was reproducible.

The table shows that the entropy change of the S_C–D transition increases from 1·4 in the $n=16$ member to $3{\cdot}8\,\mathrm{J\,mol^{-1}\,K^{-1}}$ for the $n=22$ member, i.e. with increasing n. For all ANBCs with $n \geqslant 15$, the development of a completely black area was observed at the

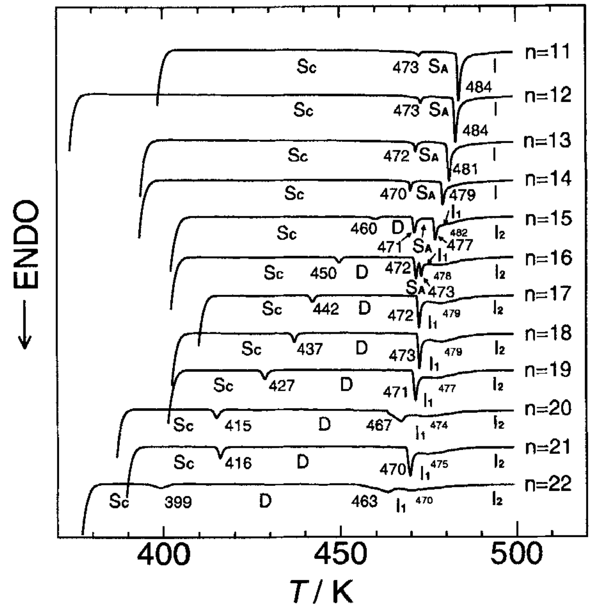

Figure 1. DSC heating curves of ANBC homologues. S_C, smectic C; S_A, smectic A; I_1 and I_2, isotropic liquid phases. In each member, the lowest temperature transition, displayed only as a tail, is a crystal–smectic C transition.

Table. Thermal parameters of ANBC homologues. The phase transition temperatures (peak temperatures) are given in Kelvin and their entropy changes in parentheses in J mol^{-1} K^{-1}†.

n	C_1		C_2		S_C		D		S_A		I_1		I_2
11	●			397 (68·4)	●			473(0·7)	●	484·8)	●	~480 (5)	●
12	●	365 (9·3)	●	372(101·6)	●			473(1·2)	●	484(7)	●	~480 (5)	●
13	●			392(101·6)	●			472(1·6)	●	481(7)	●	~480 (5)	●
14	●			392 (93·1)	●			470(1·7)	●	479(6)	●	~480 (6)	●
15	●			400(118·1)	●	460(0·7)	●	471(2·8)	●	477(4)	●	482 (9)	●
16	●	352(12·2)	●	401(106·4)	●	450(1·4)	●	472(2·9)	●	473(2)	●	478(12)	●
17	●			408(130·9)	●	442(1·9)	●	472(5·3)			●	479(11)	●
18	●	338(12·3)	●	401(118·1)	●	437(2·1)	●	473(6·2)			●	479(14)	●
19	●			400(152·5)	●	427(2·8)	●	471(6·4)			●	477(14)	●
20	●	352(16·8)	●	385(122·9)	●	415(3·3)	●	467(4·8)			●	474(15)	●
21	●			387(169·2)	●	416(3·6)	●	470(6·9)			●	475(14)	●
22	●	362(29·1)	●	376(154·4)	●	399(3·8)	●	463(3·8)			●	470(18)	●

† Obtained from DSC data in the first heating process.

S_C–D transition temperature on heating, on both orthoscopic and conoscopic observation with crossed polarizers, as Demus *et al.* reported [2, 17, 18]. However, in the longer alkoxy homologues, the number of black areas became larger, the size smaller and the shape more irregular. These results suggest that ordering of the D phase gradually decreases with increasing *n*.

It is interesting that on the heating, the DSC curves (see figure 1) for ANBCs with $n \geqslant 15$ show a broad endothermal peak at 470–480 K in the isotropic liquid region, an effect reported earlier [19] for the materials studied by Gray *et al.* The corresponding broad exothermic peak was also observed around 480 K on the cooling process. The entropy change was roughly estimated to be ~13 J mol^{-1} K^{-1}, regardless of the alkoxy chain length. On microscopic observation between crossed polarizers, sticky droplets appeared above the clearing point between two untreated glass slides, but began to flow around 480 K. This peak may not be associated with the existence of the D phase from the following facts: even in the $n = 11$–14 members, which do not exhibit the D phase, this anomalous peak certainly exists around 480 K. In figure 1, the endothermal peaks corresponding to the S_A–I phase transition also show a shoulder on the higher temperature side, and on cooling, a broad exotherm was distinctly observed around 480 K, above a sharp S_A–I peak. Our preliminary IR study for the $n = 16$ member has indicated that dissociation of carboxylic acid dimers occurs noticeably around 480 K. Consequently, it seems that the endothermal peak around 480 K is related to a dissociation of ANBC dimers.

Figure 2 shows a plot of the phase transition temperatures versus number of carbons (*n*) in the alkoxy group for the ANBC series. Clearly, the D phase occurs in the alkoxy homologues with $n > 15$, and as *n* increases from 16 to 22, the temperature range of the D phase becomes wider with lowering of the S_C–D transition temperature and a small decrease in the clearing temperature. In the $n = 22$ member, the S_C–D transition temperature lies near 399 K, and the temperature range of the D phase extends over 64°. As *n* increases from 15, the higher temperature side of the S_C phase region is eroded by the widening D phase region, and the observed narrowing of the S_C phase region results.

Lydon noticed that the molecular lengths of the aromatic and aliphatic parts are almost equal in the $n = 16$ and 18 members of the ANBCs and suggested that a balance

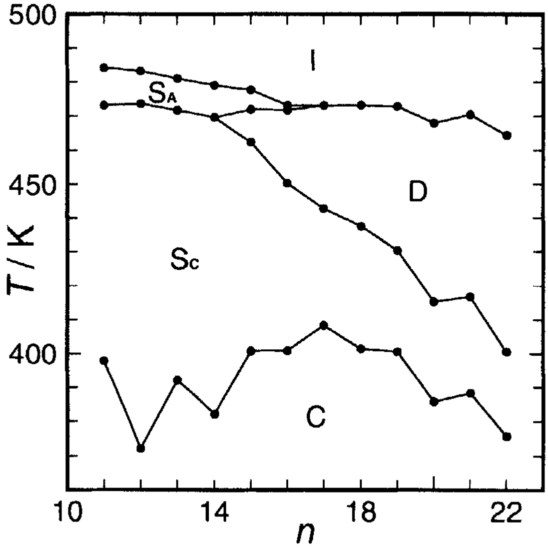

Figure 2. Phase transition temperature versus carbon number of the alkoxy group (n) in ANBC homologues.

between the two lengths may be important for the appearance of the D phase [20]. The ratio of the length of the aliphatic to aromatic parts was estimated to be 1·8 for $n=16$ and 2·0 for $n=18$. However, we emphasize that the 'stable' D phase appears in seven ANBC homologues from $n=16$ to 22, for which the ratio ranges from 1·8 to 2·4. Consequently, our results indicate that an increased ratio expands the temperature region of the D phase.

As already mentioned, based on structural studies of the D phase, two types of model have been proposed; (1) a cubic lattice model, where micellar assemblies of ANBC dimers lie in the lattice sites [4, 6]; (2) ANBC dimers constituting cylinders which are linked together to form two interwoven three-dimensional networks [5, 20], just as proposed by Luzzati and Spegt for certain optically isotropic lipid phases [21]. When the molecular length of ANBC varies, the lattice parameter should be straightforwardly proportional to the molecular length in the former model, whereas it should not in the latter. The present work therefore gives a powerful key to deciding which model is correct, because the molecular lengths of the ANBCs exhibiting the stable D phase range from ~30 Å for $n=16$ to ~38 Å for $n=22$. Structural studies by X-ray diffractometry are progressing in our laboratories.

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