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Shinichi Yano[a]; Yasuaki Mori[a]; Shoichi Kutsumizu[a]
[a] Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu, Japan

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Mesomorphic phase transitions of 4,4′-bis(ω-hydroxyalkoxy)-azoxybenzenes

Appearance of isotropic mesophase

by SHINICHI YANO*, YASUAKI MORI and SHOICHI KUTSUMIZU
Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-11, Japan

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Mesomorphic phase transitions of 4,4′-bis(ω-hydroxyalkoxy)-azoxybenzenes (number of carbons in the alkoxy group $n=2, 3, 6, 8, 11$ and 12) have been studied by differential scanning calorimetry (DSC) and polarized optical microscopy. For the $n=8$ compound, an optically isotropic (OI) mesophase reminiscent of the smectic D phase was observed in the temperature range of 400–411 K between smectic C (below 400 K) and nematic (above 411 K) phases. On the other homologues used here; the $n=2$, 3 and 6 compounds had only a nematic phase and the $n=11$ and 12 compounds had only a smectic C phase. This preliminary work points out that the thermal and optical properties of the OI phase for the $n=8$ compound are very similar to those of the smectic D phase.

Azoxybenzene derivatives are well known as liquid-crystalline compounds. 4,4′-Bis(*n*-alkoxyazoxy)benzene homologues exhibit a nematic phase for alkoxy chain lengths shorter than the hexyloxy homologue and a smectic phase for alkoxy chain lengths longer than the decyloxy homologue [1]. This work was undertaken in order to study mesomorphic phase transitions of a homologous series of 4,4′-bis(ω-hydroxyalkoxy)benzene (HAA) (see A in figure 1) and to examine how the terminal OH group affects the mesogenicity. In the course of this work, we found the appearance of an optically isotropic mesophase reminiscent of the smectic D (S_D) phase found for the $n=8$ member of HAA.

In 1957 an isotropic mesophase was first observed for two members ($n=16$ and 18) of the 4′-*n*-alkoxy-3′-nitrobiphenyl-4-carboxylic acid (ANBC) homologous series (see B in figure 1) by Gray *et al.* [2]. This phase was defined as a smetic D by Demus *et al.* in 1968 [3]. Subsequently, the structure of the S_D phase has been studied by X-ray diffraction techniques: Diels *et al.* [4, 5] indicated that the aromatic parts of the molecules constitute spherical micelles which form the ordered cubic lattice and the long alkoxy chains have an irregular liquid-like distribution. Gray and Winsor [6, 7] pointed out that this cubic and micellar model is analogous to that observed frequently in lyotropic liquid crystals. Tardieu and Billard [8] suggested that the structure of the smectic D phase has a body centred cubic lattice (space group Ia3d), which has some analogy to certain optically isotropic lipid phases studied by Luzzati and Spegt [9]. In 1984 Gray and Goodby [10] found the smectic D phase for two members ($n=16$ and 18) of the 4′-*n*-alkoxy-3-cyanobiphenyl-4-carboxylic acid (ACBC) series (see C in figure 1) which is thermally more stable than ANBC. Etherington *et al.* [11] revealed that the structure of the S_D phase in ACBC belongs to a primitive cubic space group (P23 or Pm3) with a lattice parameter of 86 Å and that this model can also explain the S_D structure of ANBC proposed earlier.

* Author for correspondence.

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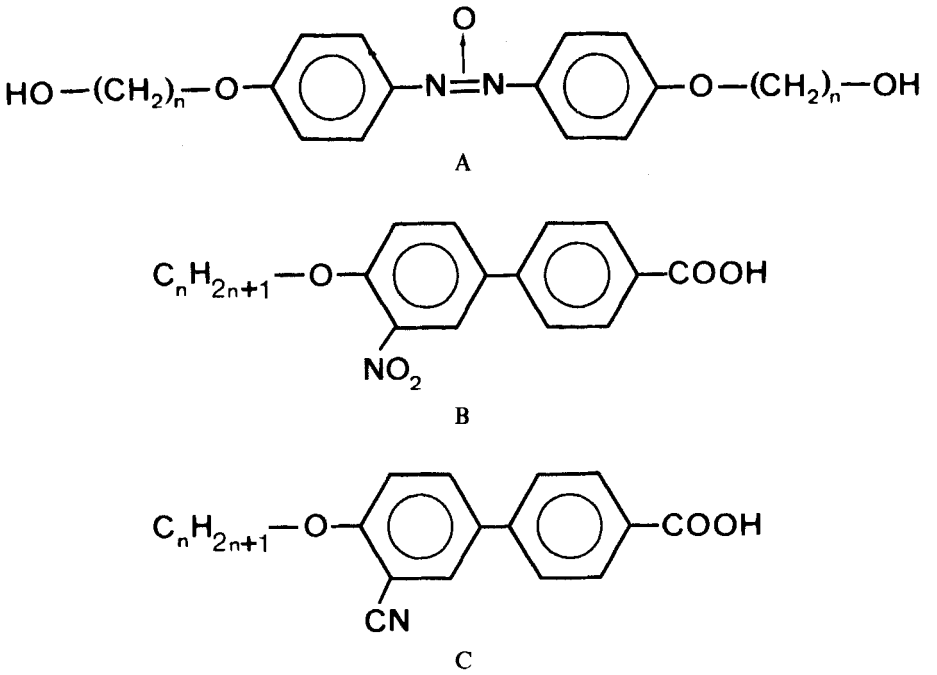

Figure 1. Chemical structures of compounds. A, HAA; B, ANBC; C, ACBC.

Although new compounds are desired exhibiting the S_D phase, so far only the four compounds of ANBC and ACBC have been found to have the so-called S_D phase, and furthermore the chemical structures of the four compounds are very similar to each other. This fact undoubtedly prevents a full characterization of the S_D phase. In this communication, we report the appearance of an optically isotropic mesophase reminiscent of the S_D phase for the $n=8$ member of the HAA series and briefly describe the phase transitions of the HAA homologues.

p-(ω-Hydroxyalkoxy)nitrobenzene was prepared by refluxing a mixture of nitrophenol (0·1 mol), K_2CO_3 (0·12 mol) and ω-bromoalcohol (0·12 mol) in acetone (200 ml) for 48 h according to conventional procedures [12]. The crude sample was purified by several recrystallizations from aqueous solution. Finally, HAA was prepared by adding glucose (0·026 mol) to 30 per cent aqueous solution of *p*-(ω-hydroxyalkoxy)nitrobenzene (0·034 mol) at 353–373 K according to the method of Gabraith and Degering [13]. The crude crystals were recrystallized several times from ethanol/chloroform (1 : 1). The crystals obtained were identified as HAA, using IR and NMR techniques and were confirmed to be fully purified by TLC and DSC.

Phase transitions were measured with a differential scanning calorimeter (Seiko Denshi, SSC 5000) at a heating/cooling rate of 5 K min^{-1} (see the table). The texture of each mesophase was determined by polarization optical microscopy (Nikon, Optiphoto-pol XTP-11) equipped with a Mettler FP-82 hot stage at a heating/cooling rate of 5 K min^{-1}.

The schematic DSC curves for HAA homologues are shown in figure 2. The $n=2$, 3 and 6 compounds (n is the number of methylene units in the alkoxy chain) show a nematic phase in the temperature ranges of 434–456 K, 410–431 K and 390–423 K,

Thermal parameters of HAA homologues. The phase transition temperatures are given in Kelvin and the entropy change in $J\,mol^{-1}\,K^{-1}$†.

n	Solid ⟶	S_C ⟶	OI ⟶	N ⟶	I
2			434 / 41	456 / 2·6	
3			410 / 51	431 / 2·3	
6			390 / 128	423 / 4·7	
8	385 / 88	400 / 0·5	411 / 8·3	414 / 14	
11	386 / 104			405 / 42	
12	383 / 86			406 / 49	

† Obtained from DSC data in the first heating process.

respectively. Conversely, the $n=11$ and 12 compounds show a smectic C (S_C) phase in the temperature range of 386–405 K and 383–406 K, respectively. The nematic and S_C phases were identified from the appearance of nematic schlieren and S_C schlieren textures, respectively, as observed by polarization optical microscopy under crossed polarizers.

The phase transition of the $n=8$ compound is very interesting. As is shown in the DSC curve of figure 2, the $n=8$ homologue melts to form a S_C phase at 385 K and transforms into an optically isotropic (OI) phase at 400 K as the temperature increases. This OI phase changes into a nematic phase at 411 K and to an isotropic liquid (I) at 414 K. The OI phase has several features of the S_D phase as is mentioned as follows. (1) In the S_C phase, the schlieren S_C texture was observed using crossed polarizers, as has already been described. At the S_C–OI phase transition temperature the development of a completely black area was observed under crossed polarizers on heating and the entire view eventually became black. However, we were not able to see the black areas with straight edges or a hexagonal shape which are characteristic of the S_D phase. Further microscopic studies are necessary for the identification of the OI phase. (2) When we pressed the OI phase by touching the cover-glass over the preparation no flashing or birefringence effect was observed. Furthermore, since no isogyre was observed under a conoscopic observation by the polarizing microscope, the OI phase observed is not a pseudo isotropic one with a homeotropic arrangement but a genuinely isotropic one. (3) The entropy change from the S_D to the OI phase shows a very small value of about $0{\cdot}5\,J\,mol^{-1}\,K^{-1}$. (4) The OI phase was viscous, compared with the isotropic liquid. (5) The sequence of the appearance of the OI phase in the successive phase transitions is similar to that of the S_D phase in ANBC and ACBC; the phase sequences are

$$\text{Solid} \xrightarrow{400\,K} S_C \xrightarrow{444\,K} S_D \xrightarrow{470\,K} S_A \xrightarrow{475\,K} I$$

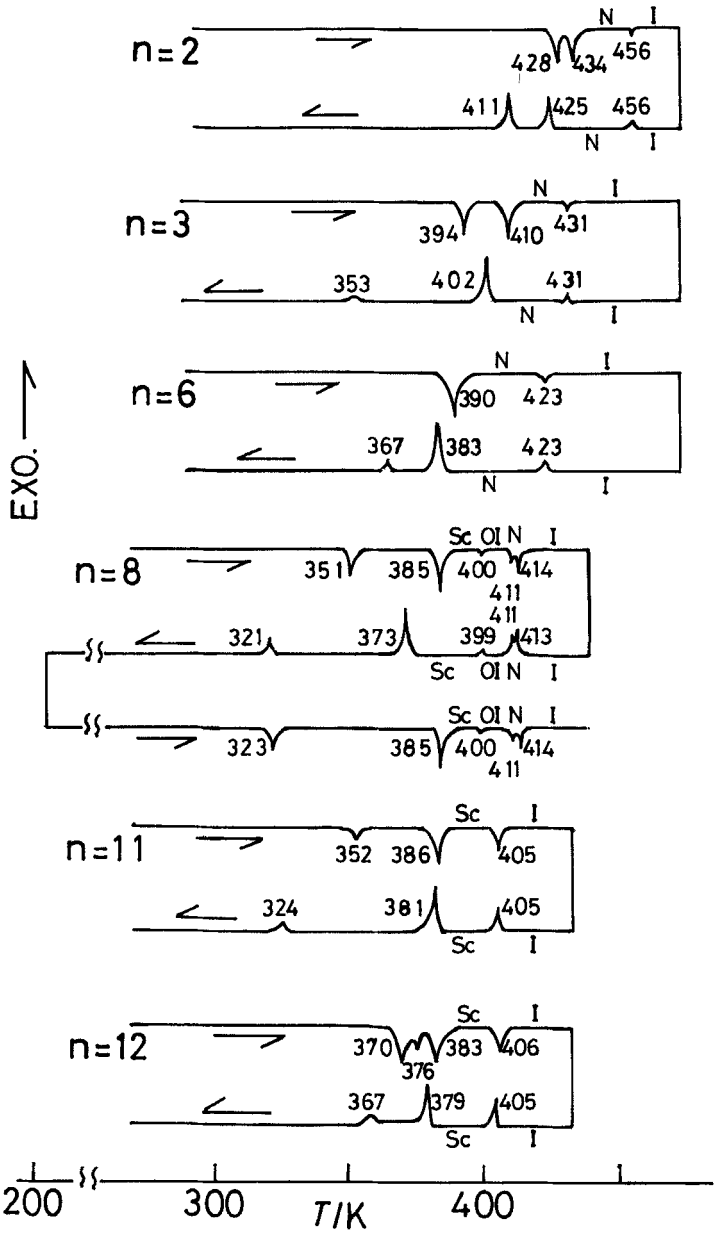

Figure 2. Schematic DSC curves of HAA homologues. N, nematic; S_C smectic C; OI, optically isotropic; I, isotropic liquid. →, heating process; ←, cooling process.

for the $n=16$ homologue in the ANBC series [5] and

$$\text{Solid} \xrightarrow{404\,K} S_C \xrightarrow{429\,K} S_D \xrightarrow{474\,K} I$$

for the $n=18$ homologue in the ACBC series [10, 11], whereas for the $n=8$ homologue of the HAA series the phase sequences are

$$\text{Solid} \xrightarrow{385\,K} S_C \xrightarrow{400\,K} \text{OI phase} \xrightarrow{411\,K} N \xrightarrow{414\,K} I.$$

(6) The ANBC and ACBC series have a hydrophilic COOH group and long hydrophobic, hydrocarbon chains and the S_D phase is observed only for the $n=16$ and 18 members. This phenomenon is also seen in the HAA series. The HAA compounds are amphiphilic. The $n=8$ member shows the OI mesophase like the S_D phase, while the $n=2$, 3, 6, 11, and 12 members do not show a OI mesophase. It is interesting to know whether the OI phase exists in the $n=7$, 9 and 10 homologues adjacent to the $n=8$ homologue and this study is now in progress.

These analogies between S_D and OI phases indicate that the OI phase is an optically isotropic mesophase reminiscent of the S_D phase. However, this phase cannot be identified as the S_D phase at present, since X-ray diffraction studies have not yet been performed. X-ray diffraction studies are in progress and will be reported elsewhere.

In conclusion, this preliminary work indicates that an optically isotropic mesophase exists for the $n=8$ member of HAA. This finding should serve to clarify the structure and properties of isotropic mesophases such as the S_D phase.

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