A cubic–cubic phase transition of 4′-*n*-hexacosyloxy-3′-nitrobiphenyl-4-carboxylic acid (ANBC-26)

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Lengthening of the alkoxyl group of 4′-*n*-alkoxy-3′-nitrobiphenyl-4-carboxylic acids to C_{26} produced two types of cubic mesophases with *Im*3*m* and *Ia*3*d* symmetries, where the *Im*3*m* cubic phase is transformed into the *Ia*3*d* cubic phase at 162 °C on heating.

Optically isotropic cubic mesophases are currently attracting much interest in the field of supramolecular chemistry because of their fundamental interest in the mysterious transformation with adjacent optically anisotropic mesophases (*e.g.* lamellar, hexagonal) and because of their biological significance.[1] They can occur in a wide range of chemical systems, such as liquid crystals, biological lipid-water, and block copolymers, and their formation depends on temperature and their molecular structure and composition. Our understanding in this field is, however, far from complete.

4′-*n*-alkoxy-3′-nitrobiphenyl-4-carboxylic acids have a relatively simple molecular structure which consists of a nitrobiphenylcarboxylic acid core and a long alkoxyl tail (see Fig. 2, top). These compounds, designated as ANBC-*n* (*n* is the number of carbons in the alkoxyl groups), were first synthesized by Gray *et al.*[2] and have been investigated by several researchers;[3–6] they show a cubic phase denoted cubic D (CubD) on both heating and cooling when $n \geqslant 16$, with the temperature region of this phase becoming wider with increasing *n* (up to $n = 22$).[3,4] For the $n = 16$ and 18 homologues, the structure type of the CubD phase has been already identified as space group *Ia*3*d*,[5,6] but the structure at the molecular level is still unclear. Here, we report a homologue having a very long chain of $n = 26$ which forms two types of cubic phases, one with *Im*3*m* symmetry and the other with *Ia*3*d* symmetry, with the *Im*3*m* cubic phase transforming into the *Ia*3*d* cubic phase at 162 °C on heating. This is the first example of a thermotropic cubic–cubic phase transition in one-component systems, although two examples have been reported in lyotropic binary or ternary mixtures on varying the water content.[7–9]

The $n = 26$ homologue, ANBC-26, was prepared by three steps: first, *n*-hexacosyl bromide was prepared by a Grignard-type reaction between *n*-hexadecyl bromide and 1,10-dibromodecane, and then, according to the established method of Gray *et al.*,[2] the obtained bromide was reacted with 4′-hydroxybiphenyl-4-carboxylic acid to give 4′-*n*-hexacosyloxybiphenyl-4-carboxylic acid (ABC-26), finally, nitration of ABC-26 gave ANBC-26. The final white powder product was purified by repeated recrystallization from ethanol, and the purity was checked by elemental analysis, thin layer chromatography, ^1H NMR, and differential scanning calorimetry (DSC).

The DSC trace of ANBC-26 shows the following phase sequence on the first heating curve (1H): crystal 1·86 °C·crystal 2·103 °C·smectic C (SmC)·123 °C·cubic I (Cub I)·162 °C cubic II (Cub II)·194 °C· structured liquid (I_1)·200 °C·isotropic liquid (I_2), with associated entropy changes of 86, 124, 6, 0.3, 9 and 15 J mol^{-1} K^{-1}, respectively. Identification of the phase type was by both texture observation using a polarizing optical microscope and small-angle X-ray scattering (SAXS). The structure of the I_1 phase has been discussed elsewhere.[3,4] The cooling process is more complicated and has not been fully characterized; the phase sequence determined so far is I_2·198 °C I_1·192 °C·hexagonal columnar phase·189 °C·Cub II·93 °C·SmC 76 °C·crystal. On second heating (2H), the sample showed crystallization of residual glassy domains at 79 °C, but was otherwise identical with the 1H scan.

Fig. 1 shows the SAXS patterns of ANBC-26 at (a) 130.4 °C and (b) 170.4 °C, on heating, where $q = (4\pi/\lambda)\sin\theta$, $\lambda = 0.154$ nm and 2θ = scattering angle (Mac Science M18XHF X-ray generator and Huxley–Holms optics). At 130.4 °C, 11 observed peaks are arranged almost symmetrically with respect to the beam stopper (not shown here), showing the following ratios of spacings: $\sqrt{3}:\sqrt{4}:\sqrt{5}:\sqrt{6}:\sqrt{7}:\sqrt{8}:\sqrt{9}:\sqrt{10}:\sqrt{12}:\sqrt{13}:\sqrt{15}$. Since the ratios $\sqrt{7}$ and $\sqrt{15}$ are not compatible with any cubic lattices, the sequence of numbers must be doubled. Therefore, the obtained ratios are $\sqrt{6}:\sqrt{8}:\sqrt{10}:\sqrt{12}:\sqrt{14}:\sqrt{16}:\sqrt{18}:\sqrt{20}:\sqrt{24}:\sqrt{26}:\sqrt{30}$, which is characteristic of a body-centered cubic symmetry *Im*3*m*, and thus the parameter of the unit cell is $a = 20.02 \pm 0.02$ nm. The pattern abruptly changed at *ca.* 155 °C on heating, and at 170.4 °C [Fig. 1 (b)], only two peaks with a ratio of $\sqrt{6}:\sqrt{8}$ are seen. The pattern was very often dissymmetric with respect to the beam stopper, as shown in the inset, reflecting orientation of the Cub II domains in the glass capillary tube. Since ANBC-26 is achiral, only the space group *Ia*3*d* matches the absence of diffractions with lower indices (100), (110), (111), (200) and (210). The cell parameter is estimated as $a = 12.30 \pm 0.04$ nm. The higher-temperature Cub II phase has the same symmetry as

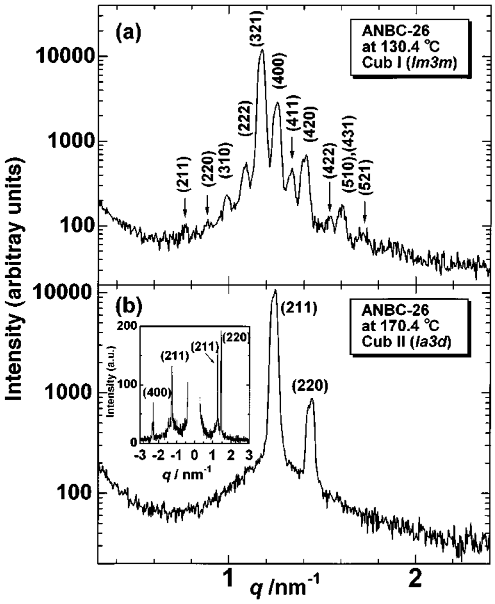

Fig. 1 SAXS patterns of ANBC-26 recorded (a) at 130.4 °C and (b) at 170.4 °C, on heating. Miller indices are also shown. In (b), the inset shows a second pattern for the same sample under the same thermal conditions.

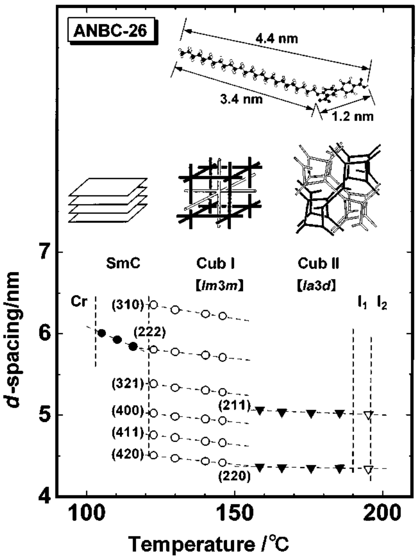

Fig. 2 Plots of *d*-spacing *vs*. temperature for ANBC-26 on heating. The molecular structure of ANBC-26 and model structures of the SmC, Cub I and Cub II phases are shown in the upper and middle part of this figure, respectively.

the CubD phase of ANBC-16[5] and −18.[6] On the other hand, the cubic phase of a 3′-cyano analogue with n = 18 (4′-*n*-octadecyloxy-3′-cyanobiphenyl-4-carboxylic acid) was identified in space group *Im*3*m*,[6] and this phase and the lower-temperature Cub I phase are of the same type.

ANBC-26 thus shows three liquid-crystalline phases, the SmC phase with a lamellar structure, and two types of cubic phases, one with *Im*3*m* symmetry and the other with *Ia*3*d* symmetry, on heating. Schematic models for these three structures are depicted in the middle part of Fig. 2. According to the models proposed for lyotropic systems by Luzzati and coworkers,[9] both cubic phases are visualized as two sets of networks of rods, which are interwoven but not connected. For the *Im*3*m* cubic phase, the rods are connected 6-by-6 at right angles so that they are directed parallel to one of three lattice axes, while in the *Ia*3*d* cubic phase, the rods are connected 3-by-3, forming two sets of helix-like networks, where each helix is linked with other four helices. In ANBC-26, the aromatic part and CO_2H group form these jointed rods, while the aliphatic chain fills out the free space between the rods.

In order to gain insight into the transformation process along the SmC–Cub I (*Im*3*m*)–Cub II (*Ia*3*d*) phase sequence, the *d*-spacings of diffraction peaks are plotted *vs*. temperature in the lower part of Fig. 2. Several interesting points are noted:

(1) The layer thickness of the SmC phase decreases as the temperature approaches the SmC–Cub I transition temperature. When the SmC layer is transformed into the SmA layer, the tilt angle of the molecular long axis against the layer normal usually reaches zero and thus the layer thickness increases. Therefore, the ‘thinning’ of the SmC layers may be characteristic of the SmC phase that exhibits any cubic phase at the higher temperature side.

(2) At the SmC to Cub I transition, the SmC layer thickness is equal to the (222) interplanar distance of the Cub I phase with *Im*3*m* symmetry. This suggests the existence of the so-called epitaxial relation[10] between the SmC layer planes and the (222) planes of the Cub I phase. In the *Im*3*m* cubic phase with a cell parameter *a*, one 6-by-6 connection point is located at (000) and the other at ($\frac{1}{2}a,\frac{1}{2}a,\frac{1}{2}a$), and the distance between them is $(\surd 3)a/2$, while the (222) spacing is given by $(\surd 3)a/6$. Hence, three layers should exist between the two connection points.

(3) In the Cub I phase, the diffraction of highest intensity is the (321) peak while the (211) diffraction peak is the highest in the Cub II phase; both spacings, however, show a discontinuity at the Cub I to Cub II phase transition.

(4) In the Cub I phase temperature range, the unit cell parameter *a* decreases with increasing temperature, showing a *negative* thermal volume expansion $[(1/a^3)(d(a^3)/dT) = -4 \times 10^{-2}\ K^{-1}]$. This trend continues but is greatly reduced ($-6 \times 10^{-4}\ K^{-1}$) for temperatures in the Cub II phase range. Bruce and coworkers reported a similar negative thermal volume expansion ($-1.5 \times 10^{-3}\ K^{-1}$) for the *Ia*3*d* cubic phase of a silver(I) alkoxystilbazole complex.[11] It seems that negative thermal volume expansion is characteristic of cubic mesophases (fluid nature).

Finally, we comment on two issues. The first relates to the molecular structure characteristics of ANBC-26. A shorter alkoxyl homologue, *e.g.* ANBC-18, shows an *Ia*3*d* cubic phase, and the length of the aliphatic chain is estimated at 2.2 nm in the extended form, which is about twice the length of the aromatic core moiety (1.2 nm). For ANBC-26, the aliphatic chain length is 3.4 nm, about three times larger than the core length (see Fig. 2). The lengthening of the aliphatic chain unexpectedly produced two types of cubic phases on heating. Moreover, this lengthening also much improved the thermal stability among this series of compounds, as confirmed by thermal gravimetry.

Second, paying attention to the location of the methyl end groups in the two cubic lattices, they form curved interfaces so as to wrap the jointed rods. These interfaces are alternative sets of description for cubic phases and are denoted infinite periodic minimal surfaces (IPMS); three fundamental cubic IPMS have been reported, the Schwarz P and D and Schöen Gyroid G surfaces, which correspond to three bicontinuous cubic phases with symmetries *Im*3*m*, *Pn*3*m* and *Ia*3*d*, respectively.[12] Hyde *et al*. pointed out that three bicontinuous cubic IPMS are mathematically interrelated to each other by a Bonnet transformation *without change in curvature*.[12] This means that phase transitions between the three cubic phases should occur without heat exchange, provided that only the elastic energy of the system is taken into consideration. This may be a reason why only one type of cubic phase has been observed to date in a given thermotropic cubic system; also our observation of a very small entropy change (0.3 J mol^{-1} K^{-1}) for the Cub I–Cub II phase transition is consistent with this expectation.

In conclusion, ANBC-26 shows an interesting polymorphism, including two cubic mesophases with *Im*3*m* and *Ia*3*d* symmetries, and a structured liquid I_1 phase. We anticipate that our finding will lead to a more complete understanding of cubic molecular organization and its transformation to and from other types, especially in thermotropic liquid crystalline systems.

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