Two Cubic Phases of 1,2-Bis(4′-*n*-alkoxybenzoyl)hydrazines (BABH-*n*)

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The structure type of bicontinuous cubic phase formed by 1,2-bis(4′-*n*-alkoxybenzoyl)hydrazines (BABH) was strongly dependent on the alkoxy chain length, showing the phase sequence of *Ia*3*d*–*Im*3*m*–*Ia*3*d* with lengthening the chain.

Among various liquid crystalline (LC) phases, thermotropic cubic (Cub) phase is attracting increasing attention in these days.[1–3] In this phase, both local mobility and a three-dimensionally periodic molecular arrangement are realized by relatively simple rodlike molecules. The self-organization is qualitatively understood, but still far from complete, especially concerning which type of Cub phases is preferred.

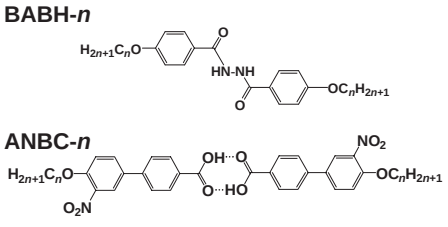
1,2-Bis(4′-*n*-alkoxybenzoyl)hydrazines (BABH-*n*, where *n* in the code is the number of carbon atoms in the alkoxy chain) and 4′-*n*-alkoxy-3′-nitrobiphenyl-4-carboxylic acids (ANBC-*n*) are such Cub-phase forming molecules.[1–3] Scheme 1 shows their chemical structures. Since in the latter system hydrogen-bonded dimers are the basic units constructing the self-organized structures, the chemical structures of both systems are common in that they are composed of a rigid aromatic core at the center and a flexible aliphatic tail at each end. In the ANBC-*n* series, we found that the formation of the Cub phase is strongly dependent on the chain length:[4,5] an *Ia*3*d* type is formed for $n = 15$–18 and an *Im*3*m* type is seen for $n = 19$–21, and further increase of *n* to, e.g., $n = 22$ or 26 causes two types in the same heating sequence with the *Im*3*m* type in the low temperature side. This finding revealed that the alkoxy chain length *n* is crucial for the Cub-phase formation. A question then arises whether the dependence of the Cub-phase type on *n* is specific to the ANBC-*n* series. This is a key to understand factors for differentiating one Cub-phase type from another. To consider the above question, the BABH-*n* system is a suitable candidate. This compound was first synthesized by Schubert et al.[6] The phase-transition behavior is expected to be influenced by the alkoxy chain length and hydrogen-bonding strength, but only three members with $n = 8$–10 were investigated by Demus et al.;[7] the three members exhibit Cub and smectic C (SmC) phases.

Another aspect to note is that the lamellar type SmC phase is formed in the low temperature side of the Cub phase in the ANBC-*n* series,[4,5] while in the BABH-*n* series the reverse order is seen in three homologues with $n = 8$–10.[7] Such different phase behaviors are explained reasonably by a quasi-binary system picture,[8–10] which predicts the possibility that the same order as in the ANBC-*n* series is seen in the BABH-*n* series when the alkoxy chain is lengthened further than $n = 10$.

From those two reasons, we began to perform a systematic research concerning the phase behaviors of the BABH-*n* series[11] and surprisingly, unexpected phase behavior was found including two types of Cub phases, which is very similar to the case of ANBC-*n* series mentioned above. The preliminary results are presented in this letter.

The preparation route of the BABH-*n* compounds was basically the same as used by Schubert et al.[6] Phase-transition temperatures were determined by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). For the BABH-*n* compounds examined in this work, two LC phases, SmC and Cub phases, were recognized; the POM photo of the former phase was characterized by the appearance of a typical SmC schlieren texture under crossed polarizers, and the transition to the latter phase was easily identified by a slow growth of completely dark texture and thus optically isotropic areas with polygonal shapes. The BABH-*n* compounds typically show two or three crystalline (Cr) phases but identification of those phases is not completed at this stage.

Figure 1 shows the phase diagram of the BABH-*n* series as functions of temperature (*T*) and alkoxy chain length (*n*), where crystal–crystal phase transitions are neglected. The data for $n = 8$–10 are essentially the same with the previous report by Demus et al.[7] While the Cub phases were detected for all members with $6 \leq n$ both on heating (2H, 2nd heating) and on cooling (1C, 1st cooling) and only on cooling for the $n = 5$ member, the SmC phase was only seen for $n = 8$–10 and in the higher temperature



Scheme 1.

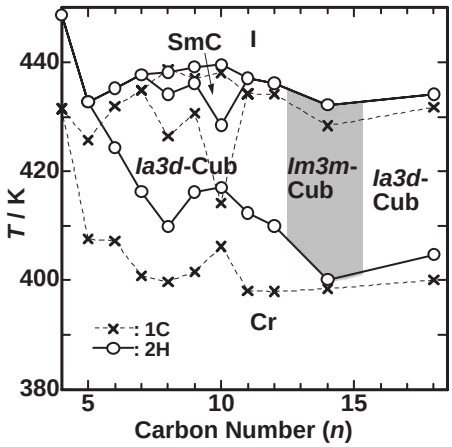


Figure 1. Phase diagram of BABH-*n*.

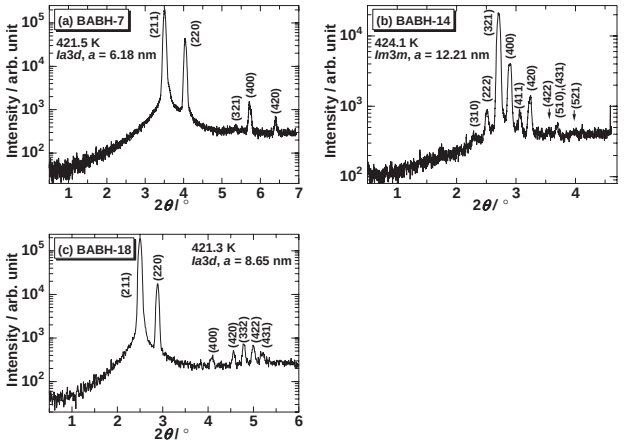


Figure 2. XRD patterns of two Cub phases formed by (a) BABH-7, (b) BABH-14, and (c) BABH-18.

side of the Cub phase. As for the structure type of the Cub phase, X-ray diffraction (XRD) investigations are necessary, and the results showed that the structure is dependent on the alkoxy chain length n; an *Ia*3*d* type is seen for $n = 5$–12, an *Im*3*m* type for $n = 14$, and again an *Ia*3*d* type is seen for $n = 18$. Such phase behavior is very similar to that seen for the ANBC-*n* described in the Introduction.

Three selected XRD patterns are shown in Figure 2. In the experiments, the Cu Kα radiation ($\lambda = 0.154$ nm) was used and the scattered X-rays were first recorded on a two-dimensional imaging plate (IP) camera, and the intensity was then circular-averaged with respect to scattering angle (2θ) which is connected to a long-range periodicity (d) with a well-known equation of $2d \sin\theta = \lambda$. Figure 2a is for the $n = 7$ member at 421.5 K, and two intense and three much weaker peaks are visible. The ratios of reciprocal d were $\sqrt{3}$:$\sqrt{4}$:$\sqrt{7}$:$\sqrt{8}$:$\sqrt{10}$, where the number inside $\sqrt{\ }$, or that times integer, should correspond to $h^2 + k^2 + l^2$ when the diffraction is assigned to (hkl) planes. Since the (hkl) planes with $h^2 + k^2 + l^2 = 7$ and 15 are not possible, the sequence of numbers must be doubled.[5] Since BABH-7 is achiral, only the space group *Ia*3*d* matches the absence of diffractions with lower indices (100), (110), (111), (200), and (210). As often seen for other Cub phases, the pattern on cooling tended to become spotlike on the IP image, reflecting the sample consisting of a small number of larger domains in the glass capillary tube. The cell parameter is estimated as $a = 6.18 \pm 0.01$ nm. The space group *Ia*3*d* is the same with that of the Cub phase of BABH-8 previously reported.[12] The structure of the *Ia*3*d*-type Cub phase is well described by a pair of interpenetrating infinite networks with 3-by-3 connections or G-type infinite periodic minimal surface (IPMS) model; one of the two incompatible parts of the molecules is located at the network rods in the former model, while is divided by the surface in the latter.[1–3] In Figure 2c, for a long chain member with $n = 18$ at 421.3 K, a similar conclusion was obtained with $a = 8.65 \pm 0.01$ nm.

Figure 2b is the circular-averaged pattern for $n = 14$ at 424.1 K. In this case, much larger number of peaks were seen, showing the following ratios of reciprocal d: $\sqrt{5}$:$\sqrt{6}$:$\sqrt{7}$:$\sqrt{8}$:$\sqrt{9}$:$\sqrt{10}$:$\sqrt{12}$:$\sqrt{13}$:$\sqrt{15}$. From the same reason mentioned above, the sequence of the numbers must be doubled, and thus, the obtained ratios are $\sqrt{10}$:$\sqrt{12}$:$\sqrt{14}$:$\sqrt{16}$:$\sqrt{18}$:$\sqrt{20}$:$\sqrt{24}$:$\sqrt{26}$:$\sqrt{30}$, which is characteristic of a body-centered cubic symmetry *Im*3*m*, and thus the cell parameter is $a = 12.21 \pm 0.01$ nm. The intensity variation with 2θ is very similar to that observed for other *Im*3*m*-type Cub phase in thermotropic systems,[5] for which we proposed a "doubled" structure of P-type IPMS.[10,13] Very recently, Zeng, Ungar, and Clerc reported a more sophisticated model by analyzing single-domain diffraction patterns;[14] although they did not say so, it can be said that, boldly speaking, their model is essentially identical with our model,[10,13] except for the minute structure such as the octahedral connection of rods at the body center and eight corners of the Cub lattice.

The most important conclusion in this work is that in addition to the ANBC-*n* series the BABH-*n* series also show two types of Cub phases, the formation of which is dependent on the alkoxy chain length n. This not only implies that the BABH-*n* series is the second example for one-component thermotropic LC systems that exhibit two Cub phases with *Ia*3*d* and *Im*3*m* symmetries but also demonstrates that the phase sequence of *Ia*3*d*–*Im*3*m*–*Ia*3*d* with lengthening the chain is a general trend for the Cub-phase forming molecules having a central polar core with one flexible chain at each end (see Scheme 1). It is clear that systematic research in terms of the chain length n we have been progressing is useful and undoubtedly will contribute to the understanding of factors differentiating between the two thermotropic Cub phases of *Ia*3*d*- and *Im*3*m*-types in the near future. The detailed investigation of the Cub phases in the BABH-*n* series, including, for example, temperature variation of lattice parameters and hydrogen bonding, is certainly worthwhile and in progress in our laboratories.

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