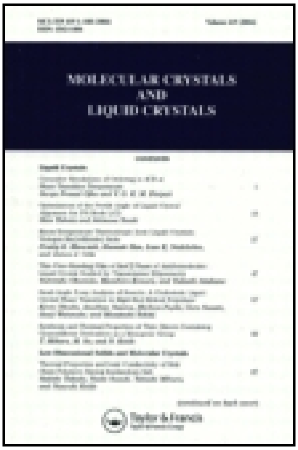

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X-ray Characterization of Two Cubic Phases and a Structured Liquid Phase of 4′-n-Alkoxy-3′-nitrobiphenyl-4-carboxylic Acids (ANBC-n)

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X-ray Characterization of Two Cubic Phases and a Structured Liquid Phase of 4′-*n*-Alkoxy-3′-nitrobiphenyl-4-carboxylic Acids (ANBC-*n*)

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The cubic D (CubD) and structured liquid (I_1) phases of 4′-*n*-alkoxy-3′-nitrobiphenyl-4-carboxylic acids (ANBC-*n*, where *n* is the number of carbons in the alkoxy group) have been investigated by X-ray diffraction techniques. The type of the CubD phase was identified as *Ia3d* for the homologues with *n*=15, 19, 20, 22, and 26, similarly to those of *n*=16 and 18. On the basis of the model proposed by Luzzati and Spegt, the diameter (*D*/Å) and the length (*L*/Å) of the constituent rod are estimated and discussed. The structure of the I_1 phase and its dependence on *n* are also discussed. For *n*=26, very surprisingly, another cubic phase with *Im3m* symmetry was observed at the lower temperature side of the *Ia3d* cubic phase on heating.

Keywords: cubic phase; structured liquid; 4′-*n*-alkoxy-3′-nitrobiphenyl-4-carboxylic acids

INTRODUCTION

4'-*n*-alkoxy-3'-nitrobiphenyl-4-carboxylic acids (designated as ANBC-*n*, where *n* is the number of carbons in the alkoxy groups) are well known for exhibiting both optically isotropic cubic (CubD) and other optically anisotropic mesophases such as smectic A and C (SmA and SmC) phases.[1] These compounds were first synthesized by Gray et al.[2], investigated by Demus et al.[3,4], Diele et al.[5], and others[6-17]. The structure of the CubD phase of n=16 and 18 has been already identified as space group $Ia3d$,[6,8,12] but the cubic lattice contains more than one thousand molecules, and thus, it is very difficult to deduce the packing at the molecular level from the lattice dimension and the packing symmetry obtained.

How the alkoxy chain length *n* influences the formation of the CubD phase was a question that initiated our studies on this phase. It has been revealed that the CubD phase appears enantiotropically when $n \geq 16$ and only on the first heating for n=15; the temperature region of the CubD phase becomes wider with increasing *n* (to n=26, see Figure 1, top).[9,15,16] In X-ray diffraction (XRD) studies, the spacing in the small-angle region often contains the experimental error of a few Å, and moreover, the actual molecular length in mesophases like the CubD phase should be some 10 % smaller than the fully extended length. These situations have also made it hard to determine unambiguously the molecular organization of the CubD phase.

The present work took notice of the fact that the length of ANBC-*n* *dimer* in the fully extended form varies from 58 Å for n=15 to 85 Å for n=26, far beyond the XRD experimental errors. How the variation of the molecular length changes the lattice dimension of the CubD phase is of much interest and such information is expected to elucidate the molecular organization of this phase. This paper reports the results of the XRD investigations on the homologues of *n*=15, 16, 18-20, 22, 26. The structural features of the CubD and a structured liquid (I_l) phases are discussed.

EXPERIMENTAL

All ANBC-*n* were prepared according to the established method.[2,18] The purity was checked by thin layer chromatography, ^{1}H-NMR (JEOL JNM-α-400), differential scanning calorimetry (DSC) (Seiko Denshi SSC 5000), and elemental analysis. The phase transitions were determined by DSC, microscopic textures (Nikon Optiphot-pol XTP-11 polarizing optical microscope and Mettler FP 82 hot stage) and X-ray diffraction (XRD) patterns.

XRD patterns were obtained with powder samples filled in thin glass capillaries by using monochromatized CuKα radiation. The following two setups were used: (A) When recorded on two-dimensional films, a Rigaku RU300B X-ray generator (operated at 45 kV and 150 mA) and an Enraf Nonius precession camera were used, and the sample-to-film distance was 100 mm. The sample capillaries (0.5 mm diameter) were placed in an air flux and the temperature was controlled within ±1 C. (B) When recorded on one-dimensional position-sensitive proportional counter (PSPC), a Mac Science M18XHF X-ray generator (40 kV and 30 mA) and the Huxley-Holms optics were used. The sample capillaries (1.5 mm diameter) were placed in a Mettler FP 82HT hot stage, and the temperature was controlled within ±0.1 C.

RESULTS AND DISCUSSION

Figure 1 shows the phase diagram of ANBC-*n* (in the top) and how the d-spacings of the innermost rings of the SmC, CubD, SmA, and I_l phases depend on the number of carbons in the alkoxy group (*n*) (in the bottom). The four phases showed a halo around 4 to 5 Å in the wide-angle region of the XRD pattern, reflecting the liquid-like state of alkoxy chains in these phases.

In the small-angle region, the innermost ring of the CubD phase is the (211) diffraction of *Ia3d* cubic lattice. As seen in the bottom part of Figure 1, the spacing increases linearly with *n*. Strictly speaking, the spacing varies with temperature even in the CubD temperature range of the same *n*, but the dependence is very small; for *n*=16, for example, the variation was found within 0.4 Å with a temperature increase of 15 K, almost comparable to the experimental errors. The spacings of the SmC and I_1 phases, on the other hand, correspond to their layer thickness, and their *n* dependences are curved upward. In the SmC phase, the tilt angle of the molecular long axis against layer normal was estimated on the basis of the dimer length in the fully extended form. Estimated values ranged between 42 and 46 °, almost independent of *n*. These values, however, are presumably overestimated, because the actual alkyl tail should be shrunk in the SmC phase from its all *trans* form.

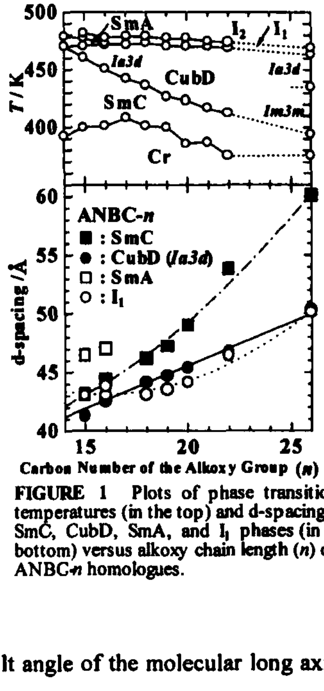

FIGURE 1 Plots of phase transition temperatures (in the top) and d-spacings of SmC, CubD, SmA, and I_1 phases (in the bottom) versus alkoxy chain length (*n*) of ANBC-*n* homologues.

The I_1 phase appears at the higher temperature side of the CubD/SmA phase. As reported previously, this phase is completely optically isotropic[4,7,9] and shows a relatively low viscosity of 10^0 P or less, which is 10^3 times lower than that of the SmC phase.[10] Nevertheless, the XRD pattern shows a sharp ring in the small-angle region. Moreover, in the DSC experiment, further heating of the I_1 phase gives a broad endothermic hump centered at a temperature about 5 K higher than the CubD to I_1 (or the SmA to I_1) phase transition temperature.[4,7,9] Above this temperature, in the I_2 phase, the sharp XRD ring disappears. Therefore, the I_1 phase is a structured liquid. In other words, this phase is a transient state into the true liquid I_2, although the I_1 phase is a thermodynamic equilibrium one. The infrared studies also revealed that a significant dissociation of COOH dimers into monomers starts to occur at around 460 K, just below the CubD to I_1 (or the SmA to I_1) phase transition temperature; about 85 % of COOH groups are in the dimer in the CubD phase, whereas about a third is in the monomer at the I_1 phase temperatures. These results suggest that the dissociation of COOH dimers destabilizes the CubD phase to produce the I_1 phase, and thus, it has been proposed that the I_1 phase contains clusters of molecules forming a layered structure similar to the SmA layers but the degree of long-range ordering is considerably lower compared with the SmA phase.[11] Similar discussions have been made in terms of "lattice melting" by Goodby et al.[20] and from a thermodynamic point of view by Saito, Sorai, and their collaborators[13,14].

In Figure 1, the layer spacing of the I_1 phase is about 62-74 % of ANBC-*n* dimer length, while in the SmA phase of n=15 and 16, the spacing is 77-80 % of the corresponding dimer length. Hence, the alkoxy chains of different layers may be interdigitated with each other. A similar model has been proposed for a structured liquid state of *cis*-9-octadecenoic acid.[19]

Figure 2 dipicts the *Ia3d* structure proposed by Luzzati and Spegt for the cubic phase of strontium alkanoates[21] and by Tardieu and Billard for the CubD phase of ANBC-*n*.[6] In the *Ia3d* structure, rod micelles are connected three-by-three to form two sets of three-dimensional networks which are interwoven. In ANBC-*n*, both the hydrogen-bonded COOH and aromatic

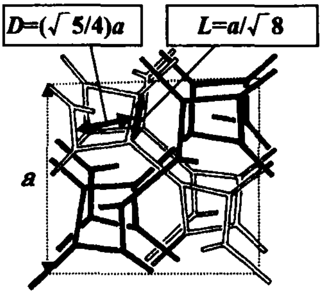

FIGURE 2 Schematic representation of *Ia3d*-cubic phase (Luzzati and Spegt model). ***D***, ***L***, and ***a*** are the diameter and length of rod, and the cell dimension, respectively, and ***D*** is approximated to a distance between the midpoints of two non-connecting rods shown above. Note that $D \sim L$ for actual rod micelles and white and black rods only depict the locations of the center of the rods.

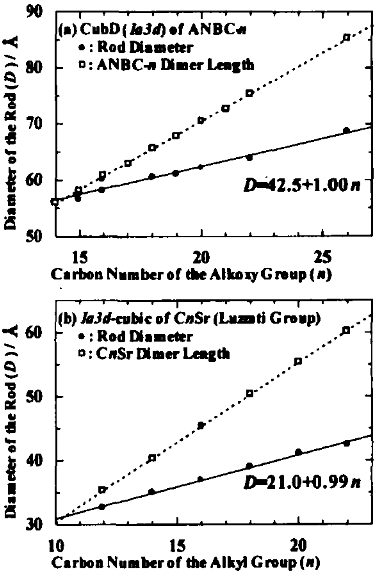

FIGURE 3 Plots of rod diameter (***D***) of *Ia3d*-cubic phase versus carbon number (***n***) of the aliphatic tail for (a) ANBC- *n* and (b) strontium alkanoates (C*n*Sr).

parts constitute the core part of ANBC-*n* dimer, being 23.8 Å long, and the core is located at the center of the rod. As shown in Figure 2, the rod diameter (*D*/Å) may be approximately given by the following equation: $D=(\sqrt{5}/4)a$, where *a* is the lattice constant of the CubD phase. Figure 3 shows plots of *D* versus *n* for (a) ANBC-*n* and (b) strontium alkanoates (C*n*Sr), where the latter plot was obtained using the data in ref 21. In both cases, the dependence of *D* on *n* is well reproduced by a linear equation of *n*: $D=42.5+1.00n$ for ANBC-*n*, and $D=21.0+0.99n$ for strontium alkanoates. Each value of *D* should be compared with the (fully extended) length (2*l*) of ANBC-*n* dimer/C*n*Sr. The data of *D* and 2*l* of ANBC-*n* are also listed in Table 1. In ANBC-*n*, $2l \geqq D$ when $n \geqq 15$, where the number 15 is the minimum number of carbon atoms in the alkoxy group

TABLE 1. Structural data for the CubD phases of ANBC-*n*

n	2*l*/Å	*T*/K		*a*/Å	space group	*D*/Å	*L*/Å	*N*/Å^{-1}
15	58.0	466	(B)	101.3	*Ia3d*	56.6	35.8	1.54
16	60.8	457	(A)	104.1	*Ia3d*	58.2	36.8	1.58
		459	(B)	107.5	*Ia3d*	60.1	38.0	1.62
18	65.7	455	(A)	108.0	*Ia3d*	60.4	38.2	1.67
19	67.8	449	(A)	109.5	*Ia3d*	61.2	38.7	1.59
20	70.6	441	(A)	111.2	*Ia3d*	62.2	39.3	1.62
22	75.4	433	(A)	114.4	*Ia3d*	63.9	40.4	1.62
26	85.2	396	(B)	201.1	*Im3m*	?	?	
		449	(B)	123.1	*Ia3d*	68.8	43.5	1.72

2*l*, dimer length; *a*, lattice constant; *D*, rod diameter; *L* rod length; *N*, number of molecules per unit length of the rod. Type of the experimental setup used is shown in parentheses (see Experimental section).

that produces the CubD phase (see Figure 1, top), and for *n*=26, *D* is 81 % of 2*l*. The same situation is seen in strontium alkanoates; $2l \geqq D$ when $n \geqq 11$, and for *n*=22, *D* is 71 % of 2*l*. The increments of *D* with *n* are the same in both series and 1.0 Å per *n*. This value corresponds to twice the carbon-carbon length in the molten state. In fact, in the columnar mesophases of dirhodium(II) tetracarboxylates, the intercolumnar distance was reported to increase with 0.9 Å per *n*.[22] On the other hand, the difference between the *D* values at *n*=0 for these two homologous series is 21.5 Å, which is mainly due to their different core size: the core size of C*n*Sr is about 8 Å, and the difference between the two is 16 Å.

Neglecting the short gap at each end of the rod[21], the length of the rod (*L*) is equal to $a/(\sqrt{8})$. The number of molecules (*N*) per unit length of the rod in the CubD phase was calculated on the assumption that the density (ρ) is 1 g/cm^3 ($N = \rho a^3 N_A / 24M$, where N_A is Avogadro's number and *M* is molecular mass), and summarized in Table 1. The value of *N* slightly

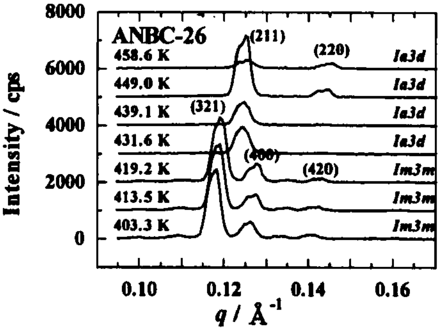

FIGURE 4 X-ray diffraction patterns of ANBC-26 as a function of temperature in the CubD phase range on heating. Temperature and the phase type are shown in the left and right sides of each curve, respectively, and only main diffraction peaks are indexed.

increases with *n*, from 1.54 $Å^{-1}$ for n=15 to 1.72 $Å^{-1}$ for n=26, but considering that the density presumably slightly decreases with *n*, it would be better to say that the density is ~1.6 $Å^{-1}$, independent of *n*. The wide-angle XRD pattern of ANBC-*n* showed that the distance between the cores along the rod is ~4 Å, and 6 molecules are present in the distance of ~4 Å because $4 \times 1.6 = 6.4 \sim 6$. Since the molecules exist as the dimer in the rod,[11] it is concluded that *one slice of the rod* contains three ANBC-*n* dimers. This picture supports the model proposed by Guillon and Skoulios[23]. Moreover, it is of much interest that the molecular organization in one slice of the rod in the CubD phase is unchanged when the dimer length changes from 58 Å for n=15 to 85 Å for n=26.

Figure 4 shows the XRD patterns of ANBC-26 at various temperatures in the CubD phase on heating ($q=(4\pi/\lambda)\sin\theta$, $\lambda=1.54$ Å, and 2θ =scattering angle). Very surprisingly, the pattern changed abruptly from 419.2 to 431.6 K. Indexing those diffraction peaks revealed that the lower-temperature cubic phase is characterized by space group *Im3m*, while the space group of the higher-temperature cubic phase is *Ia3d*, the same as other CubD phase of ANBC-*n* homologues. This transition was also detected at 435 K by DSC (5 K/min). This is the first example of a thermotropic cubic-cubic phase transition in one-component systems; in lyotropic binary or ternary mixtures, where the phase behavior is a function of the water content, two examples were reported.[24-26] The more detailed discussion on this cubic-cubic transition will be described separatedly in the near future.[17] Here, a new question arises where and how this new type of cubic phases appears in the phase diagram of ANBC-*n*, and further investigations are in progress.

In summary, the present X-ray studies revealed the molecular organization of the CubD and I_1 phases of ANBC-*n*. The rod diameter and length of the *Ia3d* CubD phase were estimated on the basis of the model proposed by Luzzati and Spegt. It was shown that the rod diameter for n=15 is nearly equal to, and for n=22 about 20 % smaller than, the molecular length of ANBC-*n* dimer, and for all *n*, one slice of the rod contains three ANBC-*n* dimers. This picture supports the model proposed by Guillon and Skoulios. It was also revealed that the I_1 phase contains clusters of molecules forming a layered structure similar to the SmA layers, and the alkoxy chains of different layers may be interdigitated with each other. For n=26, another cubic phase with *Im3m* symmetry was observed at the lower temperature side of the *Ia3d* cubic phase on heating.

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References

[1] S. Diele and P. Göring, in *Handbook of Liquid Crystals,* (eds D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, V. Vill) (Wiley-VCH, Weinheim, 1998), Vol. 2B, pp. 887–900.
[2] G. W. Gray, B. Jones. and F. Marson, *J. Chem. Soc.*, 393 (1957).
[3] D. Demus, G. Kunicke, J. Neelsen, and H. Sackmann, *Z. Naturforsch.*, **23a,** 84 (1968).
[4] D. Demus, D. Marzotko, N. K. Sharma, and A. Wiegeleben. *Kristall. Tech.*, **15**, 331 (1980).
[5] S. Diele, P. Brand, and H. Sackmann, *Mol. Cryst. Liq. Cryst.*, **17,** 163 (1972).
[6] A. Tardieu and J. Billard, *J. Phys. Coll.*, **37,** C3–79 (1976).
[7] G. W. Gray, In *Zehn Arbeiten Uber Flüssige Kristalle,* Kongress-und Tagung-berichte der Martin-Luther-Universität, Halle-Wittenberg, 1986, pp. 22–42.
[8] A.-M. Levelut and Y. Fang, *Colloque de Physique, Colloque No. 7,* **51,** C7–229 (1991).
[9] S. Kutsumizu, M. Yamada, and S. Yano, *Liq. Cryst.*, **16,** 1109 (1994).

[10] T. Yamaguchi, M. Yamada, S. Kutsumizu, and S. Yano, *Chem. Phys. Lett.*, **240,** 105 (1995).
[11] S. Kutsumizu, R. Kato, M. Yamada, and S. Yano, *J. Phys. Chem., B,* **101,** 10666 (1997).
[12] A. M. Levelut and M. Clerc, *Liq. Cryst.*, **24,** 105 (1998).
[13] K. Saito, A. Sato, and M. Sorai, *Liq. Cryst.*, **25,** 525 (1998).
[14] A. Sato, K. Saito, and M. Sorai, *Liq. Cryst.*, **26,** 341 (1999).
[15] S. Kutsumizu, T. Yamaguchi, R. Kato, and S. Yano, *Liq. Cryst.*, **26,** 567 (1999).
[16] S. Kutsumizu, T. Yamaguchi, R. Kato, T. Ichikawa, and S. Yano, *Mol. Cryst. Liq. Cryst.*, in press.
[17] S. Kutsumizu, T. Ichikawa, S. Nojima, and S. Yano, *Chem. Comm.*, 1181 (1999).
[18] G. W. Gray, J. B. Hartley, and B. Jones, *J. Chem. Soc.*, 1412 (1955).
[19] M. Iwahashi, Y. Yamaguchi, T. Kato, T. Horiuchi, I. Sakurai, and M. Suzuki, *J. Phys. Chem.*, **95,** 445 (1991).
[20] J. W. Goodby, D. A. Dunmur, and P. J. Collings, *Liq. Cryst.*, **19,** 703 (1995).
[21] V. Luzzati and P. A. Spegt, *Nature*, **215,** 701 (1967).
[22] A.-M. Giroud-Godquin, J.-C. Marchon, D. Guillon, and A. Skoulios, *J. Phys. Chem.*, **90,** 5502 (1986).
[23] D. Guillon and A. Skoulios, *Europhys. Lett.*, **3,** 79 (1987).
[24] W. Longley and T. J. McIntosh, *Nature*, **303,** 612 (1983).
[25] K. Larsson, *Nature*, **304**, 664 (1983).
[26] P. Mariani, V. Luzzati, and H. Delacroix, *J. Mol. Biol.*, **204,** 165 (1988).