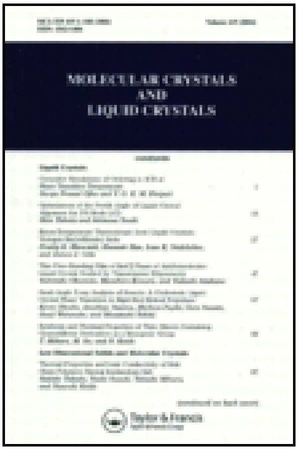

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Cubic Phases of 4'-n-docosyloxy-3'-nitrobiphenyl-4-carboxylic Acid (ANBC-22)

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CUBIC PHASES OF 4′-*n*-DOCOSYLOXY-3′-NITROBIPHENYL-4-CARBOXYLIC ACID (ANBC-22)

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Dilatometric experiments have been performed on 4′-n-docosyloxy-3′-nitrobiphenyl-4-carboxylic acid (ANBC-22) which exhibits two types of thermotropic cubic phases (Cub I and II) on heating. Although the unit lattices of both Cub I and II, determined by X-ray diffraction measurements, slightly but certainly shrink with increasing temperature, the thermal expansion coefficients in both temperature regions were found to be positive. Thus, this study provided an experimental evidence that the number of molecules constructing the unit lattice of the two Cub phases decreases with temperature. Some aspects of the structural features of the Cub phases are discussed.

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Keywords: 4′-*n*-alkoxy-3′-nitrobiphenyl-4-carboxylic acids; dilatometry; hydrogen bonding; thermotropic cubic phase; X-ray diffraction

INTRODUCTION

4′-*n*-alkoxy-3′-nitrobiphenyl-4-carboxylic acids (designated as ANBC-*n*, where *n* is the number of carbon atoms in the alkoxy groups) are well known for exhibiting thermotropic cubic (Cub) phases [1–14], and two lattice types (*Ia3d* and *Im3m*) have been reported, the formation of which is strongly dependent on the alkoxy chain length *n*. When $15 \leq n \leq 18$, the *Ia3d*-Cub phase is formed, and for $19 \leq n \leq 21$, the *Im3m* type is seen, both on heating and cooling (except for $n = 15$, where the Cub phase is observed only on the first heating of the virgin sample) [12–14]. Since one 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. Other complementary studies are demanded. At present, the structure of the *Ia3d*-Cub phase is considered a bicontinuous type [4,9,10,12,14,15], which is most commonly seen in lyotropic Cub phases. Compared to the *Ia3d*-Cub phase, the lattice dimension of the *Im3m*-Cub phase is 50–60% larger, which is puzzling regarding the molecular packing. Very recently, we found that much longer homologues of $n = 22$ and 26 exhibit the two Cub phases successively on heating in the sequence smectic C (SmC)-*Im3m*-*Ia3d*-isotropic liquid (I), while on cooling the *Ia3d* phase is supercooled and transformed directly into the SmC phase [13,14].

To get insight into the molecular packing in both types of the Cub phases, in the present work, dilatometric experiments were carried out for the $n = 22$ homologue (ANBC-22); the exact number of molecules in the Cub lattice was determined, although the number is usually deduced from the assumption that the density is $1\,\mathrm{g\,cm^{-3}}$. Such information may also be an aid for understanding the shrinking of the Cub lattice with increasing temperature.

EXPERIMENTAL

ANBC-22 was prepared according to the established method [1,16]. 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 thermograms, microscopic textures (Nikon Optiphot-pol XTP-11 polarizing optical microscope and Mettler FP 82 hot stage) and X-ray diffraction (XRD) patterns (Mac Science M18XHF X-ray generator with the Huxley-Holms optics and a Mettler FP 82HT hot stage). Infrared (IR) spectra were recorded using a Perkin-Elmer system 2000 IR spectrometer equipped with a heated cell and a controller (S. T. Japan 0019-201 and 0019-200). Dynamic viscoelastic measurements were carried out using a Rheometric Dynamic Stress Rheometer DSR.

Thermal expansions were measured at a heating rate of ca. 0.5 K min^{-1} using a glassy capillary dilatometer (length, 590 mm; inner diameter, 0.6 mm; cell volume, ca. 10 cm^3). The sample was first melted at 438 K for 45 min in a vacuum oven, and then, slowly cooled to room temperature. The obtained lumps of the sample was carefully immersed in liquid mercury *in vacuo* to avoid the formation of voids on the surface of the sample. The volume change was calculated from a reading of the height of mercury in the capillary of the dilatometer. The density at 298 K was obtained separately using a glassy pycnometer with toluene as the solvent.

RESULTS AND DISCUSSION

Figure 1 shows (a) the DSC heating trace (rate: 5 K min^{-1}), and (b) the storage modulus (G', open circle) and loss modulus (G'', open square) and (c) the Cub lattice parameters (a) as a function of temperature (T) for ANBC-22. As mentioned in the Introduction, ANBC-22 exhibits two Cub phases on heating, *Im3m*-Cub I phase and *Ia3d*-Cub II phase, in going from low-temperature side, but on cooling, only one type, the *Ia3d*-Cub II phase, is formed. The temperature variation of the Cub lattice dimensions in (c) reflects the phase behaviour. Another feature to note in (c) is a shrinking of the two Cub lattices with increasing temperature. Provided that the **apparent** thermal expansion coefficient (α) is defined as $(1/a^3)(\mathrm{d}(a^3)/\mathrm{d}T)$, although not exact from a thermodynamic point of view, the values of α are: $-1.3\times10^{-3}\,\mathrm{K}^{-1}$ for the *Im3m*-Cub I on heating, $-6\times10^{-4}\,\mathrm{K}^{-1}$ on heating and $-3\times10^{-4}\,\mathrm{K}^{-1}$ on cooling for the *Ia3d*-Cub II. The Cub I to Cub II phase transition was detected at 454 K by adiabatic calorimetry and the transition entropy was estimated as 0.37 J $\mathrm{mol}^{-1}\,\mathrm{K}^{-1}$ [13]. The DSC trace in (a) does not show any anomaly around that temperature, but very surprisingly, the plots of G' versus T and G'' versus T in (b) show a small but significant jump at 453 K.

Figure 2 shows the dilatometric results, plots of (a) the molecular volume (V_m) and (b) the thermal expansion coefficient (α) versus T. The value of α, defined as $(1/V_\mathrm{m})(\mathrm{d}(V_\mathrm{m})/\mathrm{d}T)$, was estimated by use of the least squares polynomial fit for seven data points involving three successive temperatures above and below the objective temperature. In the V_m-T curve in (a), an abrupt increase ($\Delta V_\mathrm{m}/V_\mathrm{m}\approx 7\%$) is seen around 376 K and a slight

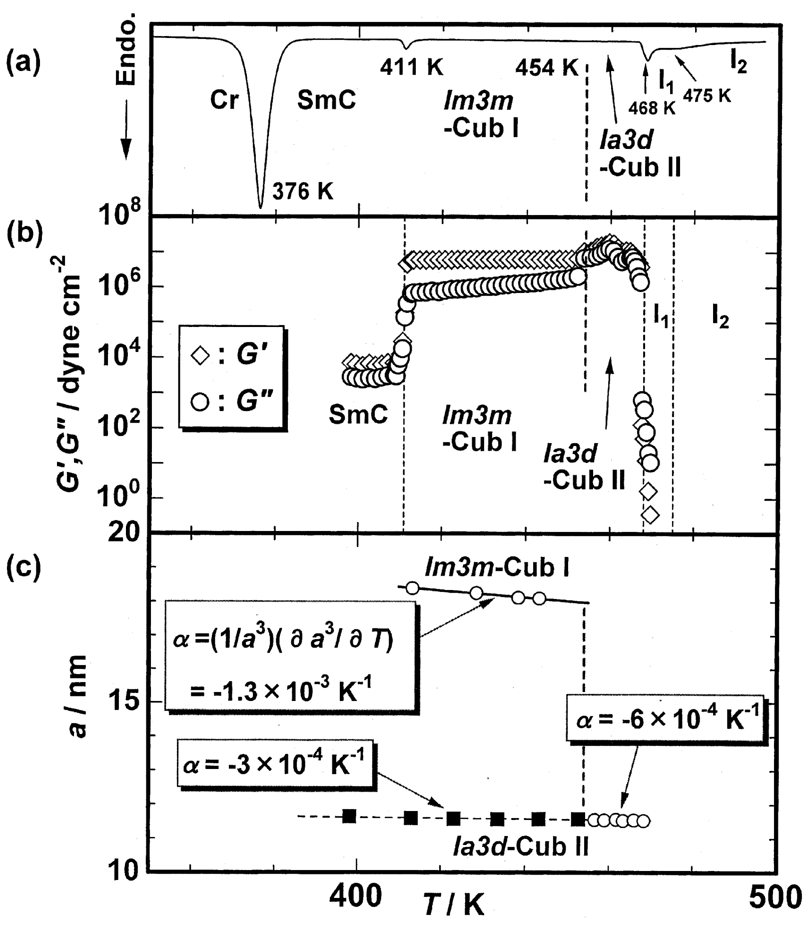

FIGURE 1 (a)DSC heating trace, and (b) the storage modulus (G') and loss modulus (G'') and (c) the Cub lattice parameters (a) as a function of temperature (T) for ANBC-22; figure b is reprinted form ref 7 with modification, Copyright (1995), with permission from Elsevier Science.

but definite increase (0.6%) is visible at 409 K. The former is due to the transition to the smectic C (SmC) phase and the latter corresponds to the SmC to Cub I phase transition. Unfortunately, we could not detect any definite change corresponding to the Cub I to Cub II phase transition; in the α-T plot in (b), a faint peak or a step at 450 K, reproduced by the duplicate measurements, seems to correspond to the transition. The transition enthalpies ΔH were precisely determined by adiabatic calorimetry and the values are 73.96, 1.98, and 0.17 kJ mol^{-1} for the transitions from

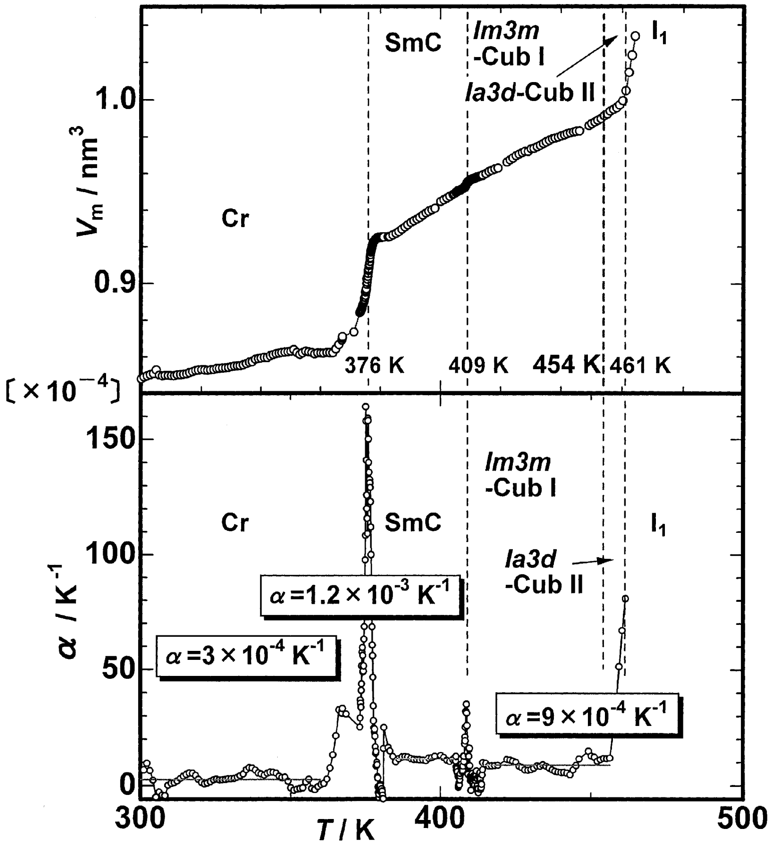

FIGURE 2 Plots of (a) the molecular volume (V_m) and (b) the thermal expansion coefficient (α) versus T.

Cr to SmC, from SmC to Cub I, and from Cub I to Cub II phases, respectively [13]; the ratio is 7 : 0.19 : 0.016. Assuming that a correlation exists between $\Delta V_m/V$ and ΔH for these transitions, $\Delta V_m/V_m$ for the Cub I to Cub II phase transition should be on the order of 0.02%, which is within the experimental errors of the present studies.

In Figure 2a, the linear fits of V_m as a function of T in the SmC and Cub phases except the transition regions gave the following results: $V_m = 0.5058 + 0.0011 \times T$ for the SmC phase ($383.2\,K \leq T \leq 408.2\,K$), $V_m = 0.6282 + 0.0080 \times T$ for the Cub I and II phases ($410.9\,K \leq T \leq 459.2\,K$), where V_m in nm^3.

In the α-T curve in (b), the average values of α are: $3 \times 10^{-4}\,K^{-1}$ for the crystalline (Cr) state ($298.2\,K \leq T \leq 360.2\,K$), $1.2 \times 10^{-3}\,K^{-1}$ for the SmC phase and $9 \times 10^{-4}\,\mathrm{K}^{-1}$ for the Cub region including both the Cub I and II phases. To our best knowledge, there has been only one report presenting the dilatometry result involving the Cub phase region. It was the study on 1,2-bis(4-*n*-octyloxybenzoyl)hydrazine by Demus *et al.* [17] and the Cub phase is of *Ia3d* type [18]. The reported value ($8.8 \times 10^{-4}\,\mathrm{K}^{-1}$) and the value of ANBC-22 are almost the same. For the SmC phase, the value of ANBC-22 is in quite consistent with the literature value for the same phase (for example, $1.3 \times 10^{-3}\,\mathrm{K}^{-1}$ for 4,4′-bis(*n*-octadecyloxy)azoxybenzene [19] and $\approx 1 \times 10^{-3}\,\mathrm{K}^{-1}$ for *n*-amyl 4-(4-*n*-dodecyloxybenzylideneamino)-cinnamate [20,21]). It should be noted that the values are in the order $\alpha(\mathrm{SmC}) > \alpha(\mathrm{Cub}) > \alpha(\mathrm{Cr})$.

In the two Cub regions, the α values obtained from dilatometry are positive, while the apparent α determined by the X-ray measurement are negative. This implies that the number of molecules contained in the unit lattice (N) should decrease with increasing temperature and the plot is presented in Figure 3. The value of N changes from ca. 6500 at 412 K to ca. 5900 at 450 K, with a decrease of 10%, in the *Im3m*-Cub I phase region, and changes from ca. 1550 at 454 K to ca. 1510 at 461 K, 3% decrease, in the *Ia3d*-Cub II region. This is not so surprising considering that there is no positional order in the molecular level such as normal crystals have. The Cub phases are, however, macroscopically three-dimensionally ordered with cubic symmetry, resulting from a micro-segregation between the paraffinic tail and the aromatic core parts of the ANBC-22 molecule, similarly to the lyotropic Cub phases. Therefore, the change in N with temperature suggests that the two molecular parts do not show the same thermal expansion.

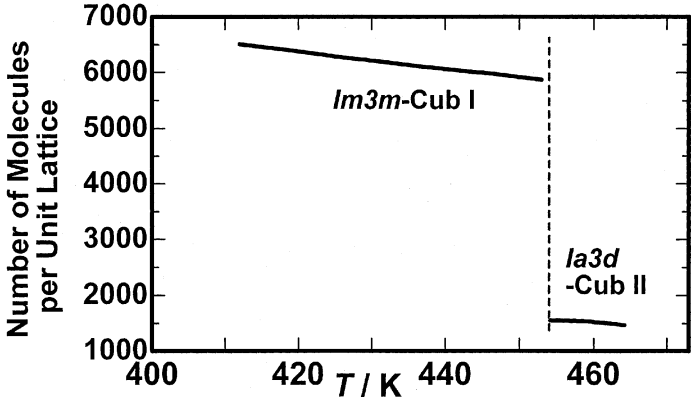

FIGURE 3 Plot of the number of molecules per Cub unit lattice versus T for ANBC-22 on heating.

What are different between the Cub I and II phases of ANBC-22? As seen from Figure 1, the symmetry of the Cub lattice changes from $Im3m$ to $Ia3d$, followed by a change in elasticity. To obtain microscopic information, we re-examine the IR spectral results which was published before finding the existence of the two Cub phases on heating [8]. Figure 4 shows (a) the temperature variation of the asymmetric C-H stretching vibration frequency of methylene groups ($\nu_{as}(\text{C-H})_{CH_2}$) and (b) the van't Hoff plot for dimer-monomer equilibrium constant (K_d) versus reciprocal temperature, derived from the decomposition of the carbonyl stretching vibration (ν(C=O)) peak. Here, K_d is linked to the heat of dissociation (ΔH) through the relation $\ln(K_d) = -\Delta H/RT + \Delta S/R$, where the variables are their usual meanings. In (a), as temperature is raised, the $\nu_{as}(\text{C-H})_{CH_2}$ frequency shifts towards higher frequency with a distinct jump at the transitions. Since the higher frequency shift implies the development of the conformational disorder in the alkoxy tails, the result derives an important conclusion that the alkoxy tails in the Cub I and II phases is more disordered than in the SmC phase, being completely molted just as in the isotropic liquid I_1 and I_2.

In (b), the temperature variation is roughly divided into three straight lines, characterized by different ΔH values. Here, a thing to note, which was not pointed out previously, is that when temperature goes from the Cub I into the Cub II phase regions, the state of terminal COOH groups changes into a state where the dissociation is strongly promoted by raising temperature. Thus, it is concluded that the core linkage due to hydrogen-bonded COOH groups becomes weaken when the Cub I phase is transformed into the Cub II phase.

We will discuss the average shape of ANBC-22 molecules in the SmC and Cub I and II phases. In the SmC phase, the tilt angle is reasonably assumed to be ≈ 20 deg, as expected from the tilt angle of the same phase for ANBC-n with $n = 14$–17 determined by X-ray diffractometry [14]. The core length is estimated as 2.384 nm by using Chem3D software and the layer spacing was determined to be 5.22 nm at 403 K by X-ray diffractometry. Using these values, the volume ratio of the paraffinic tail to aromatic core parts of ANBC-22 in the SmC phase can be estimated as 1.3 : 1. Since the corresponding weight ratio is 1.2 : 1, the molecular shape is well approximated as being rod-like.

For the Cub phase, the paraffinic tail behave as in the isotropic liquid state as mentioned above. Guillon *et al.* [22] reported that the volume of a molten methylene group V_{CH_2} (in nm^3) does not depend on the compound considered, and at a given temperature T (in K),

$$V_{CH_2} = 0.02103 + 2.023 \times 10^{-5} \times T.$$

According to this equation, the value at 423 K is 0.02959 nm^3, and the volume of the paraffinic tail of ANBC-22 is calculated as 0.6510 nm^3. From

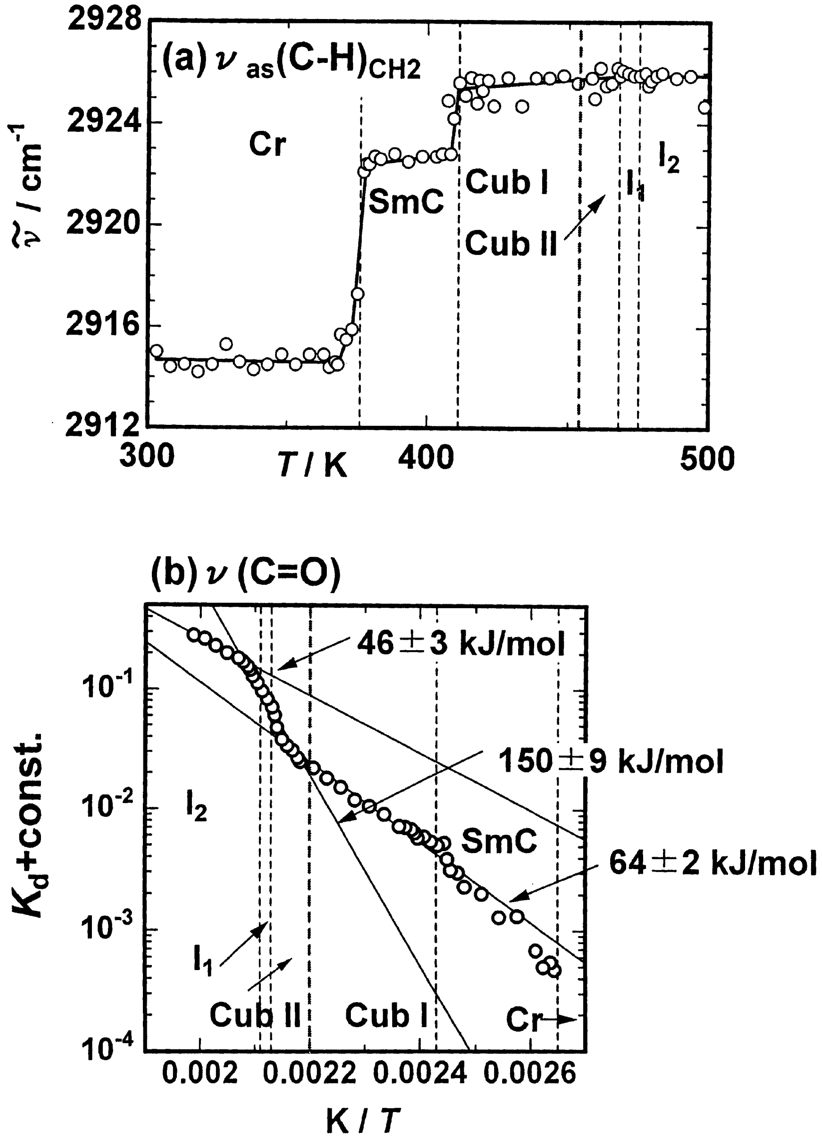

FIGURE 4 (a)Temperature dependence of the asymmetric C-H stretching vibration frequency of methylene groups (ν_{as}(C-H)$_{CH_2}$ and (b) van't Hoff plot for the dimer-monomer equilibrium constant (K_d) versus reciprocal temperature; reprinted from ref 8 with modification, Copyright (1997), with permission from American Chemical Society.

Figure 2, the molecular volume at 423 K in the Cub I phase is 0.9673 nm^3. Thus, the volume ratio of the paraffinic to aromatic parts of ANBC-22 in the Cub I phase at 423 K was estimated as 2.058 : 1. Likewise, the ratios at 443 K (in the Cub I), 455 K and 461 K (in the Cub II) were found to be 2.049 : 1, 1.975 : 1 and 1.981 : 1, respectively. The estimation is fairly rough but reveals an important feature regarding a change in the average molecular shape from the SmC to the Cub I phases, that is, changing from a rod to a truncated cone with the paraffinic part expanded, which would cause a mismatch of the surface area between the aliphatic flexible chains and the aromatic rigid core parts and undulate the SmC layer structure, just like in the case of the lyotropic Cub phases [23]. Furthermore, the above estimation also reveals that a substantial contraction of the core part occurs at the transition, which was previously pointed out by Saito, Sorai and coworkers from a thermodynamic point of view [11]. A slight decrease in the ratio of the paraffinic to aromatic parts seen on elevating temperature suggests that the degree of mismatch of the surface area between the two parts caused by one molecule decreases with temperature, resulting in the less number of molecules needed for one Cub lattice; the larger degree of the mismatch of the surface area would require the more molecules to relax a distortion (or a frustration) present in the structure. This is the reason for the shrinking of the Cub lattice with increasing temperature. As for the Cub I to Cub II phase transition, we could not get a definite conclusion, but it is probable that weakening of the core linkage, suggested by IR, would contribute to putting the shape slightly back towards a rod shape. This speculation is also supported by the fact that the lattice dimension of the $Ia3d$-Cub II phase of ANBC-22 is significantly shorter than the extrapolated value form the data for ANBC-n with $n = 15$–18 [14].

In summary, the phase behaviour of a curious cubic mesogen ANBC-22 was investigated by a combination of the X-ray diffraction and dilatometry studies. Although the unit lattices of the Cub I and II phases, determined by the X-ray measurement, slightly but certainly shrink with increasing temperature, the thermal expansion coefficients obtained were positive in both temperature regions. By combining these results, changing of the average molecular shape along with the transitions SmC → Cub I → Cub II was deduced.

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