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X-ray studies of the layer thickness in smectic phases

Stanisław Urban[a]; Jan Przedmojski[b]; Joanna Czub[a]
[a] Institute of Physics, Jagiellonian University, 30-059 Kraków, Poland [b] Physics Department, Warsaw University of Technology, 00-662 Warsaw, Poland

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X-ray studies of the layer thickness in smectic phases

STANISŁAW URBAN*, JAN PRZEDMOJSKI† and JOANNA CZUB
Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Kraków, Poland
†Physics Department, Warsaw University of Technology, 00-662 Warsaw, Poland

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X-ray investigations of nine smectogenic substances exhibiting the smectic A_d, A_1 and crystalline E phases were performed at various temperatures. X-ray patterns yielded the layer thickness d (A_d, A_1 phases) and orthorhombic unit cell parameters (E phase). The layer thickness of the A_d phase in 4′-*n*-alkyl-4-cyanobiphenyls (*n*CBs) has different temperature coefficients for shorter ($n=8-10$) and longer ($n=12-14$) members, which is explained as resulting from two competing effects: a weakening with temperature of the intermolecular association energy that favours an increase in d, and the increasing number of conformers which reduces the molecular length. A small anisotropy of the thermal expansivity in the smectic phases was found by comparing the linear quantity $d(T)$ with the linearized bulk characteristic of the system, $V^{-3}(T)$, where $V=1/\rho$ is the specific volume, ρ is the density. Differences between the slopes of the two quantities are less in the case of the A_1 phase of two *n*DBTs (5-*n*-alkyl-2-(4′-isothiocyanatophenyl)-1,3-dioxanes). The present X-ray data and recent results of studies of the low frequency relaxation process in these compounds (under atmospheric as well as elevated pressures) give a consistent picture of molecular reorientations around the short axes in the smectic phases.

1. Introduction

Rod-like molecules arranged in smectic layers can be characterized by two order parameters [1]: $S=\langle P_2(\cos\theta)\rangle=\langle 3\cos^2\theta-1\rangle/2$ describing the average orientation of the long axes with respect to the director **n**; and $\sigma=\langle\cos(2\pi z/d)\rangle$ being a measure of the density wave along the layer normal z [2], thus describing the layer structure (θ is the angle which the long axis forms with the director and d is the layer thickness). In the orthogonal phases (SmA, SmB, E, …) the z-axis lies along **n**, whereas for tilted phases (SmC, K, …) both these axes form angles that depend on the temperature. For tilted phases, yet another order parameter has to be introduced. In addition, the smectic phases may be divided into the *liquid*-like phases with no arrangement of the molecular centres of mass in the layers (A, C), and the *crystal*-like phases where such arrangements within the layers (and probably between the layers) are present (B, E, K, …). It was well established that the orientational order parameter S is practically temperature-independent in the smectic phases, in contrast to its behaviour in the nematic phase (e.g. [3, 4]). By comparison the variation of the σ-parameter and the layer thickness d with temperature has been less studied [5–19].

To the best of our knowledge there are several issues concerning smectic phases which still await experimental elucidation: (i) does the layer thickness d vary with temperature in a similar fashion in liquid-like and solid-like phases? (ii) does d vary with temperature in the same way for short and long members of a given homologous series? (iii) does the thermal expansivity show a noticeable anisotropy in smectic phases? (iv) can the ratio (volume of the molecule itself)/(volume per molecule in the unit cell), called the *packing parameter*, be useful for distinguishing between the ‘smectic rotator phase’ and a true crystal phase? (v) can X-ray data be helpful in the explanation of the dynamic properties of molecules in particular phases?

In order to find answers to at least some of these questions we have undertaken X-ray measurements as a function of temperature for several smectogens belonging to different homologous series. The following phases were examined: SmA_1, SmA_d and E. The results will be discussed with other available data on the substances examined. In particular, the layer spacing data $d(T)$ will be compared with the molar volume $V(T)=1/\rho(T)$ (ρ is the density) characterizing a bulk property of the system. The relationship between the

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*Corresponding author. Email: ufurban@cyf-kr.edu.pl

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rotational dynamics of molecules around their short axes and their arrangements in the smectic layers will be discussed.

2. Experimental

All the substances studied were synthesized in the Institute of Chemistry, Military University of Technology, Warsaw. Their chemical formulae, acronyms used and temperatures of phase transitions are shown in the table.

X-ray measurements were performed using an X'Pert (Philips) diffractometer equipped with Cu radiation monochromatized by an absorption Ni filter and proportional counter. Aligned thin layer as well as non-aligned thick layer samples were used. The intensity of the scattered diffracted beam was strongly dependent on the preparation conditions of the samples. It was measured during step-wise change of the scattering angle with the temperature constant within ±0.2 K. The value of the scattering angle was checked using the diffraction data for 8OCB (octyloxycyanobiphenyl) in the SmA_d phase, taking into account the layer spacing determined by Leadbetter *et al.* [7]. Besides possible systematic errors, the accuracy of the estimation of *d*-values is better than ±0.02 Å.

3. Results

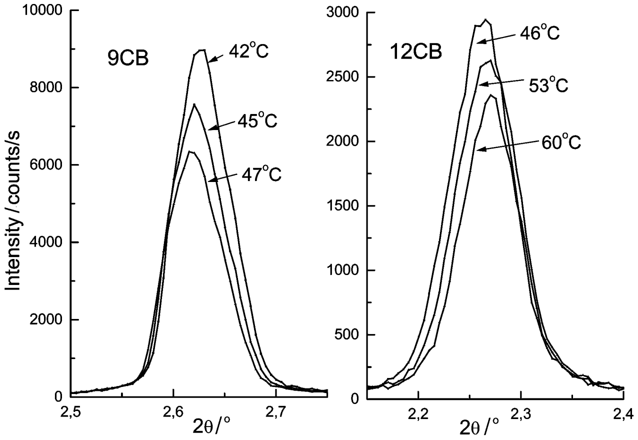
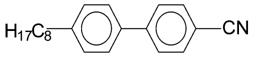
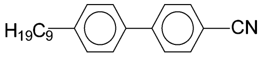
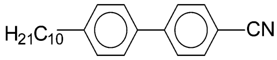
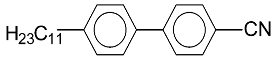
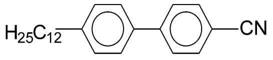
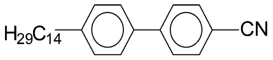
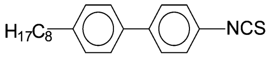
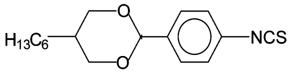
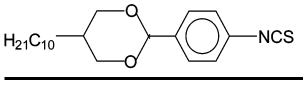


Figure 1. X-ray patterns (intensity versus scattering angle) of smectic peak recorded at three temperatures within the SmA phase of (*a*) 9CB and (*b*) 12CB. The angle corresponding to the position of maximum yields the layer spacing *d*.

Figures 1 and 2 show typical X-ray patterns obtained for the SmA and E phases, respectively. In the SmA phase the peaks observed yielded only the layer spacing *d*. For the crystal-like E phase five to eight reflections were observed in different runs which enabled the determination of the orthorhombic unit cell parameters.

Figure 3 presents the layer spacing *d* versus temperature determined for all known smectogenic members of the *n*CB series. The data agree well with those determined for a few of substances by other authors (open symbols) [6–9, 12–14]. The inset shows a clear linear dependence of *d* on the alkyl chain length for longer members, with a jump between 10CB and two shorter members, 9CB and 8CB, for which the SmA phase is preceded by the nematic phase. The *d*(*n*) dependence for $n \geqslant 10$ is approximated by $d = 22.5 + 1.38n$, which can be compared with $d = 19.0$ +

Table. Chemical formulae, acronyms and phase sequences of the substances examined.

Chemical formula	Acronym	Phase sequence (°C)
	8CB	Cr 16.0 SmA_d 32.6 N 40.0 I
	9CB	Cr 39.2 SmA_d 47.0 N 49.4 I
	10CB	Cr 40.5 SmA_d 50.3 I
	11CB	Cr 51.2 SmA_d 56.9 I
	12CB	Cr 45.2 SmA_d 58.5 I
	14CB	Cr 55.1 SmA_d 62.4 I
	8BT	Cr 30.4 E 69.4 I
	6DBT	Cr 34.5 SmA_1 79.0 I
	10DBT	Cr 61.0 SmA_1 79.5 I

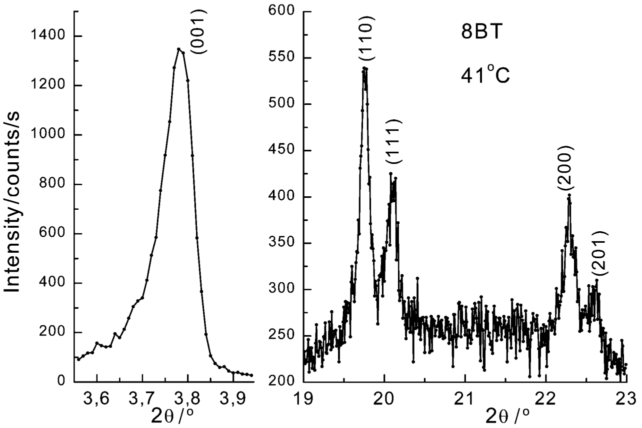


Figure 2. Typical X-ray patterns (intensity versus scattering angle) measured for 8BT in the E phase. The Miller indices correspond to the orthorhombic cell with lattice parameters presented in figure 4.

1.816n reported by Ocko [13] for $8 \leqslant n \leqslant 12$. One can also note different slopes of the $d(T)$ behaviour which will be analysed further in detail.

Figure 4 displays the temperature dependence of the orthorhombic unit cell parameters a, b and c, as well as the unit cell volume, the calculated density assuming $Z=2$ molecules in the unit cell (open points) and the experimental density data (full points) [20]. As is usually observed, the calculated density is larger than the measured density. It should be added, however, that the unit cell consisting of $Z=4$ molecules with a doubling of the lattice parameter c may be more probable. This statement arises from calculations performed with the aid of the Cerius 2 program[†]. We tried to build a crystal cell by minimization of the intermolecular interaction energy with adjusted unit cell parameters and selected $P2_12_12$ and $Pba2$ space groups, according to the suggestions given by Diele *et al.* [11]. A realistic density value and a compensation of the dipole moments within the cell were achieved for $Z=4$ and the $P2_12_12$ space group. Nevertheless, the assumption $Z=2$ does not further influence our conclusions.

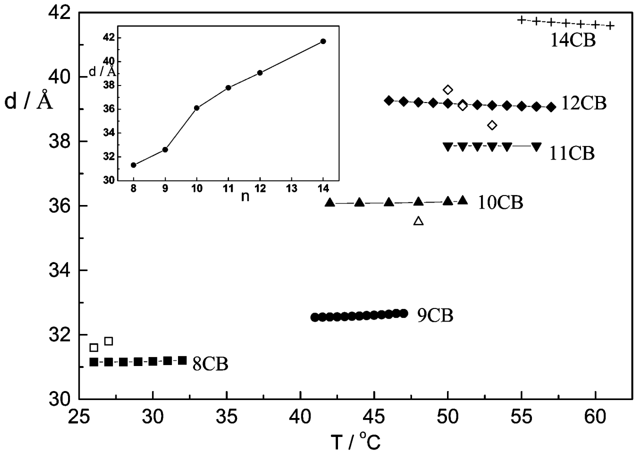


Figure 3. Layer spacing determined for the SmA phase of nCBs. Open points are from refs [7] (8CB, 10CB, 12CB), [9] (12CB), [13] (12CB) and [14] (8CB, 12CB). Inset shows the dependence of the layer spacing on the alkyl chain length.

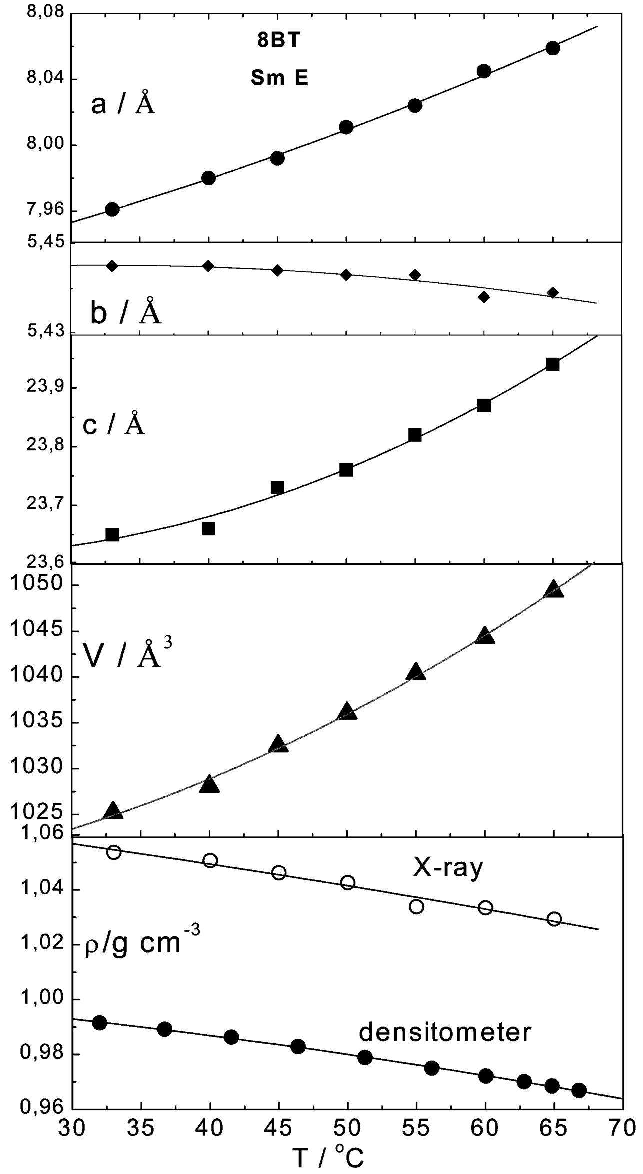


Figure 4. Temperature dependence of the unit cell parameters, the volume of the unit cell and the density measured by Schmalfuss *et al.* [20] and calculated from X-ray data for the E phase of 8BT.

[†] These calculations were provided by ACK CYFRONET AGH according to project No MNiI/SG/2800/UJ/029/2004.

4. Discussion

In order to analyse the dependence $d(T)$ for members of the nCB series the data from figure 3 are presented in figure 5 as $[d_{\mathrm{tr}}-d(T)]/d_{\mathrm{m}}$ vs. n plots, where d_{tr} and d_{m} were taken at the transition to a higher temperature phase (N or I) and in the middle of the smectic phase, respectively. It is evident that the slopes for the three shorter members differ from the slopes for the two longest members, with almost zero effect for 11CB. This may be explained as follows: for cyano-compounds the layer spacing d is incommensurate with the molecular length l calculated for the all-*trans*-configuration ($d \approx 1.4\ l$) [6–10]. With increasing temperature two opposing effects have to be considered: a reduction of the dipole–dipole association energy which may lead to an increase in d; and an increase of the number of kinks in the alkyl chain which may result in a reduction of the molecular length. The first effect seems to dominate for $n<11$, whereas the second is distinctly more effective for $n>11$; for the case of 11CB the effects are balanced. The broader molecular shape of 14CB results in relatively short relaxation times and a low activation barrier for molecular rotations around the short axis, as was established using the dielectric relaxation method [16] (these quantities are very close to those obtained for 8CB in the SmA phase).

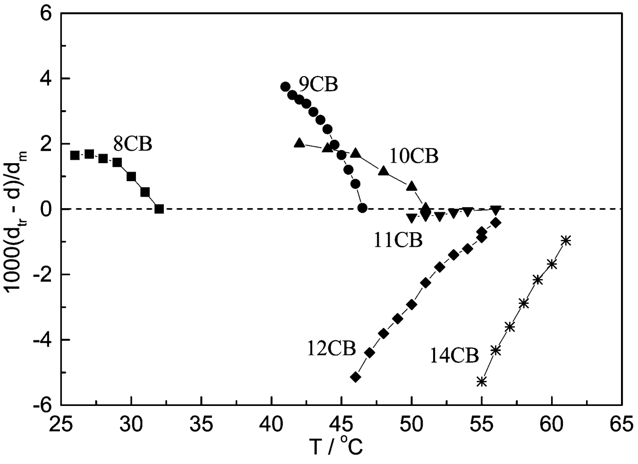


Figure 5. Plots of $(d_{\mathrm{tr}}-d)/d_{\mathrm{m}}$ versus temperature for the SmA phase of nCBs (d_{tr} corresponds to the SmA–N or SmA–I transitions, d_{m} is taken at the middle of the SmA phase).

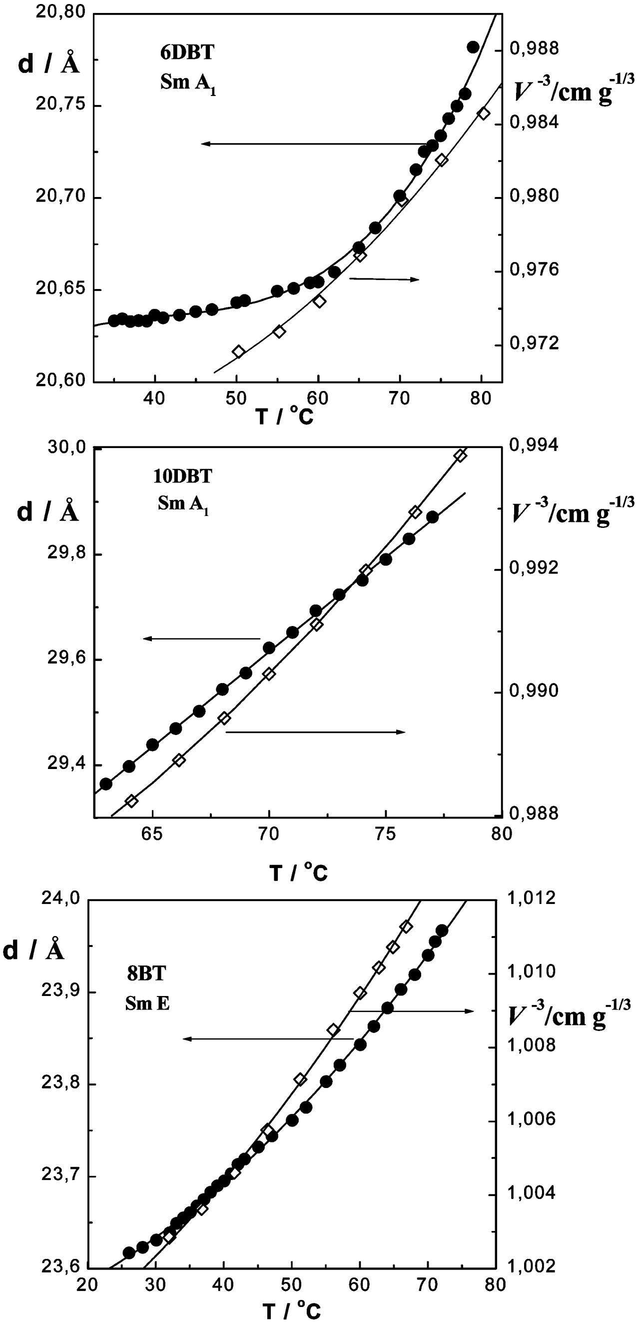


Figure 6. Temperature dependence of the layer spacing (left-hand scale) and the third root of the specific volume (right-hand scale) for 6DBT, 10DBT and 8BT in the smectic phase. Density data are from ref. [20].

It is widely known that LC phases show a considerable anisotropy in their physical properties. However, the anisotropy of the thermal expansivity seems to have received little attention. One possible way to study this is to compare the bulk expansivity characterized by the specific volume $V=1/\rho$ with the temperature dependence of the layer spacing $d(T)$ which characterizes the expansion in the preferred direction of a smectic phase. Figures 6 and 7 show the temperature dependence of the layer spacing d (filled symbols and left-hand scale) and, for comparison of the linear values, the third root of the specific volume V^{-3} (open symbols and right-hand scale) for smectics with monomolecular layers and for those nCBs for which the density data

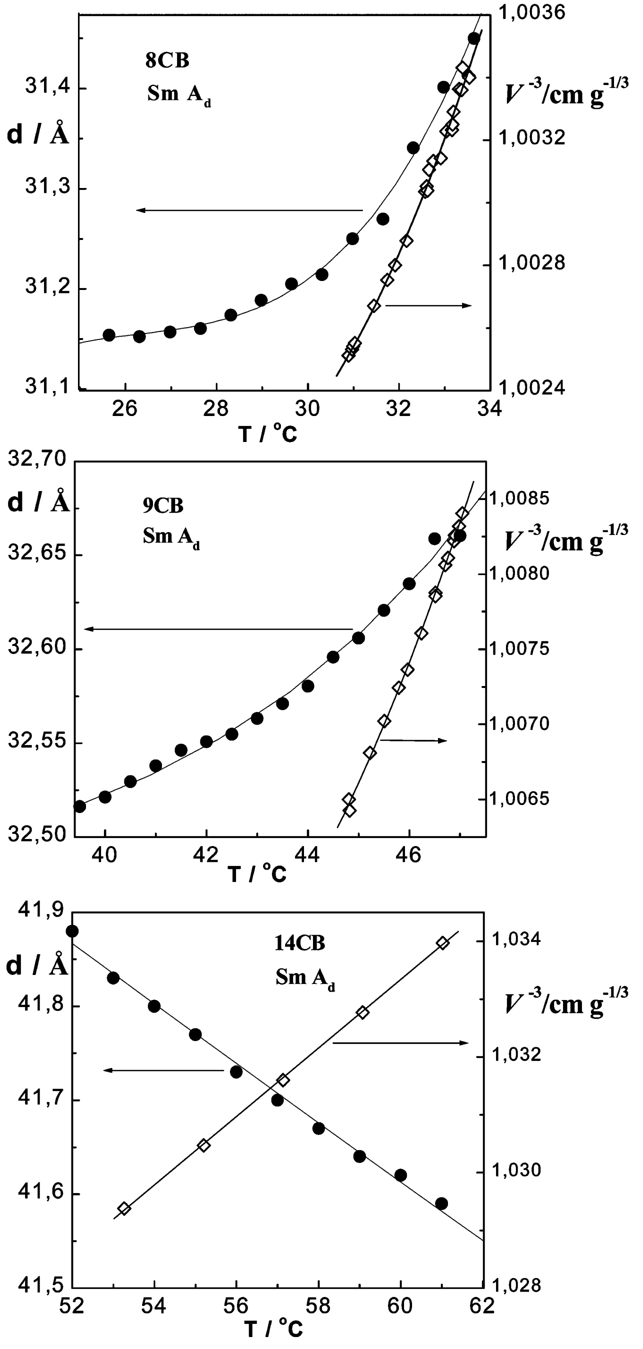


Figure 7. Temperature dependence of the layer spacing (left-hand scale) and the third root of the specific volume (right-hand scale) for three *n*CBs. Density data are from refs [28] (8CB, 9CB) and [20] (14CB).

are available. In the former cases (6DBT, 10DBT, 8BT) both parameters behave similarly with temperature, although the slope for the bulk seems to be a little steeper than that in the preferred direction. However, for the SmA$_d$ phase of *n*CBs one observes two important differences: (i) the steepness of $d(T)$ and $V^{-3}(T)$ differ markedly (especially at low temperatures); (ii) for 14CB (and probably for 12CB) the dependences have opposite slopes.

It seems justified to conclude that the thermal expansivity shows a small anisotropy which is more pronounced for the SmA$_d$ phase due to the competing effects mentioned already. This supports the suggestion given by Madhusudana *et al.* [21, 22] for explaining the decrease of the activation barrier hindering the molecular rotations around the short axes in the SmA phase in relation to the N phase. These authors claimed that this is due to anisotropic packing effects: the volume expansion causes an expansion mainly within the smectic layer, whereas the layer spacing hardly varies with temperature.

Looking at the X-ray data presented in figure 4 for the E phase of 8BT, one can see an agreement of the *c*-parameter with the length of the molecule l (=21.1 Å for the most extended conformation). This suggests an alignment of the molecular long axes with the *c*-axis of the unit cell. The value of the *b*-parameter, being independent of temperature, is typical for substances with aromatic cores [10, 11] and should correspond to the molecular diameter. If so, the lattice constant a reflects the intermolecular distance in the cell.

Both a and c increase with temperature, which results in an increasing unit cell volume, $V_{\mathrm{u.c.}}$, and decreasing density. Expansion of the *c*-parameter in the E phase of 8BT reveals why the layer structure can be destroyed by increasing pressure with an induction of the N phase [23, 24]; thus, the molecules can move along the preferred axis, which may lead to the destruction of the layer structure. It should be added that, in contrast to other smectic phases, the layer thickness of the B phase (hexatic or crystalline) does not change with temperature [17–19] and the high pressure studies of the substances with the B$_{\mathrm{cr}}$–I transition revealed no induction of the N phase [25].

$V_{\mathrm{u.c.}}$ changes with temperature within the E phase of 8BT almost linearly from 1025 to 1050 Å^3 (figure 4). Taking $Z=2$ molecules/cell, we can calculate the packing parameter $p=ZV_{\mathrm{mol}}/V_{\mathrm{u.c.}}$, where V_{mol} was calculated using the Cerius 2 program assuming all-*trans*-configuration ($V_{\mathrm{mol}}=331.81$ Å^3). Thus, we have $p=(0.647-0.632)$ within the phase. Similar values were obtained for other compounds in the E and B phases [10, 26], whereas in the crystalline phase of 6CB and 7CB the p values are greater (0.731 and 0.724, respectively). It seems that molecular rotations around the short axes are possible if the free volume in the unit cell is sufficiently large, say 35% of $V_{\mathrm{u.c.}}$. The pressure studies of the low frequency relaxation process in the E phase of 8BT yielded two important pieces of information about this motion [23, 24]. First, the activation volume, being the measure of difference of volumes occupied by a molecule in the activated and ground states, consists of 20% of the molar volume. Second, the isochoric activation energy is less than half the isobaric activation enthalpy for the flip–flop molecular motion in the E phase. The former indicates that a molecule can overcome the energy barrier due to large fluctuations of the intermolecular distances which can be reached if there is sufficient free room in the unit cell. The latter means that both temperature and volume effects determine the molecular rotations around the short axes to the same extent. Thus, information coming from the high pressure and X-ray studies gives a consistent picture of molecular rotations around the short axes in the LC phases.

5. Summary

The temperature dependence of the layer thickness d for nine smectogenic substances was determined with the aid of X-ray diffraction. Thermal expansion in the preferred direction was compared with thermal expansion in the bulk; a small anisotropy was established. It seems that $d(T)$ behaves similarly in the liquid-like and crystal-like phases, whilst it is sensitive to the mode of layer building (monomolecular or partly double-molecular layers). The $d(T)$ depends markedly upon the alkyl chain length in the nCB homologous series. The X-ray data enable the determination of the free volume in the cell and can elucidate the dynamic properties of molecules established in the dielectric relaxation studies under elevated pressure.

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