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X-ray studies on the crystalline E phase of the 4-*n*-alkyl-4′-isothiocyanatobiphenyl homologous series (*n*BT, *n*=2–10)

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X-ray diffraction measurements were carried out on nine members of the isothiocyanatobiphenyl homologous series (*n*BT) in their smectic E (SmE) phase, with the aim of estimating the layer thickness and deriving orthorhombic unit cell parameters for the SmE phase. The data obtained are discussed in relation to molecular reorientation motion around the short axis in that phase.

Keywords: X-ray diffraction; smectic E phase; packing parameter; molecular reorientation

1. Introduction

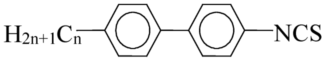
In calamitic liquid crystalline substances a variety of smectic phases can be divided into two classes: *liquid*-like phases with no arrangement of the molecular centres of mass in the layers (smectic A and C) and *crystal*-like phases where such arrangement within the layers (and probably also among the layers) is substantial (smectic B, E, K, G, etc.) (*1, 2*). The structure of the smectic E phase has been the subject of several X-ray diffraction studies (*1, 3–8*). They lead to the conclusion that the molecules form an orthorhombic array within the layers, and that the layers are correlated with each other with the correlation range between 300 and 1000 layers (*1*). In spite of the close-packed arrangement in all smectic phases the molecules perform rotational motions around their principal inertia axes (*9–13*). These motions, especially the reorientation around the short axis, require the better understanding of its relationship with the molecular arrangements in the layers. This issue has already been somewhat addressed for certain substances (*3–8*, *12, 13*).

The dynamics of the isothiocyanatobiphenyl homologous series (*n*BT) molecules in the SmE phase are being studied using dielectric spectroscopy measurements (*14–17*), under elevated pressure (*18, 19*) and the NMR technique (*20*). The flip-flop molecular jumps in the SmE phase occur with relatively long relaxation times and large activation barriers (10^{-2}–10^{-6} s and over 70 kJ mol^{-1}, respectively) (*7, 14*), whereas the spinning motions (including internal motions) observed by the NMR technique are very fast over low barriers (~10^{-11} s, 20 kJ mol^{-1}) (*20*).

In the present paper, the results of X-ray studies of nine members of one homologous series with a SmE phase are presented. This enables us to discuss the rotational freedom of molecules in relation to the ratio of 'the molecular lengths to the layer thickness' and to the packing parameter (i.e. the ratio of the volume of molecule itself to the unit cell volume per molecule). Temperature variations of several characteristics of the molecular arrangement in the layers are also presented.

2. Experimental

The substances studied belong to the 4-*n*-alkyl-4′-isothiocyanatobiphenyl homologous series (*n*BT, see Scheme 1).



Scheme 1. Structure of the 4-*n*-alkyl-4′-isothiocyanatobiphenyl homologous series (*n*BT).

For *n*=2–10, the *n*BT compounds exhibit only one liquid crystalline phase, the SmE phase. In the eleventh and twelfth members, a smectic A phase is additionally reported (*14, 15, 20, 21*), as shown in Figure 1. At elevated pressure, the SmE phase transforms to liquid-like phases (*21*).

The *n*BT substances were synthesised in the Institute of Chemistry, the Military University of Technology, Warsaw, Poland, along the preparative route described elsewhere (*14*). X-ray studies were carried out using an X'Pert PRO (PANalytical) diffractometer with the Cu K$_\alpha$ radiation (λ=1.540589 Å) and a graphite monochromator. The sample temperature was stabilised with an accuracy of ±0.1°C using a continuous flow cryostat

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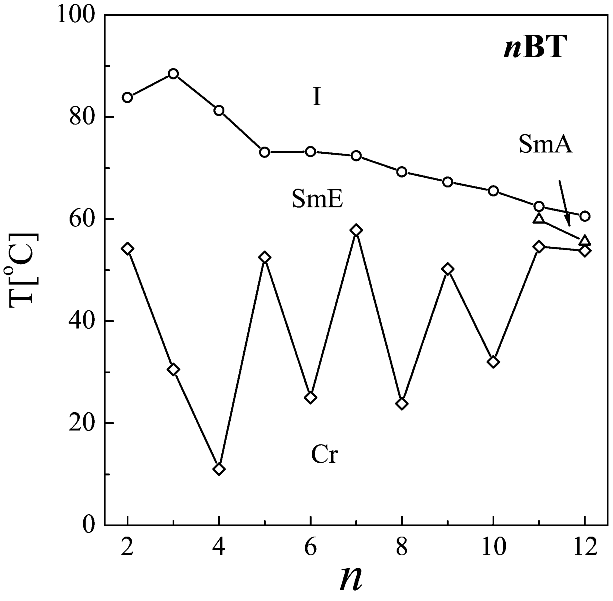

Figure 1. Transition temperatures of the *n*BT compounds.

supplied by Anton Paar Co. Details of sample preparation are given in a previous paper (*7*). The measurements were performed during cooling. After each cooling stage the sample was held for about 5 min in order to reach equilibrium. Due to the supercooling effect, the crystallisation temperatures were lower than those shown in Figure 1 by about 10°C.

3. Results and discussion

Sample diffraction patterns for the SmE phase of four *n*BTs are presented in Figure 2. Between five and eight Bragg reflections detected in different experimental runs could be indexed assuming the orthorhombic unit cell. For 6BT some extra unidentified reflections were detected, recurreing in different measurement runs. The X-ray data at selected temperatures within the SmE phase of all substances are summarized in Table 1. X-ray diffraction study of 11BT and 12BT in the SmE and SmA phases was a subject of the previous paper (*7*). Diffraction patterns recorded in the SmA phase were dominated by one strong (001) and one weak (002) reflections, corresponding to the layer and bilayer thicknesses, respectively.

Figure 3 shows the dependence on *n* of the layer thickness, *d*, and the molecular length, *L* (*d* was taken at the middle of the temperature range of the SmE phase). The molecular lengths, *L*, were calculated using the AM1 method, as implemented by the Mopac program (*22*). The *L* values were taken as a distance between two outermost atoms in the *all-trans* molecular conformation and are presented in Table 1. The X-ray data for 4BT and 8BT agree well with those determined by other authors (*5, 6*).

In the SmA phase of 11BT and 12BT the ratio d/L exceeds 1.24, indicating partially bi-layered arrangement of molecules, as in the cyanobiphenyl compounds (*23, 24*). The corresponding ratios observed for the SmE phase are close to 1.1 in all nBT compounds (compare data in Table 1).

For the SmE phase the orthorhombic unit cell parameters were determined and the unit cell volume, V_{uc}, was calculated. The *a* and *b* lattice parameters were temperature independent and the unit cell volume was driven by the temperature behaviour of the *c* lattice parameter. The values obtained for the *b* lattice parameter are typical for compounds with the aromatic cores (*3, 4, 6, 25*), and should correspond to the molecular diameter. The *a* lattice parameter represents the distance between the centres of mass of the neighbouring molecules in the cell. The X-ray density, $\rho=ZM/N_A V_{uc}$ ($Z=2$ is the number of molecules in the cell, M is the molar mass, N_A is the Avogadro's number), could therefore be calculated. Figure 4 presents the densities of eleven *n*BTs as a function of temperature. The ρ value for 8BT obtained in this way is by ca. 5% larger than that obtained from the dilatometric measurements (*6, 26, 27*).

The density data allowed us to calculate the thermal expansion coefficient, $\alpha=(\mathrm{d}v/\mathrm{d}T)/v$ ($v=1/\rho$ is the specific volume), with the results shown in Figure 5. The value $\alpha=6.8\times10^{-4}\,\mathrm{K}^{-1}$ obtained for 8BT from X-ray studies is somewhat smaller than $\alpha=8.4\times10^{-4}\,\mathrm{K}^{-1}$ obtained from pVT measurements (*27*).

As already mentioned in the introduction, dielectric studies revealed a molecular rotation motion around the short molecular axes (*14*), with the relaxation times and activation barriers strongly dependent on *n*, especially in the case of short molecules. Let us consider two factors that shed more light on the structural aspects of this motion. The ratio a/L changes from ca. 0.55 to 0.3 between 2BT and 12BT compounds, and it gives information about the range of fluctuations in the molecular positions within the layers, which create necessary space for the flip-flop rotation jumps of the molecules. Another interesting quantity is the so-called packing parameter defined as $p=ZV_m/V_{uc}$, where V_m is the molecule's volume calculated by the Cerius 2[‡] program assuming the all-trans conformation (the structure of the molecules had

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[‡] All computer simulations by Cerius 2 program were run on high-performance computers of The Academic Computer Centre CYFRONET AGH

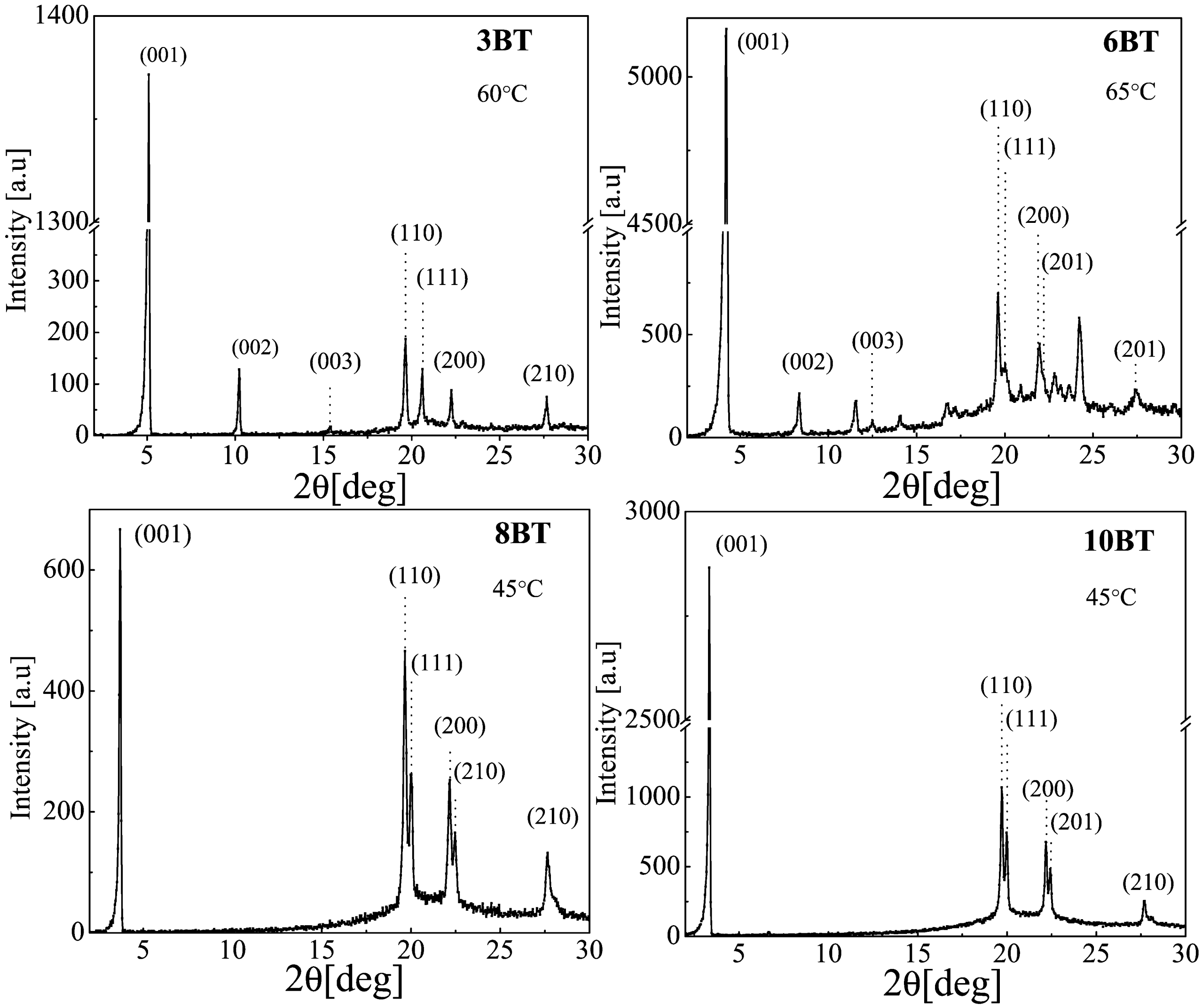

Figure 2. X-ray patterns recorded for the SmE phase of selected members of the *n*BT homologous series. Miller indices correspond to the orthorhombic unit cell.

been optimised by using AMBER force field). The dependence of the packing parameters *p* on chain length of *n*BTs is shown in Figure 6 together with the activation enthalpy determined from the dielectric relaxation studies (*14*). It can be seen that there is a clear correlation between both quantities.

The highest value of the packing parameter (ca. 0.63), was obtained for 2BT, whereas the maximum packing for a body centred hexagonal system of cylinders of equal diameter is 0.907. With increasing chain length, the *p* value systematically decreases down to ca. 0.60 for the longest molecules. (The present values of the packing parameter are smaller than those obtained in the SmE phase by Diele *et al.* for other compounds (*3, 13*); the discrepancy seems to be caused by different methods of the molecular volume calculation).

Since the *a* and *b* lattice parameters are practically the same for all substances (see Table 1) one can conclude that the increase of the *c* parameter with *n* is caused by both the increase of the alkyl chain length and the fluctuations of the centres of mass of molecules along the symmetry axes. The former seems to be responsible for the induction of the lower ordered liquid crystalline phases observed under elevated pressures for long *n*BTs (*21*). Of course, the loosely packed molecules create smaller barrier for the flip-flop rotational jumps.

4. Conclusion

From the X-ray studies in the SmE phase of nine members of the 4-*n*-alkyl-4′-isotiocyanatobiphenyl homologous series we can conclude the following.

Table 1. The X-ray data in the SmE phase of nBT compounds for n=2–12. The particular symbols mean: M−molar mass in [g/mol], d_{exp} and d_{cal} are the lattice spacing experimental and calculated, respectively, $V_{u.c.}$ is the volume of the unit cell, V_m is the volume of the molecule calculated as explained in the text, L is the molecular length calculated for the all-trans configuration, $p=2V_m/V_{u.c.}$ is the packing parameter.

Compound/ Temperature	Intensity/counts s^{-1}	d_{exp}/Å	d_{cal}/Å	Miller indices	Lattice constants/ Å	V_{uc}, V_m/Å^3
2BT	**9868**	**15.83**	**15.83**	**(001)**	$a=7.88\pm0.02$	
	431	7.97	7.92	(002)	$b=5.42\pm0.02$	$V_{uc}=676.09$
55°C	295	4.48	4.47	(110)	$c=15.83\pm0.05$	$V_m=212.34$
	548	3.98	3.98	(200)		$p=0.628$
M=239.343	156	3.93	3.83	(201)	$L=14.20$	
	255	3.2	3.2	(210)		
3BT	**1416**	**17.36**	**17.36**	**(001)**	$a=8.00\pm0.02$	
	129	8.65	8.68	(002)	$b=5.35\pm0.02$	$V_{uc}=740.86$
60°C	17	5.76	5.79	(003)	$c=17.31\pm0.05$	$V_m=229.32$
	178	4.52	4.45	(110)		$p=0.619$
M=253.37	92	4.32	4.31	(111)	$L=15.32$	
	68	4.00	4.00	(200)		
	74	3.22	3.15	(210)		
	4983	18.16	18.13	(001)		
4BT	**241**	**9.15**	**9.7**	**(002)**	$a=8.05\pm0.02$	
	68	6.11	6.04	(003)	$b=5.62\pm0.02$	$V_{uc}=799.65$
60°C	298	4.58	4.51	(110)	$c=18.16\pm0.05$	$V_m=249.30$
	1220	4.49	4.0	(111)		$p=0.623$
M=267.397	720	4.00	3.90	(200)	$L=16.59$	
	246	3.93	3.27	(201)		
	259	3.21	3.32	(210)		
5BT	**1696**	**19.7**	**19.70**	**(001)**	$a=8.00\pm0.02$	
	1310	4.52	4.59	(110)	$b=5.47\pm0.02$	$V_{uc}=862.07$
60°C	553	4.47	4.47	(111)	$c=19.70\pm0.05$	$V_m=266.18$
	890	4.00	4.00	(200)		$p=0.617$
M=281.424	298	3.23	3.29	(210)	$L=17.68$	
	2580	21.03	21.03	(001)		
6BT	**109**	**10.61**	**10.51**	**(002)**	$a=8.08\pm0.02$	
	45	7.05	7.01	(003)	$b=5.49\pm0.02$	$V_{uc}=932.9$
65°C	351	4.52	4.54	(110)	$c=21.03\pm0.05$	$V_m=277.64$
	177	4.43	4.43	(111)		$p=0.600$
M=295.451	220	4.04	4.04	(200)	$L=19.07$	
	154	3.89	3.97	(201)		
	279	3.67	3.77	(202)		
	115	3.24	3.25	(210)		
7BT	**6672**	**22.14**	**22.14**	**(001)**	$a=8.04\pm0.02$	
	671	4.51	4.51	(110)	$b=5.45\pm0.02$	$V_{uc}=969.69$
60°C	447	4.42	4.42	(111)	$c=22.13\pm0.05$	$V_m=296.50$
	381	4.02	4.02	(200)		$p=0.612$
M=309.478	263	3.96	3.95	(201)	$L=19.59$	
	132	3.23	3.23	(210)		
	165	3.21	3.20	(211)		
8BT	**669**	**23.81**	**23.81**	**(001)**	$a=8.02\pm0.02$	
	464	4.52	4.52	(110)	$b=5.47\pm0.02$	$V_{uc}=1044.63$
45°C	264	4.44	4.44	(111)	$c=23.81\pm0.05$	$V_m=315.43$
	258	4.01	4.01	(200)		$p=0.604$
M=323.505	163	3.96	3.95	(201)	$L=21.44$	
	132	3.22	3.23	(210)		
9BT	**3272**	**25.09**	**25.09**	**(001)**	$a=8.04\pm0.02$	
	1284	4.51	4.51	(110)	$b=5.45\pm0.02$	$V_{uc}=1099.38$
57°C	853	4.44	4.44	(111)	$c=25.09\pm0.05$	$V_m=332.15$
	952	4.02	4.02	(200)		$p=0.604$
M=337.532	548	3.97	3.97	(201)	$L=22.57$	
	557	3.23	2.24	(210)		
10BT	**2871**	**26.43**	**26.43**	**(001)**	$a=8.02\pm0.02$	
	1085	4.5	4.50	(110)	$b=5.44\pm0.02$	$V_{uc}=1153.1$
45°C	748	4.44	4.44	(111)	$c=26.43\pm0.05$	$V_m=347.48$
	674	4.01	4.01	(200)		$p=0.603$

Table 1. (*Continued*).

Compound/ Temperature	Intensity/counts s^{-1}	d_{exp}/Å	d_{cal}/Å	Miller indices	Lattice constants/ Å	V_{uc}, V_m/Å^3
M=351.559	471	3.96	3.97	(201)	L=23.97	
	253	3.22	3.23	(210)		
	442	28.38	28.38	(001)		
11BT	**82**	**14.20**	**14.19**	**(002)**	a=8.07±0.02	
	178	4.52	4.52	(110)	b=5.46±0.02	V_{uc}=1250.25
	161	4.46	4.47	(111)	c=28.38±0.05	V_m=365.81
58.4°C	114	4.04	4.03	(200)		p=0.585
	109	4.01	4.00	(201)	L=25.04	
M=365.586	105	3.23	3.25	(210)		
	2776	29.67	29.67	(001)		
12BT	**140**	**14.85**	**14.84**	**(002)**	a=8.05±0.02	
	535	4.51	4.51	(110)	b=5.44±0.02	V_{uc}=1299.31
50.0°C	374	4.46	4.46	(111)	c=29.67±0.05	V_m=378.59
	306	4.03	4.03	(200)		p=0.583
M=379.613	227	4.00	3.99	(201)	L=26.34	
	87	3.23	3.24	(210)		

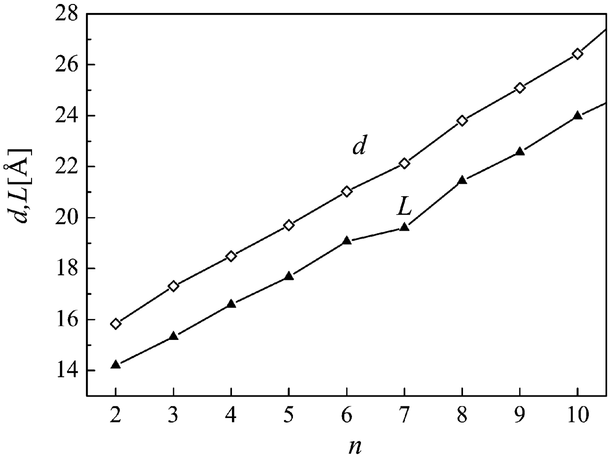

Figure 3. The values of the layer spacing, d, and the molecule length, L, versus n in the SmE phase of nBTs.

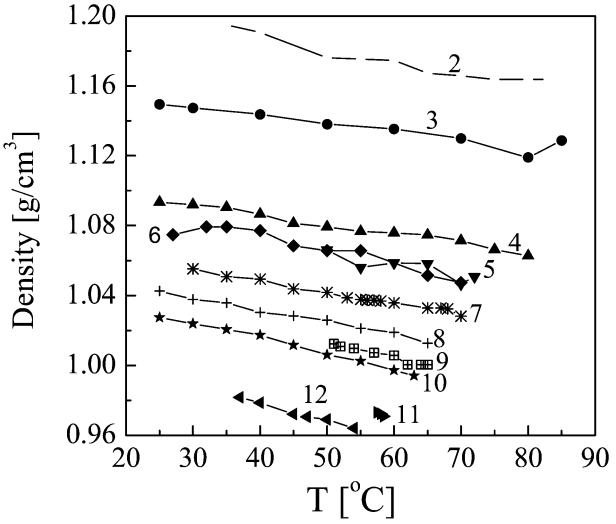

Figure 4. The temperature dependence of the density of the SmE phase of nBTs determined from the X-ray data.

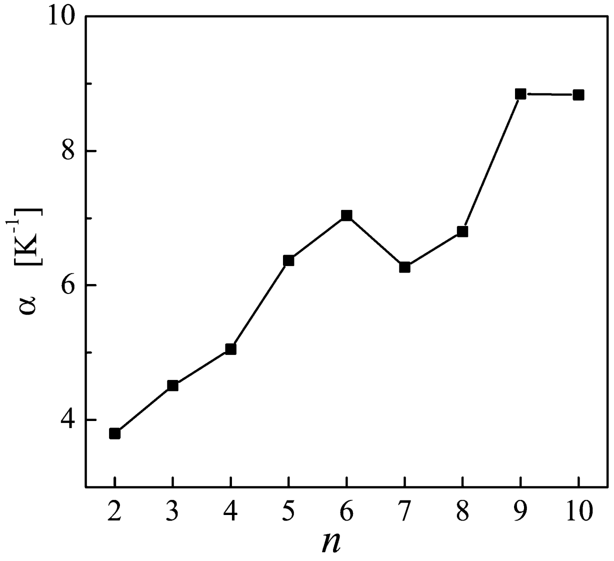

Figure 5. The volumetric thermal expansion coefficient, α, of nBTs.

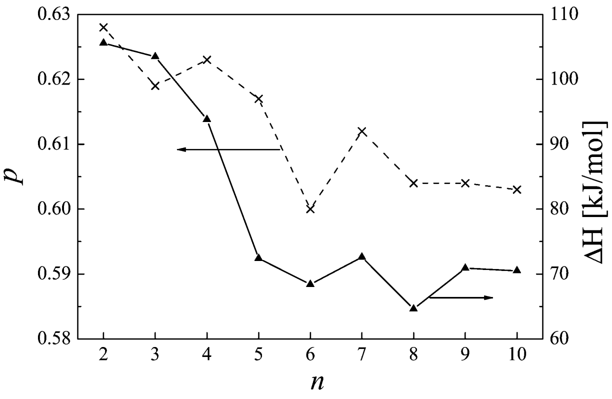

Figure 6. The dependence of the packing parameter, p, and the activation enthalpy, ΔH, for the flip-flop motions of molecules in the SmE phase of nBTs.

- The *a* and *b* lattice parameters are temperature independent and the unit cell volume is driven by the weak temperature changes of the *c* lattice parameter.
- The analyses of the layer spacing to molecular length ratio as well as that of the packing parameters indicate a strong rotation–translation coupling for the flip-flop rotation motion of molecules in the smectic E layers.
- A similarity was found between the behaviour of the packing parameter and the activation enthalpy for the flip-flop molecular motions as functions of the length of the molecules in the *n*BT series.

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