Thermodynamic Measurements on Selected Liquid Crystals at Normal and Elevated Pressures

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Densities have been determined for two 5-*n*-alkyl-2-(4-isothiocyanatophenyl)-1,3-dioxanes (6DBT, 10DBT), 4-*n*-tetradecyl-4'-cyanobiphenyl (14CB), 4-*n*-octyl-4'-thiocyanatobiphenyl (8BT) and two laterally aryl-branched mesogens 4-cyanobenzyl 5-(4-*n*-octyloxybenzoyloxy)-2-undecyloxybenzoate (4CNOUB), 3-cyanobenzyl 2,5-bis(4-*n*-octyloxybenzoyloxy)benzoate (3CNBOB). The densities have been measured in the isotropic, nematic (only 3CNBOB) and smectic phases with a vibrating tube densimeter. The densities decrease with increasing alkyl chain length within a homologous series. Furthermore the enthalpy changes accompanying the phase transitions have been determined by DSC.

Key words: Specific Volumes; Density; DSC; Liquid Crystals; Thermodynamics.

1. Introduction

Densities and specific volumes are important thermodynamic quantities. They are useful for a better understanding of the polymorphism in liquid crystals and the nature of their phase transitions [1]. Most of the liquid crystals described in the literature are derived from a rod-like shape, in particular all the compounds used for practical application in liquid crystal displays. Starting from calamitic mesogens, the molecular shape can be strongly influenced by terminal or lateral branches, which can also result in various physical properties.

The introduction of bulky groups in lateral position of calamitic molecules causes a strong change of the molecular shape [2]. So, the attachment of a phenyl ring, which can be substituted itself, to a lateral position of a three-ring mesogen by means of an odd-numbered spacer results in so-called laterally arylsubstituted mesogens [3]. The clearing temperatures of such wedge-shaped compounds are unexpectedly high, especially in comparison to laterally alkyl substituted mesogens. One reason is an intercalated packing of these molecules in smectic layers to reach a high packing density. Therefore we performed recently high-pressure DTA measurements in order to study the influence of pressure (which changes the density) on the phase transitions of 4 selected aryl-substituted mesogens [4].

Not only calamitic three-ring compounds but also two-ring mesogens can be laterally substituted by phenyl containing groups. Although small substituents, laterally attached to two-ring mesogens, reduce or prevent the liquid crystalline properties, stable meso-phases were reported for laterally 4-nitrobenzyloxycarbonyl substituted phenyl-benzoates [5]. In the homologous series of these compounds the clearing points clearly increase with growing length of the terminal chains. Due to the unexpected liquid crystalline properties of mesogens of such a nonconventional constitution, further investigations could be helpful to understand the behaviour of these compounds. First, the nitro group was substituted by a cyano one, because nitro compounds are not so stable for long-time measurements. For example, 4-cyanobenzyl 5-(4-*n*-octyloxy-benzoyloxy)-2-undecyloxybenzoate (4CNOUB) was synthesized as described for the unsaturated derivatives to compare the thermodynamic behaviour at elevated pressures with the properties of the corresponding side group polymer [6].

The following representatives have been selected for the density measurements: Two 5-*n*-alkyl-2-(4-isothiocyanatophenyl)-1,3-dioxanes (6DBT, 10DBT),

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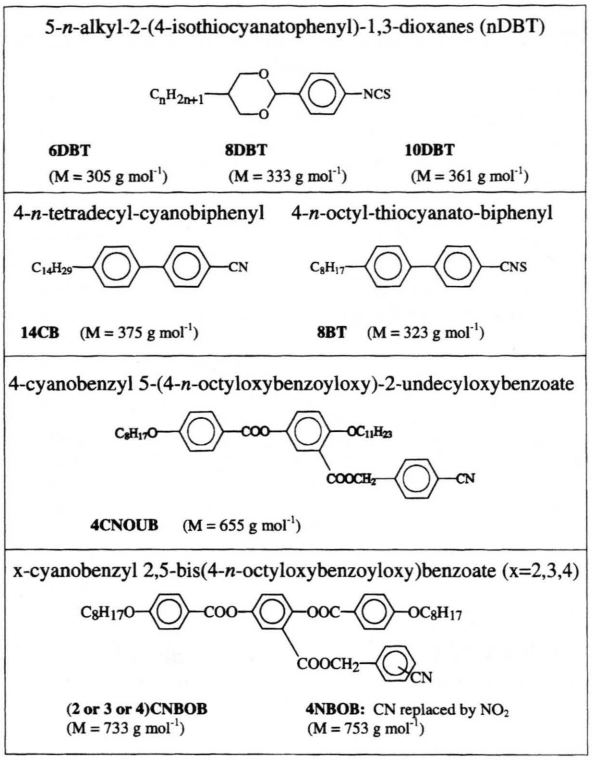

Fig. 1. Chemical structures and molar masses of the samples studied.

4-*n*-tetradecyl-4'-cyanobiphenyl (14CB), 4-*n*-octyl-4'-thiocyanatobiphenyl (8BT), two laterally aryl-branched liquid crystals 4-cyanobenzyl 5-(4-*n*-octyloxybenzoyloxy)-2-undecyloxy-benzoate (4CNOUB), 3-cyanobenzyl 2,5-bis(4-*n*-octyloxybenzoyloxy)benzoate (3CNBOB).

Moreover we employed DSC measurements on the mentioned liquid crystals and additionally on 8DBT, 2CNBOB, 4CNBOB, and 4-nitrobenzyl 2,5-bis(4-*n*-octyloxybenzoyloxy)benzoate (4NBOB) in order to determine the enthalpy changes accompanying the phase transitions. The chemical structures of the studied samples are shown in Figure 1.

2. Experimental

The laterally aryl-branched liquid crystals have been synthesized by Weissflog et al. [5, 6], the other samples were obtained from R. Dąbrowski, Institute of Chemistry, Military Academy of Technology (Warsaw, Poland). The densities at 1 atm were measured with a vibrating tube densimeter Anton Paar DMA 60. The densimeter was calibrated with octane, nonane,

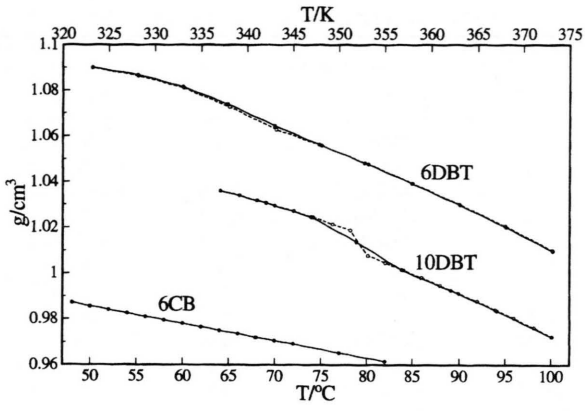

Fig. 2. Densities of 6DBT and 10DBT for increasing (•) and decreasing (o) temperature.

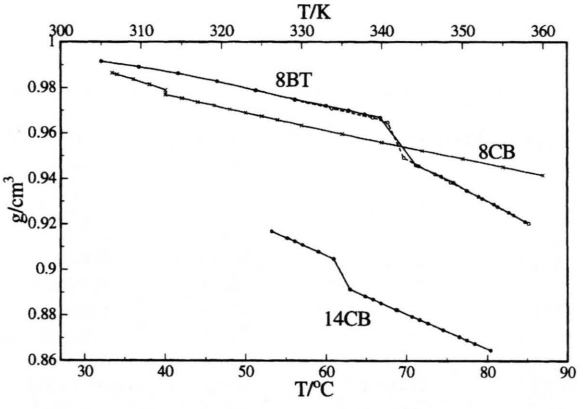

Fig. 3. Densities of 14CB and 8BT.

and decane. The temperature can be varied from room temperature to 150 °C and is measured by a Pt-100 with an accuracy of 0.05 K. The apparatus has recently been used for density measurements on liquid crystal mixtures [7]. DSC measurements have been carried out with commercially available Perkin-Elmer devices in Halle and Bochum [8].

3. Results

3.1. Density Measurements

6DBT and 10DBT

Figure 2 presents the density as a function of increasing and decreasing temperature. Detailed data are listed in Table 1. The melting point of 10DBT is considerably higher than for 6DBT, whereas the clearing points are comparable. The latter is seen as a small

Table 1. Densities at increasing and decreasing temperature for 6DBT and 10DBT.

6DBT				10DBT			
T/°C,↑	ρ/g·cm^{-3}	T/°C,↓	ρ/g·cm^{-3}	T/°C,↑	ρ/g·cm^{-3}	T/°C,↓	ρ/g·cm^{-3}
50.21	1.090070	100.17	1.009958	64.11	1.036130	100.14	0.972375
55.15	1.086866	94.99	1.020543	69.06	1.030753	98.14	0.976241
60.00	1.081500	90.06	1.030122	73.96	1.024549	95.93	0.980393
64.85	1.073991	85.01	1.039381	78.88	1.013658	93.91	0.984116
70.00	1.064493	80.18	1.047668	83.82	1.001496	91.93	0.987708
74.79	1.056224	75.08	1.055813	89.12	0.992466	89.95	0.991221
79.79	1.048127	70.18	1.062873	94.08	0.983587	87.97	0.994678
84.93	1.039301	65.07	1.072692	100.07	0.972335	85.96	0.998091
90.08	1.029839	60.10	1.080955			84.00	1.001359
95.10	1.020034	55.16	1.086434			82.06	1.004535
100.18	1.009629	50.21	1.090033			80.13	1.007654
						78.21	1.018637
						76.29	1.021470
						74.17	1.024414
						72.05	1.027139
						70.02	1.029638
						68.09	1.031891
						66.16	1.034028
						64.11	1.036134

Table 2. Densities at increasing and decreasing temperature for 14CB and 8BT.

14CB				8BT			
T/°C,↑	ρ/g·cm^{-3}	T/°C,↓	ρ/g·cm^{-3}	T/°C,↑	ρ/g·cm^{-3}	T/°C,↓	ρ/g·cm^{-3}
53.23	0.916843	80.39	0.864636	31.98	0.991498	85.19	0.920404
56.11	0.912433	78.44	0.867606	36.71	0.989166	83.26	0.924016
59.01	0.907893	76.50	0.870565	41.54	0.986298	81.32	0.927623
60.97	0.904773	74.56	0.873511	46.39	0.982870	79.39	0.931208
62.92	0.891474	72.64	0.876461	51.26	0.978900	77.46	0.934798
65.84	0.886924	70.72	0.879395	56.11	0.974961	75.52	0.938397
68.74	0.882459	68.79	0.882340	60.04	0.972132	73.59	0.941978
71.66	0.878003	66.85	0.885325	62.81	0.970118	71.65	0.945589
74.56	0.873585	64.91	0.888329	64.84	0.968543	69.72	0.949175
77.46	0.869173	62.96	0.891342	66.80	0.966921	67.77	0.964819
80.38	0.864731	61.01	0.904648	71.28	0.945978	65.83	0.966894
		59.05	0.907815	74.34	0.941080	60.74	0.970989
		57.11	0.910896	75.86	0.938195	56.09	0.974745
		55.18	0.913900	77.53	0.934738	51.27	0.978957
		53.24	0.916831	78.92	0.932153	46.39	0.982851
				80.86	0.928697	41.55	0.986267
				82.67	0.925240	36.73	0.989148
				84.75	0.921213	31.99	0.991605

step, although less pronounced for 6DBT. The density of 10DBT is distinctly lower than that of 6DBT. Also for other rod-like liquid crystals it has been found that increasing alkyl chain length causes a lowering of the density [9, 10]. Still lower is the density of 6CB [10] which has been included in Fig. 2 for comparison. It is surprising that the molecular structure of the isothiocyanatophenyldioxanes yields a so much higher density than the cyanobiphenyls. Because of its broad smectic-A phase region 6DBT is a suitable candidate for dielectric measurements [11].

14CB and 8BT

8BT has a smectic E phase and correspondingly the density jump to the isotropic phase is more strongly pronounced than for the other liquid crystals exhibiting a smectic A phase, see Fig. 3. The density of 8BT is comparable with 8CB [10] which has the same

Table 3. Densities at increasing and decreasing temperature for 3CNBOB and 4CNOUB.

3CNBOB				4CNOUB			
T/°C,↑	ρ/g·cm^{-3}	T/°C,↓	ρ/g·cm^{-3}	T/°C,↑	ρ/g·cm^{-3}	T/°C,↓	ρ/g·cm^{-3}
89.97	1.090676	150.02	1.065168	59.97	1.056566	100.02	1.024226
99.99	1.084660	145.03	1.066111	64.93	1.053202	97.92	1.025165
110.02	1.077805	140.05	1.067246	69.97	1.049709	95.92	1.026144
120.07	1.073578	134.94	1.068597	74.85	1.045715	93.95	1.027142
130.01	1.070096	129.93	1.070103	79.94	1.034968	91.95	1.028151
139.94	1.067290	125.00	1.071787	84.76	1.031931	89.99	1.029188
149.96	1.065144	119.99	1.073624	90.23	1.028820	87.93	1.030319
		114.97	1.075642	95.20	1.026236	85.85	1.031474
		110.06	1.077801	100.20	1.023802	83.96	1.032562
		105.02	1.080249			82.07	1.033727
		100.02	1.084643			79.99	1.035073
		95.01	1.087761			75.12	1.041397
		89.98	1.090672			69.96	1.049774
						65.13	1.053093
						59.97	1.056568

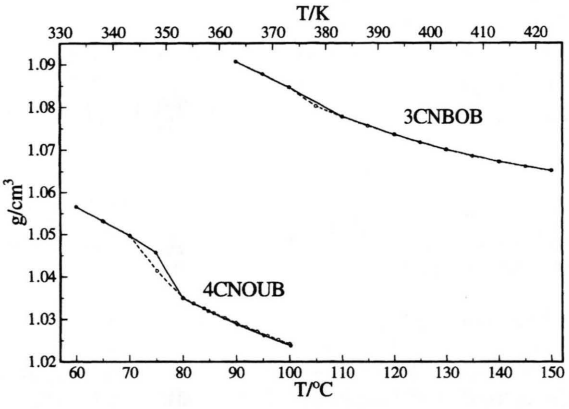

Fig. 4. Densities of 3CNBOB and 4CBOUB.

molecular core. Again we find distinctly smaller densities for 14CB with the longer chain length. Detailed density data are gathered in Table 2.

3CNBOB and 4CNOUB

These two laterally substituted mesogens were subjected to extended high-pressure studies, both with DTA and pVT measurements: 3CNBOB [4, 12], 4CNOUB [13]. The densities are plotted in Fig. 4 and listed in Table 3. The step at the nematic – isotropic transition for 3CNBOB is smaller than that at the smectic-A – isotropic transition for 4CNOUB. The densities of the four-ring mesogen are distinctly higher than for the three-ring mesogen. This is somewhat surprising because the bulky 3CNBOB with a CN-group in sterically unfavorable position was expected to have some "free space" due to unusual mixing properties [14].

Table 4. Thermodynamic properties of the investigated liquid crystals.

Sample	Transition	T/K	ΔH_m/ kJ·mol^{-1}	ΔS_m/ J·mol^{-1}·K^{-1}
6DBT	Cr → SmA	310.6	25.6	82.4
		307.7 [16]		
	SmA → Is	354.0	3.80	10.7
		352.2 [16]		
8DBT	Cr → SmA	322.8	28.4	88.0
		320.2 [16]	28.7 [16]	
	SmA → Is	356.1	3.82	10.7
		354.7 [16]	4.0 [16]	
10DBT	Cr2 → Cr1	317.7	7.37	23.2
		325.7 [16]	7.2 [16]	
	Cr1 → SmA	336.1	29.4	87.5
		334.2 [16]	30.0 [16]	
	SmA → Is	354.8	3.79	10.7
		352.7 [16]	3.8 [16]	
14CB	Cr → SmA	331.4	41.4	125.0
		327.2 [16]		
	SmA → Is	338.0	5.40	16.0
		335.2 [16]		
8BT	Cr → SmE	301.5	16.4	54.5
		295.7 [16]	18.3 [16]	61.9
	SmE → Is	345	10.3	30.2
		340.7 [16]	10.3 [16]	

3.2. DSC Measurements

Enthalpy changes determined from DSC measurements (without reference: in Halle), together with other literature data are compiled in Table 4. The Table contains also transition temperatures derived

Table 4 (continued).

Sample	Transition	T/K	ΔH_m/ kJ·mol^{-1}	ΔS_m/ J·mol^{-1}·K^{-1}
2CNBOB	Cr2 → Cr1	355.7 [8]	53.3 [8]	149.8
		358.6 [4]	56 [15]	
	Cr1 → Is	365.0 [8]	4.0 [8]	10.9
		366.9 [4]		
3CNBOB	Cr → N	363.4 [8]	42.4 [8]	116.7
		364.5 [4]		
	N → Is	374.1 [8]	3.1 [8]	8.3
		374.1 [4]		
4CNBOB	Cr → SmA	360.0 [8]	25.6 [8]	71.2
		364.3 [4]		
	SmA → Is	423.0 [8]	8.1 [8]	19.1
		422.4 [4]		
4NBOB	Cr → SmA	366.9 [8]	29.2 [8]	79.5
		368.5 [4]		
	SmA → Is	436.1 [8]	9.6 [8]	21.9
		435.5 [4]		
4CNOUB	Cr → SmA	334.2	33.7	101.7
		331.4 [13]	~34 [13]	
	SmA → Is	349.2	8.16	23.4
		348.3 [13]	~ 8 [13]	

from DTA and pVT measurements. In general DSC runs are carried out at relatively high heating rates (5 - 10 K min^{-1}) yielding higher transition temperatures than obtained with DTA or pVT measurements [4, 12, 13, 17].

Apart from 8BT, 2CNBOB and 3CNBOB all liquid crystals exhibit a smectic A phase. For the rod-like compounds 6DBT...14CB in Table 4 ΔH_{SmA-Is} amounts to ≈ 4 kJ mol^{-1}, whereas for the aryl-branched samples (which have roughly the double molar mass) $\Delta H_{SmA-Is} \approx 8$ kJ mol^{-1}. That is, the transition enthalpy smectic A – isotropic (in J/g) does practically not depend on the molecular shape, despite significantly different molecular cores.

Table 5. Volume changes for the laterally aryl-branched liquid crystals.

Sample	Transition	T/K	$(\partial T/\partial p)$/ K·MPa^{-1}	ΔV_m/ cm^3·mol^{-1}
2CNBOB	Cr2 → Cr1	355.7	0.135 [4]	20.2 [8]
	Cr1 → Is	365	0.279 [4]	3.1 [8]
3CNBOB	Cr → N	363.4	0.296 [4]	34.5 [8]
	N → Is	374.1	0.275 [4]	2.3 [8]
4CNBOB	Cr → SmA	360	0.304 [4]	21.6 [8]
	SmA → Is	423	0.241 [4]	4.6 [8]
4NBOB	Cr → SmA	366.9	0.364 [4]	28.9 [8]
	SmA → Is	436.1	0.181 [4]	4.0 [8]
4CNOUB	Cr → SmA	331.4	0.313 [13]	31.8 [13]
	SmA → Is	348.3	0.192 [13]	4.5 [13]

Masberg [8] calculated the volume changes accompanying the phase transitions for four laterally aryl-branched compounds using the Clausius-Clapeyron equation and the slopes from [4], see Table 5. The Table contains also results for 4CNOUB [13]. For the last three aryl-branched compounds $\Delta V_{SmA-Is} \approx$ 4.5 cm^3 · mol^{-1} or ≈ 0.006 cm^3 · g^{-1}. In a recent high-pressure DTA study of 6DBT, 8DBT and 10DBT somewhat larger volume changes (in cm^3 · g^{-1}) have been found [17].

Acknowledgement

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[1] W. Wedler, in D. Demus, J. Goodby, G. W. Gray, H. W. Spiess, V. Vill, Handbook of Liquid Crystals, Vol. 1, Wiley-VCH, Weinheim 1998, p. 334.
[2] W. Weissflog, in D. Demus, J. Goodby, G. W. Gray, H. W. Spiess, V. Vill, Handbook of Liquid Crystals, Vol. 2b, Wiley-VCH, Weinheim 1998, p. 835.
[3] W. Weissflog and D. Demus, Liq. Cryst. **3**, 275 (1988).
[4] C. Ernst, doctoral thesis, Ruhr-University of Bochum 1997; C. Ernst, G. M. Schneider, A. Würflinger, and W. Weissflog, Ber. Bunsenges. Phys. Chem. **102**, 1870 (1998).
[5] A. Jacobi and W. Weissflog, Liq. Cryst. **22**, 107 (1997).
[6] A. Jacobi and W. Weissflog, Mol. Cryst. Liq. Cryst. **304**, 15 (1997).
[7] S. Ernst, doctoral thesis, University of Halle-Wittenberg 1995.
[8] S. Masberg, doctoral thesis, Ruhr-University of Bochum 1999.
[9] M. Sandmann, F. Hamann, and A. Würflinger, Z. Naturforsch. **54a**, 281 (1999); **52a**, 739 (1997).
[10] M. Sandmann and A. Würflinger, Z. Naturforsch. **53a**, 787, 233 (1998).
[11] S. Urban and A. Würflinger, Z. Naturforsch. **54a**, 455 (1999).
[12] A. Würflinger, M. Sandmann, and W. Weissflog, Z. Naturforsch. **55a**, 823 (2000).
[13] A. Würflinger and W. Weissflog, Z. Naturforsch. **55a**, 936 (2000).
[14] S. Diele, A. Mädicke, K. Knauft, J. Neutzler, W. Weissflog, and D. Demus, Liq. Crystr. **10**, 47 (1991); S. Haddawi, S. Diele, H. Kresse, G. Pelzl, and W. Weissflog, Cryst. Res. Technol. **29**, 745 (1994).
[15] S. Diele, W. Weissflog, G. Pelzl, H. Manke, and D. Demus, Liq. Cryst. **1**, 101 (1986).
[16] K. Czuprynski, thesis, Military University of Technology, Warsaw 1987.
[17] A. Würflinger and S. Urban, submitted.