Pressure-Temperature Phase Diagrams for four 4,4'-Dialkylbiphenyl Compounds

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The high pressure phase behaviour of four 4,4'-dialkylbiphenyl compounds (**Cm-Cn**, m = 5, 6,7, n = 6, 7) has been studied with differential thermal analysis. The pressure dependence of the phase transitions has been determined up to 200 MPa. In one substance a pressure limited and in another a pressure induced phase was observed. Volume changes accompanying the transitions to the isotropic phase were calculated using the Clausius-Clapeyron equation and the enthalpy changes from DSC measurements at 1 atm. They are compared with the data for other two-ring compounds.

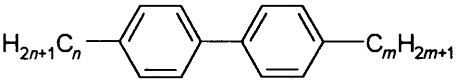
Key words: Liquid Crystals; Smectics; DTA; Phase Diagram; High Pressure.

Introduction

Liquid crystals (LC) often exhibit a complex polymorphism which can be modified by changing the molecular length in a given homologous series, by applying the hydrostatic pressure, or by varying the concentration in multicomponent systems. For the present purpose the two first factors are of a special interest. Applying the differential thermal analysis (DTA) method under pressure, we have discovered recently an induced nematic phase in some longer smectogen members of three two-ring homologous series: in two *n*-alkyl-cyanobiphenyls (10CB and 11CB) [1], in *n'*-octyl-*n*-isothiocyanatobiphenyl (8BT) [2], and in 5-decyl-2-(4'-isothiocyanatophenyl)-1,3-dioxane (10DBT) [3]. These substances possess non-symmetrical molecules with a strongly polar group -CN or -NCS at the *para*-position of the benzene ring. On the other hand, it was found for 2,3-dicyano-4-hexyloxyphenyl *trans*-4-butylcyclohexane-1-carboxylate (CNCN), having two -CN groups attached to the benzene ring at the lateral positions, that the SmA phase disappears at relatively low pressure [4]. Therefore we decided to check how the pressure influences the phase behaviour of 4,4'-dialkylbiphenyls, the two-ring homologous series consisting of non-polar and symmetric molecules. The substances belonging to this homologous series (abbreviated as **Cm-Cn**) exhibit a rich smectic polymorphism at atmospheric pressure [5 - 7] with the orthorhombic $\mathrm{SmB_{cr}}$ and several SmE phases identified by X-rays and polarising microscopy. It seemed to be interesting to investigate whether the same phase behaviour would persist with increasing pressure. We have performed DTA studies of four compounds (**C5-C6**, **C6-C6**, **C6-C7** and **C7-C7**) up to 200 MPa. The results are presented in the form of p-T phase diagrams and DTA traces.

Experimental

The studied substances have the chemical structure



Two symmetrically substituted compounds, m = n = 6 (**C6-C6**) and m = n = 7 (**C7-C7**), and two unsymmetrical substituted compounds, $m = 5, n = 6$ (**C5-C6**), and $m = 6, n = 7$ (**C6-C7**), were studied. They were synthesised as described in [5].

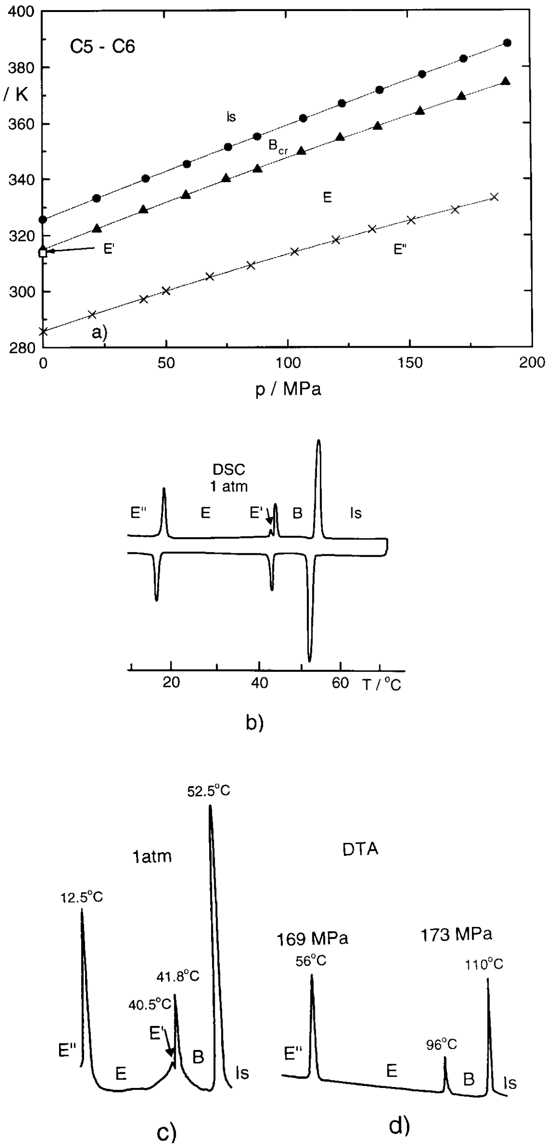


Fig. 1. $T(p)$ phase diagram (a) and characteristic DSC (b) and DTA (c, d) traces for **C5-C6**. Crystallisation of the sample could not be achieved.

Two high pressure DTA apparatuses have been used which were constructed for measurements at low (–100 °C ÷ +90 °C) [8] and high (0 °C ÷ 200 °C) [9] temperatures. DTA peaks were generated at heating rates of 1 or 2 K/min and registered with a two-channel recorder. The samples were cooled down to ca. –30 °C and annealed for several hours. However, it was found that when the annealing temperature was ca. 0 °C the sequences of the transitions were the same.

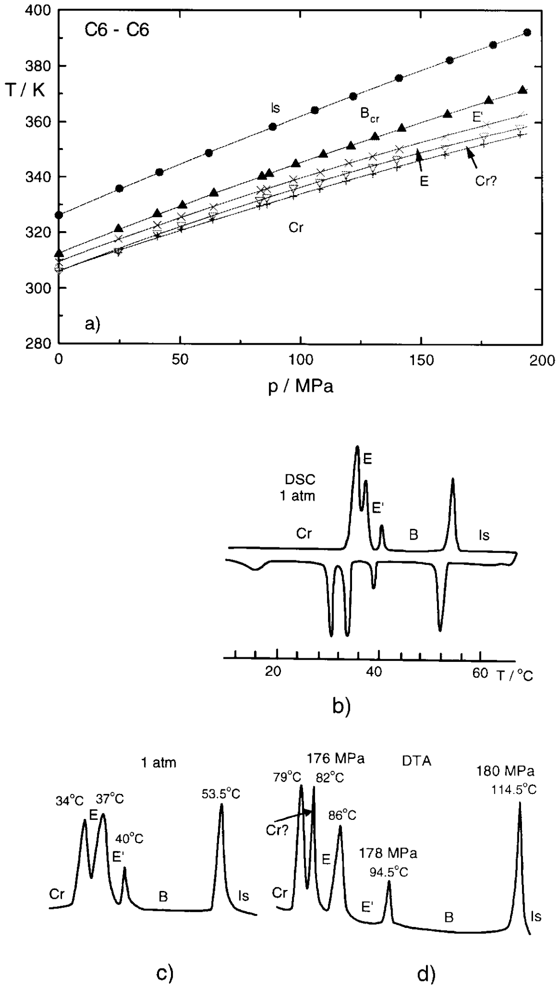


Fig. 2. $T(p)$ phase diagram (a) and characteristic DSC (b) and DTA (c, d) traces for **C6-C6**. Crystal phase was obtained after annealing of the sample at ~0 °C for 1 hour.

Results and Discussion

Figures 1 - 4 present the p-T phase diagrams established for the four **Cn-Cm** substances together with characteristic DTA traces, that are compared with the DSC traces measured at 1 atm [7]. The smectic phases B_{cr}, E, E' and E" are named according to [5 - 7]. The pressure dependence of the transition temperatures has been smoothed by polynomials. The fitting parameters obtained are gathered in Table 1.

For **C5-C6** at 1 atm we observed the same phase sequence as in the DSC measurements in the heating run ([7], Fig. 1). It has been found that increase of pressure to 20 MPa cancels the transition SmE - SmE'.

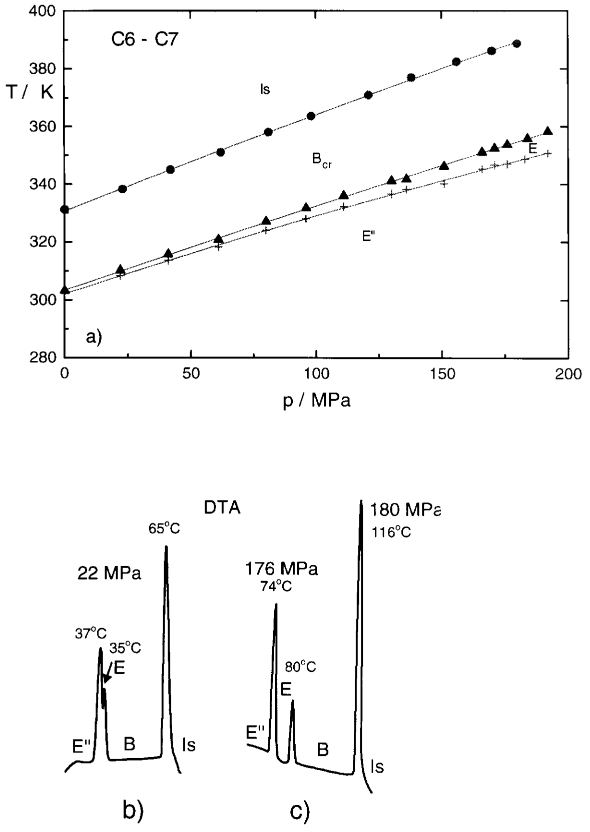


Fig. 3. $T(p)$ phase diagram (a) and characteristic DTA (b, c) traces for **C6-C7**. Crystallisation of the sample could not be achieved.

However, in the case of **C6-C6** above ca. 25 MPa a new phase transition appeared (Fig. 2) which was not detected at 1 atm. Because the splitting observed concerns the melting line, it is not clear whether the new phase is an additional crystalline or liquid crystalline phase. (It should be added that only for this substance the solidification of the sample occurred without any trouble). In the other two substances the transitions observed at 1 atm were detected up to 200 MPa.

With each substance the most pronounced peak has been recorded for the transition from the SmB_{cr} phase to the isotropic (Is) phase. This means that the isotropisation process is accompanied by a large latent heat. A similar effect was observed in the case of the transition from the SmE to Is phase for some isothiocyanato-biphenyls [2, 10, 11]. This is in contrast to the thermal effects accompanying the transitions between the liquid-like phases (N or SmA) and Is phase which are much smaller; compare Table 2, where the thermodynamic parameters characterising the isotropisation of different two-ring substances are collected. The transition enthalpy, ΔH_{cl}, and the entropy change $\Delta S_{cl} = \Delta H_{cl}/T_{cl}$ were obtained from the DSC studies at 1 atm. The volume change ΔV_{cl} at the clearing point (at 1 atm) may be calculated using the measured slopes of the clearing lines, dT/dp, and the Clausius-Clapeyron equation, $dp/dT = \Delta H_{cl}/(T_{cl}\Delta V_{cl})$. One can see that independently of the molecular structure all thermodynamic parameters differ considerably when they concern the

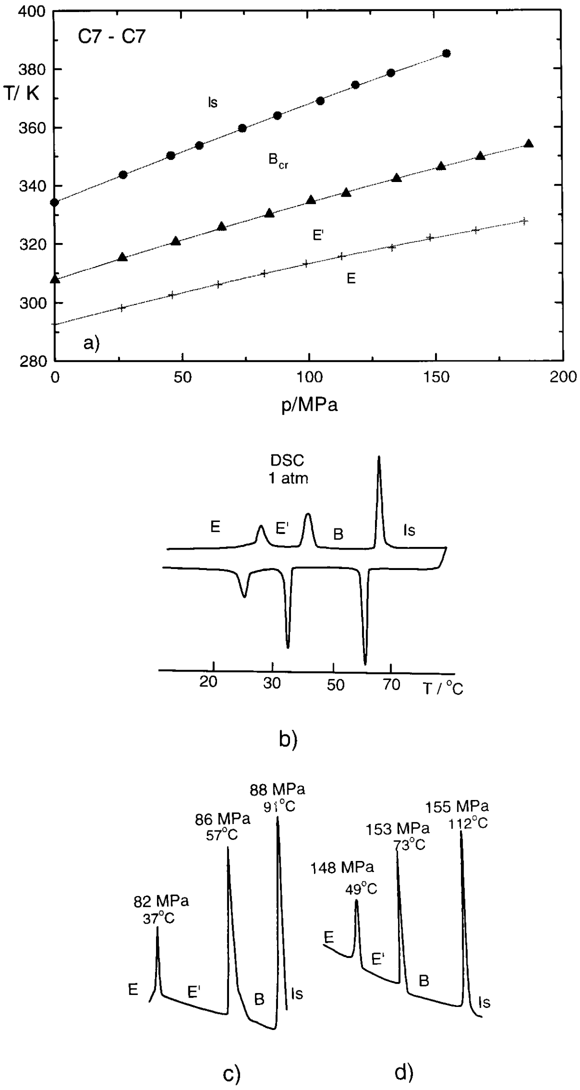


Fig. 4. $T(p)$ phase diagram (a) and characteristic DSC (b) and DTA (c, d) traces for **C7-C7**. Crystallisation of the sample could not be achieved.

Table 1. Transition temperatures, T [K] = $a+b\cdot(p\,[\mathrm{MPa}])+c\cdot(p\,[\mathrm{MPa}])^2$, for the **Cm-Cn** compounds studied with DTA.

Substance	Transition	a	b	$10^4\cdot c$
C5-C6	E'' - E	285.7	0.298	–2.31
	E - E'	313.7		
	E - B_{cr}	314.9	0.342	–1.56
	B_{cr} - Is	325.6	0.346	–0.96
C6-C6	Cr - Cr?	306.2	0.298	–2.16
	Cr? - E''	305.0	0.338	–3.46
	E'' - E	309.6	0.329	–2.74
	E - B_{cr}	312.5	0.350	–2.24
	B_{cr} - Is	326.3	0.378	–1.98
C6-C7	E'' - E	302.1	0.286	–1.69
	E - B_{cr}	303.4	0.298	–1.89
	B_{cr} - Is	330.6	0.348	–1.44
C7-C7	E'' - E	292.6	0.225	–1.92
	E - B_{cr}	307.8	0.281	–1.89
	B_{cr} - Is	334.2	0.351	–1.44

clearing of the solid-like phases ($\mathrm{SmB_{cr}}$ and SmE) and the liquid-like phases (N and SmA). This reflects large differences in the molecular arrangements in the two types of LC phases [19].

Table 2. Clearing temperature T_{cl}, the slope of the clearing line dT/dp, the experimental enthalpy ΔH_{cl} and entropy ΔS_{cl} of the transition (all at 1 atm), and the volume changes ΔV_{cl} as calculated from the Clausius-Clapeyron equation, for different substances.

Sub-tance	Phase transition	T_{cl} K	dT/dp K/MPa	ΔH_{cl} kJ/mol	ΔS_{cl} J/mol·K	ΔV_{cl} cm^3/mol
C5 - C6	Is - B_{cr}	325.7	0.346	10.0 [7]	30.7	10.6
C6 - C6		326.7	0.378	10.7 [6]	32.7	12.4
C6 - C7		331.2	0.348	11.9 [7]	35.9	12.5
C7 - C7		334.2	0.351	13.0 [6]	38.9	13.6
4BT	Is - E	355.2	0.322 [10]	11.2 [11]	31.5	10.2
8BT		345.0	0.237 [2]	10.1 [11]	29.3	6.9*
6DBT	Is - A_1	354.0	0.259 [3]	3.80 [12]	10.7	3.16*
8DBT		356.1	0.238 [3]	3.82 [12]	10.7	2.55
10DBT		354.8	0.237 [3]	3.79 [12]	10.7	2.70
5CB	Is - N	308.3	0.424 [13]	0.33 [13]	1.1	0.45*
6CB		302.4	0.390 [14]	0.26 [14]	0.9	0.34*
7CB		315.6	0.370 [14]	0.53 [14]	1.7	0.62*
8CB		313.8	0.355 [15]	0.50 [15]	1.6	0.57*
5PCH	Is - N	328.1	0.440 [16]	0.92 [16]	2.8	1.2*
6PCH		322.6	0.417 [17]	0.63 [17]	1.9	0.81*
7PCH		330.9	0.420 [18]	1.0 [18]	3.0	1.27*
8PCH		328.3	0.412 [13]	0.65 [13]	2.0	0.82*

* Values obtained from pVT measurements.

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