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High pressure differential thermal analysis of laterally substituted nematic liquid crystalline compounds

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High pressure differential thermal analysis of laterally substituted nematic liquid crystalline compounds

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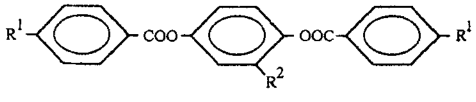
By means of high pressure thermal analysis we measured the pressure dependence of the clearing temperatures of nematic, 2-substituted hydroquinone-bis-(4-substituted benzoates) up to pressures of about 500 MPa. The clearing lines are strongly non-linear and can be well reproduced by a modified Simon–Glatzel equation. The gradients dT/dp of the clearing lines decrease strongly with increasing pressure, indicating a pronounced decrease of the transition volume with increasing pressure. Compounds with long chain lateral substituents exhibit liquid crystalline behaviour because the lateral substituents tend to have an orientation parallel to the molecular long axes. We expected that the preferred orientation of the lateral substituents would be strengthened by high pressure, demonstrated by enhanced dT/dp values. However, despite the strong deviation of the compounds from the ideal rod-like shape, the magnitudes and the trend of the data are similar to those of classical nematics.

1. Introduction

At present more than 40 000 thermotropic liquid crystalline compounds are known [1]. The majority of these compounds follows Vorländer's rule of the most linear shape of the liquid crystalline molecules [2]. However, there is a limited number of compounds which deviate from this simple rule and may be called unconventional liquid crystals [3]. Especially interesting are compounds with large flexible lateral substituents [4–11, 12]. Among these, many examples of the 2-substituted hydroquinone-bis-(4-substituted benzoates) have been synthesized [4–8] and some of these have been investigated in more detail [6, 7]. These investigations led to the opinion that the mesomorphic properties of these compounds are due to the fact that the flexible long chain lateral substituents have an orientation nearly parallel to the long axis of the basic molecule [7]. In order to obtain additional arguments for the discussion of the properties of these compounds we performed high pressure differential thermal analysis (DTA) investigations.



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Until now high pressure investigations about calamitic liquid crystalline substances have been restricted to laterally non-substituted compounds [13, 14]. With rising pressure an increase of the nematic clearing temperatures has been predicted

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theoretically [15, 16] and found by experiments [13, 14]. Especially, the slope of the clearing lines has been under discussion. Therefore, the question if laterally substituted compounds provide characteristic differences with respect to the 'classical' substances, arises.

2. Experimental

We determined the phase transitions by the aid of high pressure differential thermal analysis in a gas pressure equipment (Unipress, Warsaw, Poland). Details of the apparatus have been described previously [17, 18].

The investigated substances are compiled in table 1. We used the original substances which already have been the subject of earlier investigations given in the references.

3. Results

Since all compounds given in table 1 are nematic, we concentrated our efforts on a determination of the pressure dependence of the nematic–isotropic transition temperatures. The nematic–solid transitions showed a strong tendency to hindrance of crystallization and supercooling of the melt, especially at high pressures, and therefore such transitions could only be determined in a few cases (see figures 1–3). Substance 8O/1 (see figure 1) has at normal pressure only one solid phase. At pressures above 150 MPa, a second solid phase with a higher melting temperature appears. The solid–solid transition itself could not be observed.

The melting line of substance 8O/4*t* (see figure 2) runs in the immediate vicinity of the clearing line at somewhat lower temperatures. The thermodynamically stable area of the nematic phase increases from a temperature range of 1·4 K at normal pressure to 2·5 K at about 75 MPa.

Without problems we were able to determine the phase diagram of the substance 6/4*t* (see figure 3), although the clearing temperatures are about 50 K below the melting points. During the registration of the DTA traces, we regularly observed that, by cooling the isotropic melt of the substance, crystallization occurred immediately below the isotropic–nematic transition. At pressures above 100 MPa, however, the melt can be strongly supercooled and does not crystallize. Therefore under these conditions we did not observe the solid phase.

Table 1. List of investigated substances. X is the length-to-breadth ratio, calculated according to [7]. T_0 is the temperature of the nematic–isotropic transition at normal pressure.

	General structure I			T_0/K		
Substance	R^1	R^2	X	Measured	Reference value	Reference
8O/0	n-$C_8H_{17}O$	H	9·44	466·2	468·1	[6, 7]
8O/1	n-$C_8H_{17}O$	CH_3	7·99	430·0	429·7	[6, 7]
8O/2	n-$C_8H_{17}O$	C_2H_5	7·32	391·9	392·2	[6, 7]
8O/3	n-$C_8H_{17}O$	n-C_3H_7	6·87	371·8	371·8	[6, 7]
8O/4	n-$C_8H_{17}O$	n-C_4H_9	6·52	363·6	363·8	[6, 7]
8O/4t	n-$C_8H_{17}O$	t-C_4H_9	6·52	357·9	357·1	[6, 7]
8O/16	n-$C_8H_{17}O$	n-$C_{16}H_{33}$	4·77	341·9	342·7	[5]
6/0	n-C_6H_{13}	H	8·19	441·6	442·5	[19]
6/4*t*	n-C_6H_{13}	t-C_4H_9	5·19	308·2	308·0	[20]

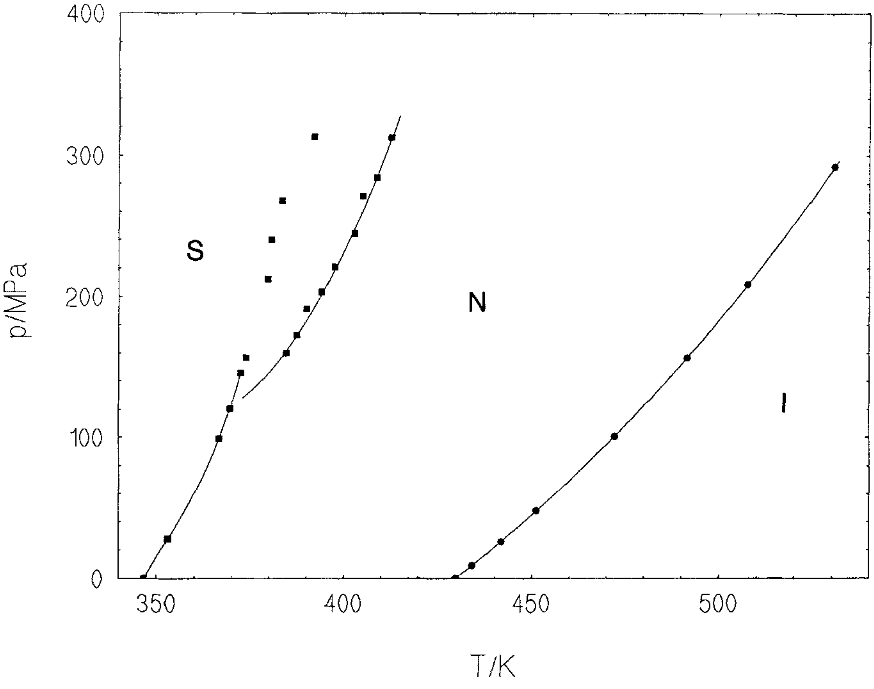

Figure 1. Phase diagram of 1,4-bis(4-*n*-octyloxybenzoyloxy)-2-methylbenzene. S, solid; N, nematic; I, isotropic.

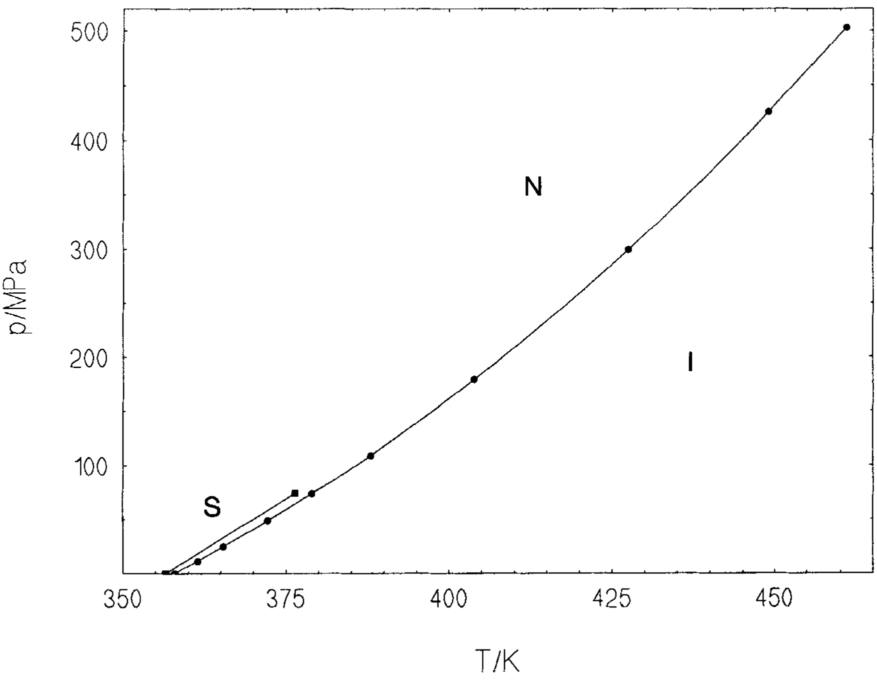

Figure 2. Phase diagram of 1,4-bis(4-*n*-octyloxybenzoyloxy)-2-*t*-butylbenzene. S, solid; N, nematic; I, isotropic.

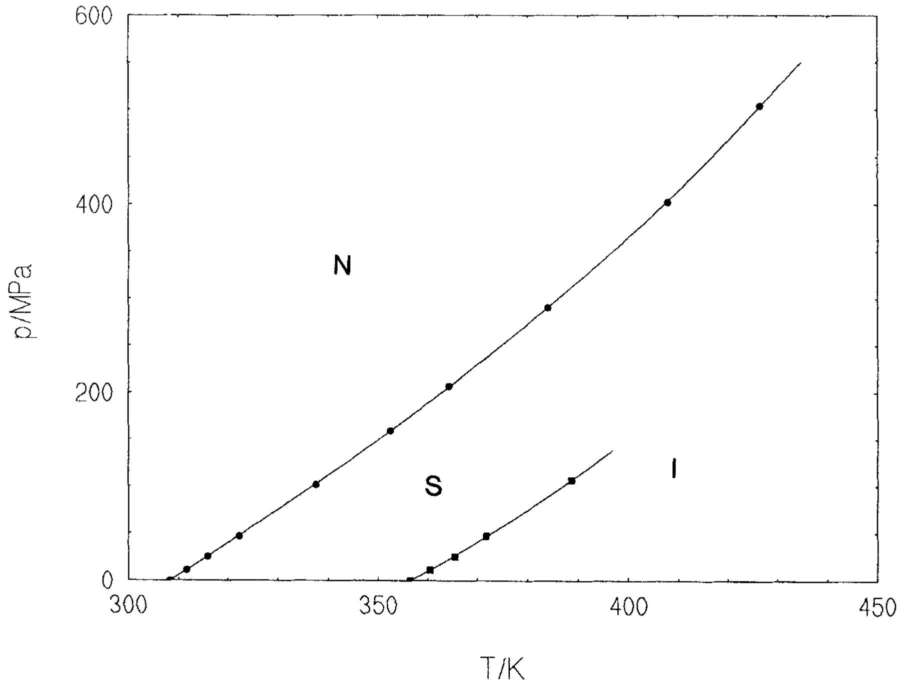

Figure 3. Phase diagram of 1,4-bis(4-*n*-hexylbenzoyloxy)-2-*t*-butylbenzene, 6/4*t*. S, solid; N, supercooled nematic; I, isotropic.

Figure 4 presents the clearing curves of all investigated compounds. All curves have been reproduced by calculation. For the clearing lines of compounds 8O/1 to 8O/16, 8O/4*t* and 6/4*t* we used the modified Simon–Glatzel equation [21]

$$T = T_0\left(1+\frac{p}{b}\right)^a \exp(cp) \tag{1}$$

where T = transition temperature (subscript 0 for normal pressure), a, b, c = constants, and p = pressure. The data used for calculations are given in table 2. For calculation of the clearing lines of substances 8O/0 and 6/0, as well as the melting lines, we used the equation

$$T = T_0 + lp + mp^2, \tag{2}$$

where l and m = constants. The data used for calculation are compiled in table 3.

Generally, during investigations of organic compounds at high temperatures, the limited thermal stability of the compounds should be taken into consideration. Therefore, after several measurements and after the last measurement at the highest pressure and temperature, we repeated the determination of the clearing temperature at normal pressure. With exception of substance 8O/1, ($\Delta T = -0{\cdot}2$ K after the measurement at 530·7 K), and the substance 8O/2, ($\Delta T = -0{\cdot}4$ K after the measurement at 500·4 K), we have not been able to detect any depression of the clearing temperatures.

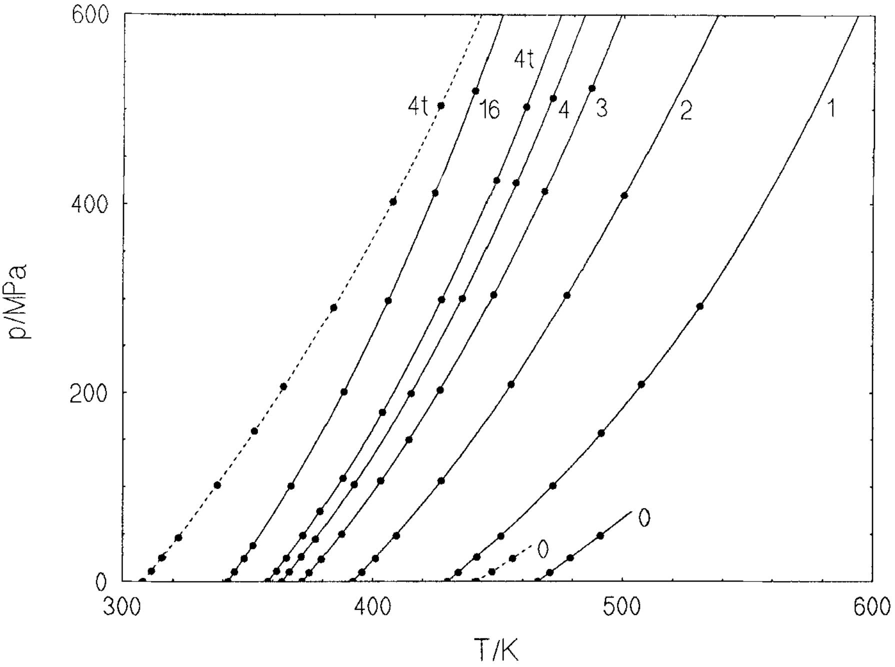

Figure 4. The clearing lines of the substances investigated in this study. The numbers at the curves indicate the number of carbon atoms in the lateral alkyl chain, *n*. (- - - -), 6/*n*; (——), 8O/*n*.

Table 2. Values of the parameters of equation (1) for the fitted clearing lines of the compounds 8O/*n* and 6/4*t*. S_T is the standard deviation of the fit.

Substance	T_0/K	*a*	*b*/MPa	$c/(10^{-5}$/MPa)	S_T/K
8O/1	430·0	0·336	276	−10·98	0·09
8O/2	391·9	0·165	193	13·70	0·05
8O/3	371·8	0·235	271	3·26	0·11
8O/4	363·6	0·236	277	2·49	0·17
8O/4*t*	357·9	0·213	255	4·15	0·03
8O/16	341·9	0·247	312	2·19	0·11
6/4*t*	308·2	0·839	649	−31·12	0·17

Table 3. Fitting results for the parameters of equation (2) for the transition lines of the compounds 8O/0, 6/0, 8O/1, 8O/4*t* and 6/4*t* (S, solid phase; N, nematic phase, I, isotropic liquid phase). T_0 is the transition temperature at normal pressure. S^1, normal pressure phase; S^2 high pressure phase.

Substance	Transition	T_0/K	*l*/(K/MPa)	$m/(10^{-4}$K/MPa^2)
8O/0	N–I	466·2	0·525	−2·1
6/0	N–I	441·6	0·597	−3·2
8O/1	S^1–N	346·6	0·250	−5·0
8O/1	S^2–N	334·3	0·378	−4·1
8O/4*t*	S–N	356·4	0·271	—
6/4*t*	S–N	356·5	0·349	−4·3

Because at higher temperatures the substances 8O/0 and 6/0 tend to decomposition, we investigated them only in the stable region in which no decomposition could be observed.

3. Discussion

In the homologous series of laterally substituted hydroquinone-bis-benzoates 8O/*n*, the clearing temperatures decrease with increasing lateral alkyl chain length, tending to a borderline temperature [4–7]. This behaviour has been explained by such preferred conformations of the lateral alkyl chains which allow a nearly parallel orientation of these alkyl chains with the long axis of the basic molecules. This explanation is consistent with van der Waals theories of the nematic state [22, 23]. In the frame of van der Waals theories, the clearing temperature decreases when the length-to-breadth ratio of the molecules is diminished and the packing fraction, (the quotient of the calculated most dense volume and the actual volume), decreases. According to the data from [7], the length-to-breadth ratios decrease in the said homologous series. However, the packing fraction at the clearing temperature increases, which means that because of the smaller length-to-breadth ratio, the minimum density necessary to stabilize the nematic state increases in the series. Since the intermolecular attraction, which in such low polar compounds is based mainly on dispersion interaction, is not very different in the homologues, the packing fractions at a common reference temperature (in [7], 70°C has been used) should be not very different. In fact, they decrease slightly in the series, which seems to be due to a small increase of the non-accessible free volume caused by the bulkiness of the lateral substituents. In accordance with the predictions of the theories, because of the increase of the packing fraction, the fractional transition volume, $\Delta V_0/V_0$ decreases. The transition enthalpy ΔH_0 and entropy ΔS_0 of the nematic–isotropic transition pass through a small maximum; selected data are given in table 4.

In table 4, we compare the calculated and measured data for $(\mathrm{d}T/\mathrm{d}p)_0$. The agreement is acceptable, considering the very small values (pretransitional effects have not been considered) of the transition enthalpies determined by differential scanning calorimetry [7].

Figure 5 presents a plot of the initial slopes, $(\mathrm{d}T/\mathrm{d}p)_0$, versus the packing fractions, which proves the distinct trend in the homologous series. The magnitude of the data is comparable to those of laterally non-substituted liquid crystals and this trend fits with the general behaviour of liquid crystals that in compounds with increasing packing fraction, because of decreasing compressibility, $\mathrm{d}T/dp$ decreases.

Figure 6 shows that $\mathrm{d}T/\mathrm{d}p$ decreases with increasing pressure, possibly to a common saturation value in the homologous series. This may be explained easily by the assumption, that with increasing pressure, because of the stronger compression of the high temperature phase, ΔV decreases remarkably. However, the transition entropy $\Delta S = \Delta H/T$ is not influenced to the same extent.

Using the volume and enthalpy changes measured at normal pressure, we found approximately $(\Delta V/\Delta H)_0 = \text{constant}$ [7]. Using our high pressure data (which are more precise than the data taken from direct ΔV and ΔH measurements) and the Clausius–Clapeyron equation

$$\frac{\Delta V}{\Delta H} = \frac{1}{T}\frac{\mathrm{d}T}{\mathrm{d}p}, \tag{3}$$

for the calculation of $\Delta V/\Delta H$, we obtain a distinct dependence on the chain length in the homologous series as well as on the pressure. This is exhibited in figure 7.

Table 4. Selected data of the nematic–isotropic transition at normal pressure.

Substance	T_0/K	$X(a)$	dT/dp(b)/K/MPa	dT/dp(c)/K/MPa	$(\Delta V_0/V\,(d)) \times 10^3$	ΔH_0/kJ mol^{-1}	ΔS_0/JK^{-1} mol^{-1}
8O/0	466·2	9·44	0·525	—	—	2·1	4·49
8O/1	430·0	7·99	0·476	0·556	4·7	2·2	5·12
8O/2	391·9	7·32	0·389	—	—	2·2	5·61
8O/3	371·8	6·87	0·335	0·400	3·5	2·34	6·29
8O/4	363·6	6·52	0·318	0·393	3·35	2·4	6·6
8O/4t	357·9	6·52	0·314	0·349	3·08	2·31	6·46
8O/16	341·9	4·77	0·278	≈0·364 (e)	≈1·4 (e)	≈1·47 (e)	≈4·3 (e)
6/0	441·6	8·19	0·598	0·603 (f)	4·31 (f)	1·76 (f)	3·98 (f)
6/4t	308·2	5·19	0·3025	—	—	—	—

(a) Length-to-breadth ratio calculated according to [7].

(b) Experimental values from p–T measurements.

(c) Calculated by use of the Clausius–Clapeyron equation from ΔH_0 and ΔV_0 [7].

(d) Data from [7].

(e) Value of the C_{12}-homologue from [7]; an asymptotical relationship within the homologous series lets us expect a similar value for the C_{16}-homologue, too.

(f) Data from [19].

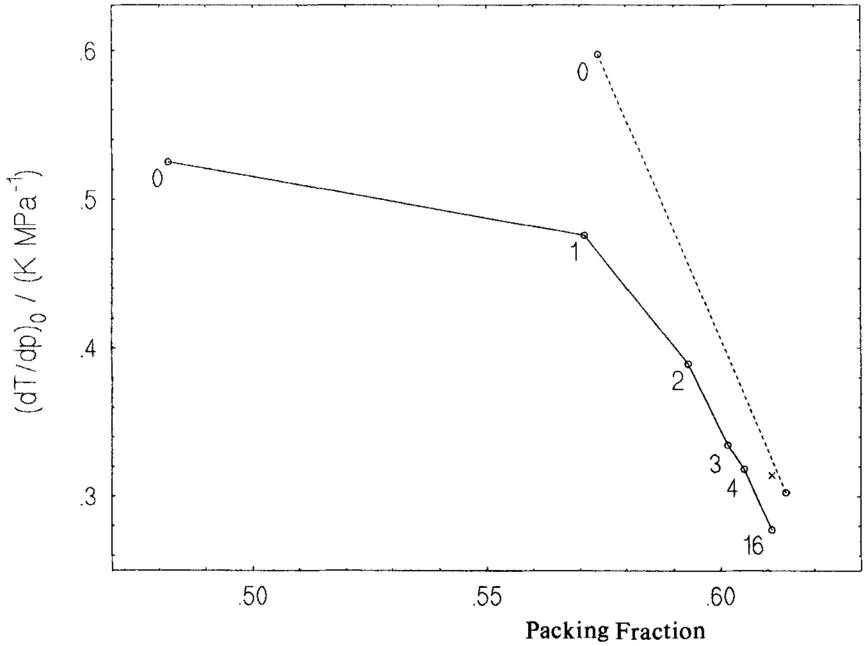

Figure 5. The relationship between the slope dT/dp of the clearing line and the packing fraction, at the clearing point, at normal pressure. The numbers at the curves indicate the number of carbon atoms in the lateral alkyl chain, n. (- - - -), 6/n; (——), 8O/n; ×, 8O/4t.

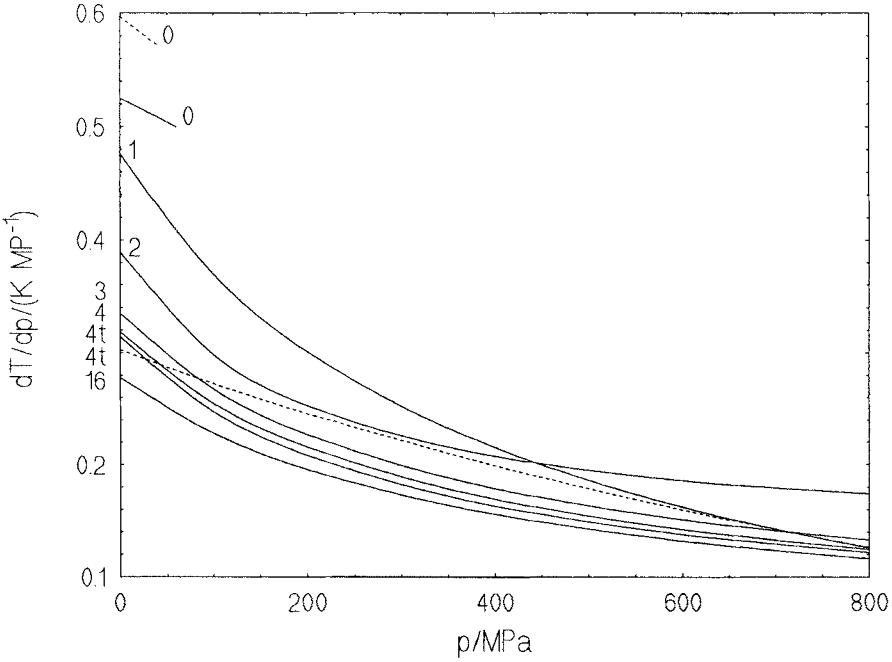

Figure 6. The pressure dependence of the slope of the clearing lines. Within the experimental range (see figure 4), the relative error of the slope does not exceed 0·027 [18]. The numbers at the curves indicate the number of carbon atoms in the lateral alkyl chain, n. (- - - -), 6/n; (——), 8O/n.

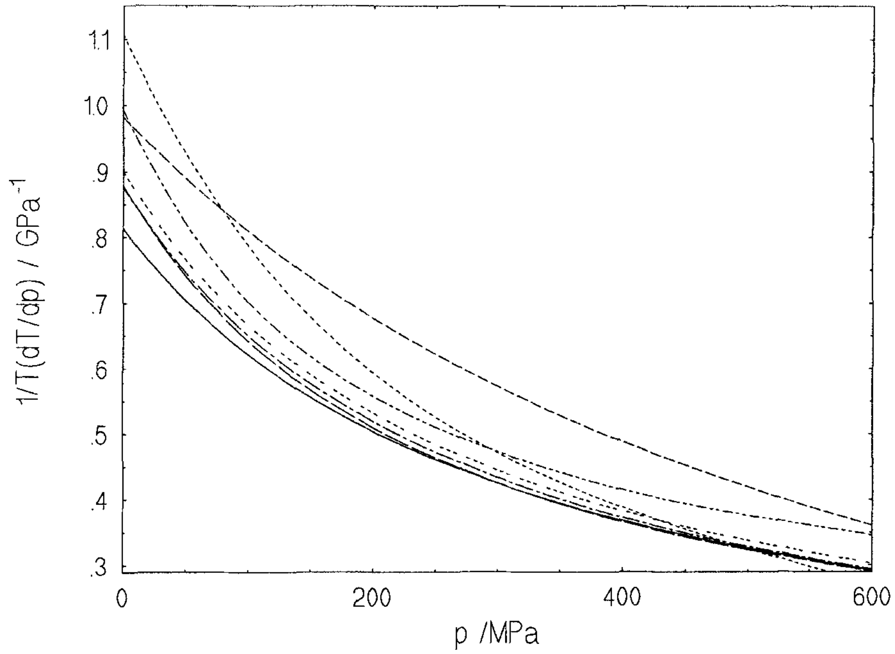

Figure 7. The pressure dependence of $1/T(\mathrm{d}T/\mathrm{d}p)$. Within the experimental range (see figure 4) the relative error of $1/T(\mathrm{d}T/\mathrm{d}p)$ is less than 0·012 [18]. (——), 6/4*t*; (- - - -), 8O/1; (—- - -—- -), 8O/2; (- - - - - - - - -), 8O/3; (-—-—-), 8O/4; (———), 8O/4*t*; (——), 8O/16.

In order to derive equation (1) from equation (3), we assumed a non-linear pressure dependence of ΔV which, together with the assumption of constant ΔH, delivers [21]

$$\frac{\Delta V}{\Delta H}=\frac{a}{p+b}+c. \tag{4}$$

Equation 4 is able to describe the experimental results, presented in figure 7, much better than the assumption

$$\frac{\Delta V}{\Delta H}=\frac{\text{const.}}{p+b}, \tag{5}$$

which is the basis on which the Simon–Glatzel equation is derived from equation 3 [21].

4. Conclusions

We have investigated the pressure dependence of the clearing temperatures of several laterally substituted compounds, among them 6 belonging to one homologous series. The clearing lines are strongly non-linear. Therefore, simple equations and also such with several adjustable constants, like the Simon–Glatzel equation, fail to reproduce these curves. The modified Simon–Glatzel equation [21], which in principle allows a change of the sign of the transition volume at the clearing point, is well suited for the description of these curves.

Due to the influence of the lateral substituents, the initial slopes, $(\mathrm{d}T/\mathrm{d}p)_0$, decrease in the homologous series. This behaviour is mainly determined by the remarkable decrease of ΔV in the series; the changes in the transition entropy are less pronounced.

With increasing pressure, the dT/dp data decrease, possibly to a common saturation value in the series. Furthermore, we assume that this behaviour is determined by the decrease of ΔV with increasing pressure.

Comparing the pressure dependence of the clearing temperatures of the laterally substituted compounds with those of more rod-like laterally non-substituted substances, there is no remarkable difference in the magnitude and trend in the data. Especially, we did not find any evidence for the idea that, with increasing pressure, the long lateral substituents would be forced to more stretched configurations; this should lead to higher dT/dp values with increasing pressure [24]. However, the experiments prove the reverse. Despite the large deviations of the individual molecules from the rod-like shape, from a macroscopic standpoint, the laterally substituted compounds behave akin to 'classical' nematics.

The experimental part of this work has been performed in the Martin-Luther University, Halle, FB Chemie.

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