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High pressure differential thermal analysis of nematic compounds with different molecular shapes

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By means of high pressure differential thermal analysis we measured the pressure/temperature phase diagrams of several nematic compounds with different molecular structures. Using pressures up to about 500 MPa we found strongly non-linear clearing curves. This behaviour is interpreted as changes from 'weak' intermolecular potentials to 'hard' potentials, or using thermodynamic arguments, strong pressure dependence of the volume discontinuity at the clearing transitions.

1. Introduction

The ideal shape of the 'classical' liquid crystalline compound is the slim stiff rod. However, many examples are known in which the molecular shape deviates considerably from this idealized model [1]. Only a few physical properties have been measured for such compounds. Recently we have investigated the pressure dependence of the clearing temperatures of compounds with lateral long chain substituents [2]. In all compounds the clearing temperatures have been enhanced by high pressure. The p/T curves showed strongly non-linear behaviour.

In order to compare the properties of compounds with different molecular shapes, here we include some substances with enhanced molecular biaxiality and non-aromatic cyclohexane carboxylic acids in the high pressure investigations.

2. Experimental

The phase transitions under enhanced pressure were determined by differential thermal analysis (DTA) in a gas pressure equipment, described previously [3, 4].

The investigated substances are collected in table 1. The substances N1, N2 and NB were synthesized using the methods indicated in [5]. The substance 4H and the mixture 4/6H (50 mol% 4H, 50 mol% 6H) were commercial products. The investigated substances can be classified into two groups: compounds with a bulky core (N1, N2, NB) and non-aromatic compounds (4H, mixture 4/6H). Apart from the above mentioned compounds we have included in our considerations COC and CG, using the data measured by Feyz and Kuss [9] and fitting them in the same manner as our own results.

Some compounds tended to thermal decomposition at higher temperatures, so that the phase diagrams could be investigated only at relatively low temperatures and pressures. The progress of the decomposition was checked by comparative measurements of the clearing points at normal pressure between some measuring cycles and after the last clearing point determination at high pressure, i.e. after the strongest thermal stress of the substance (see table 2).

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Table 1. Structures and clearing temperatures at normal pressure T_0 values (measured and reference) for compounds studied.

Compound	Structure	R	T_0 /K	
			Measured	Reference value
N1		$n\text{-C}_6\text{H}_{13}$	388.8	393.2 [6]
N2		$n\text{-C}_6\text{H}_{13}\text{O}$	450.6	454.0 [6]
NB		$n\text{-C}_6\text{H}_{13}$	385.5	386 [6]
4H		$n\text{-C}_4\text{H}_9$	364.1	367 [7, 8]
6H		$n\text{-C}_6\text{H}_{13}$	—	370 [7, 8]
COC		$\text{CH}_3\text{-(CH}_2\text{)}_7\text{-CH=CH-(CH}_2\text{)}_8\text{-}$	—	311.9 [9]
CG		$\text{CH}_3\text{-C=CH-(CH}_2\text{)}_2\text{-C=CH-CH}_2\text{-}$ CH_3 CH_3	—	325.0 [9]

Table 2. Maximal depression of clearing points ΔT_d ; maximal pressure p_m of measured point which was used for the fitting calculations; number of data points n .

Substance	P_m/MPa	$\Delta T_d/\text{K}$	n
N1	25.5	0	3
N2	119.6	0.3	6
NB	409.6	0.1	11
4H	255.3	0.1	7
4/6H	183.8	0.2	6
COC [9]	300.0	?	17
CG [9]	300.0	?	17

3. Results

For the compound N2 and the mixture 4/6H we only determined clearing lines. Compound N1 has very low thermal stability. Its phase diagram, shown in figure 1, is not affected by thermal decomposition, but measurements at higher pressures and temperatures had to be avoided. For the compounds N1 and NB (see figures 1 and 2), the clearing lines run below the melting lines in the supercooled metastable regions, which become more obvious on comparing the numerical data. Owing to the higher dT/dp slope of the melting lines, the monotropic character of the nematic phases increases in both cases. The same behaviour has been found in the laterally substituted compound 2-*tert*-butylhydroquinone bis(4-*n*-hexylbenzoate) [2].

For the compound 4H the clearing line is crossed by another phase transition line at about 466 MPa and 464 K (see figure 3). The size of the DTA peaks and the ability of this transition to supercool indicate a melting line. The experimental points have been determined with increasing temperature. Because the extrapolation of this line does not hit the melting point at normal pressure, we infer the existence of a high pressure solid phase. The intersection of both the lines indicates a triple point solid/nematic/isotropic with the nematic phase at the low pressure side. Such behaviour seems to be very rare and is only known for cholesteryl nonanoate [10, 11].

The clearing lines are strongly non-linear. Therefore, in order to obtain a good fit for the compounds N2, NB, 4H, 4/6H, COC and CG (table 3), we used the modified Simon-Glatzel equation [12]

$$T = T_0(1 + p/b)^a \exp(cp), \quad (1)$$

where a , b and c are constants. The clearing line of N1 and the melting lines could be reproduced well (table 4) with the simpler equation

$$T = T_0 + mp + np^2, \quad (2)$$

where m and n are constants. For the calculations we only used measured values with a depression less than 0.3 K (see table 2). In none of the cases did the difference between the measured and calculated values exceed 0.3 K.

Within the experimental range, the relative error of the slope dT/dp (see figure 4) does not exceed 0.046, with the exception of compounds N2 and NB where the relative error at the two borders of the measuring range rises up to 0.075 and 0.053, respectively.

Within the experimental range the relative error of the curvature (see figure 5) does not exceed 0.16, with the exception of N2 and NB where the relative error at the two borders of the measuring range rises up to 0.71 and 0.28, respectively.

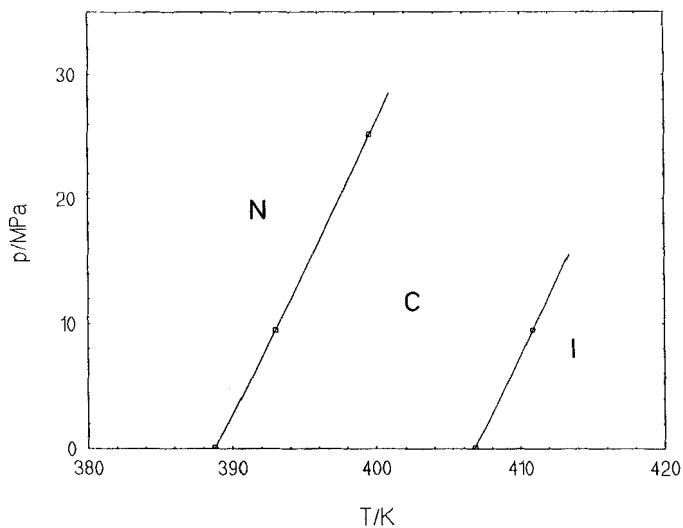


Figure 1. p/T diagram of compound N1. I, isotropic; C, crystal; N, nematic. ○, C-I; □, N-I (supercooled).

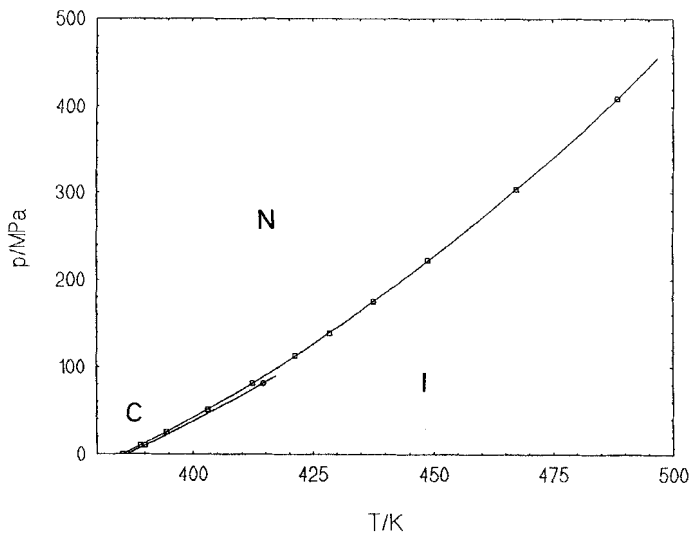


Figure 2. p/T diagram of compound NB. ○, C-I; □, N-I (supercooled).

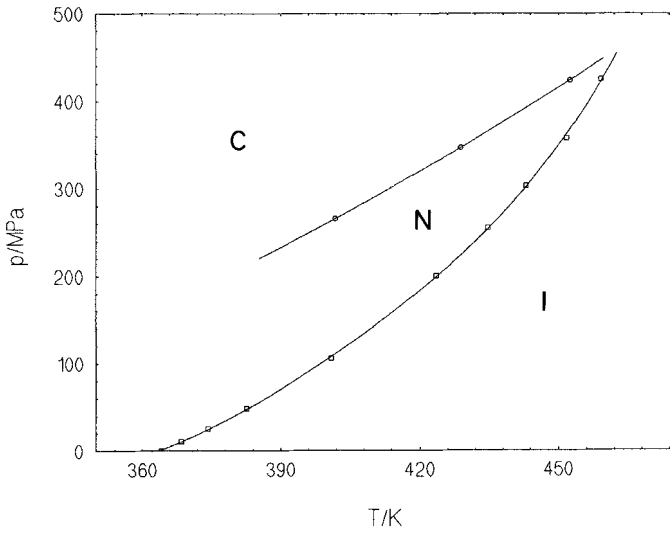


Figure 3. p/T diagram of compound 4H (4-*n*-butylcyclohexane carboxylic acid). \circ , C-N; \square , N-I.

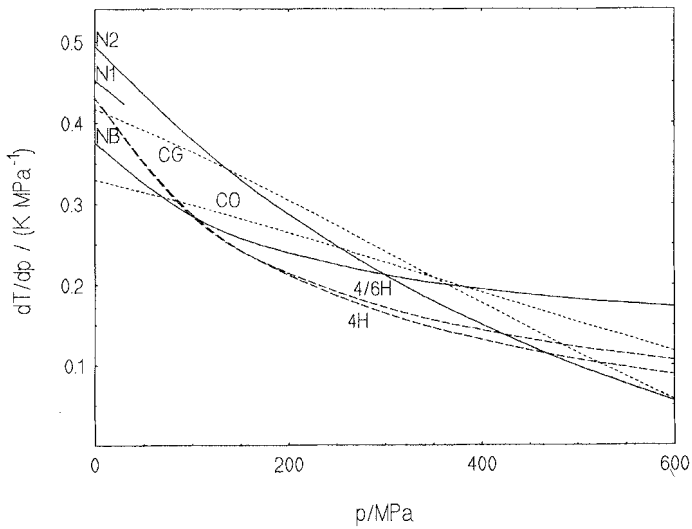


Figure 4. Pressure dependence of the slope of the clearing lines.

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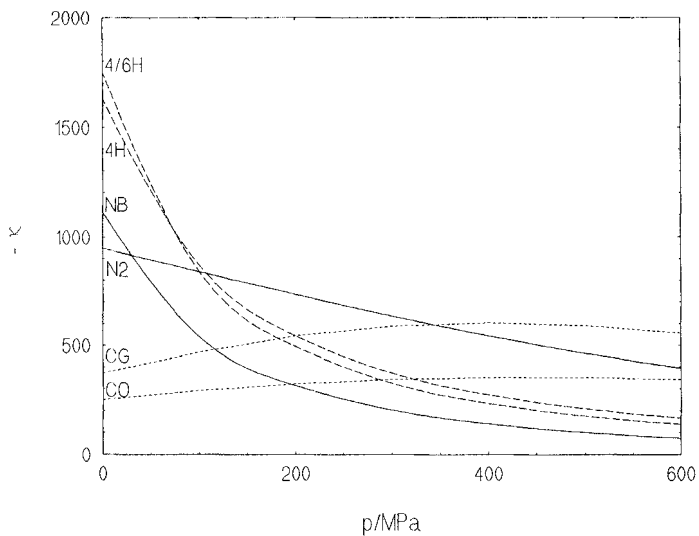


Figure 5. Curvature K of the clearing curves (numerical data using the units p/GPa , T/K).
 $[K = [(d^2T/dp^2)/(1 + \{dT/dp\}^2)^{3/2}]$.

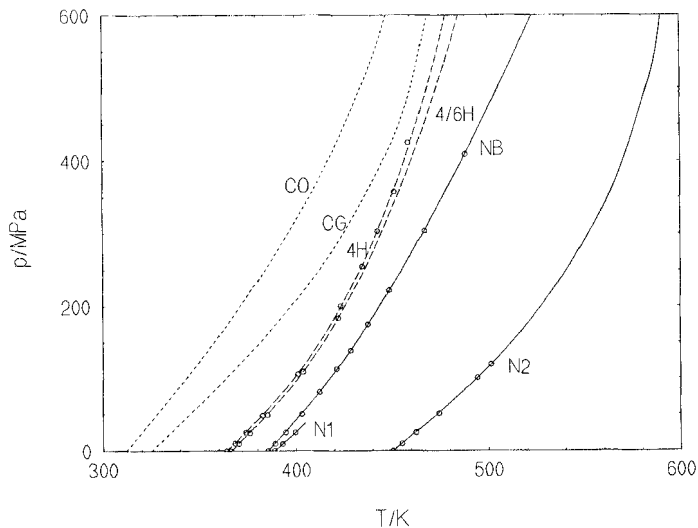


Figure 6. p/T diagram of the clearing lines of several compounds.

4. Discussion

Generally, for all the investigated substances, and in the whole experimental range, the clearing temperatures increase with increasing pressure (see figure 6). Compound N2 showed the largest increase (calculated for 300 MPa, 101.5 K), in compound 4H we found the smallest (for 300 MPa, 78.2 K). This increase in the clearing temperature with increasing pressure is in agreement with the van der Waals theories of the nematic state [13, 14]. The molecular-statistical theories of the van der Waals type use intermolecular potentials with attractive and repulsive parts. The repulsion because of the elongated molecular shape (expressed as length to breadth ratio) is strongly anisotropic and, in the frame of the theory, it is coupled with the isotropic attraction stemming mainly from dispersion interaction. In order to obtain the nematic phase for a given length to breadth ratio a critical packing fraction, $PF = V_B/V$ (V_B = hypothetical molar volume of the most dense packing according to an increment system of Bondi, V = actual molar volume), is necessary [13, 14]; graphical plots are presented in [15, 16]. Because the packing fractions are derived from actual volumes, they are temperature dependent. This critical packing fraction can be achieved either by the internal attractive forces, which always tend to contract a system hereby competing with the repulsive forces, or by external enhanced pressure. So the enhancement of the attractive forces or of the external pressure likewise will increase the clearing temperatures [15]. Compounds with low packing fractions possess 'weak' intermolecular potentials; those with high packing fractions have 'hard' intermolecular potentials (pronounced repulsion).

The slope dT/dp is different in the investigated compounds and decreases with increasing pressure (see figure 4). Generally, nematic phases with small packing fractions (nematic phases existing at high temperatures or in such compounds with very

Table 3. Values of the parameters for the fitted clearing lines (equation (1)) of the compounds N2, NB, 4H, 4/6H, COC and CG. Measured data points see [4] and [9], respectively; T_0 is the clearing temperature at normal pressure, S_T is the standard deviation of the experimental data with respect to the fit using equation (1).

Substance	T_0/K	a	b/MPa	$c \times 10^5/MPa$	S_T/K
N2	450.6	0.693	409	-59.22	0.07
NB	385.4	0.161	190	12.57	0.15
4H	364.1	0.235	181	-11.70	0.15
4/6H	366.4	0.195	161	-3.62	0.02
COC	311.9	2.427	1085	-117.71	0.17
CG	325.0	3.071	955	-180.34	0.10

Table 4. Values of the parameters for the fitted transition lines (equation (2)) of the compounds N1, NB, 4H. Measured data points see [4]: C = solid, N = nematic, I = isotropic phase.

Compound	Transition	T_0/K	$m/KMPa^{-1}$	$n/KMPa^{-2}$
N1	N/I	388.8	0.453	-10
N1	C/I	406.8	0.436	—
NB	C/I	386.4	0.382	-4.2
4H	C/N	297.6	0.437	-1.7

low attractive forces as non-aromatic compounds) have large dT/dp values (up to about 0.6 KMPa^{-1}). Nematic phases with high packing fractions (nematic phases with low clearing temperatures, highly polar compounds, compounds with large aromatic moieties) exhibit smaller dT/dp , in our examples down to about 0.5 KMPa^{-1} .

Our results fit well in this general framework. The p/T curves are strongly non-linear. Partly this is caused by the chemical nature of the compounds. On the other hand, in most investigations, only relatively low pressures up to 200 MPa (for example [17, 18]) have been used and under these circumstances the transition curves may usually be approximated quite well by straight lines. Using higher pressure, the curvature of the transition lines became obvious [11]. The non-aromatic compounds 4H, 4/6H and COC as well as CG have relatively high dT/dp for normal pressure and a strong decrease with increasing pressure (see figure 4). This indicates a change from a 'weak' intermolecular potential to a 'hard' potential showing pronounced repulsive forces. Every two molecules of the carboxylic acids 4H and 4/6H form two hydrogen bridges, resulting in the formation of dimers [19]. In the analogous 4-*n*-alkoxybenzoic acids, the molecules are strongly associated even above the clearing temperature [20]. We may assume a similar behaviour for the acids 4H and 4/6H. Therefore we cannot expect anomalies leading to re-entrant behaviour, as Cladis *et al.* [21], have found in compounds with strongly polar substituents.

In compounds with bulky cores the packing fraction is relatively low because of a certain degree of non-accessible free volume [22]; this means a relatively weak potential despite the aromatic nature of the compounds. Probably enhanced pressure considerably diminishes this free volume, changing the potential to a more hard character. In compounds with lateral substituents we found quite similar behaviour [3], especially in those with relatively high clearing temperatures.

As the curvatures displayed in figure 5 indicate, the clearing lines of compounds N2, NB, 4H, 4/6H straighten with increasing pressure. This trend agrees with theoretical predictions [23, 24, 25]. On the other hand, COC and CG show increasing curvatures of the transition lines. The theoretically expected behaviour cannot be found inside the experimental range, and we do not have an explanation for this behaviour.

5. Conclusions

We have measured the p/T phase diagrams for several nematic liquid crystal materials having different molecular structures. Using pressures up to about 500 MPa, we found strongly non-linear clearing curves. The non-linearity may be explained by changes from 'weak' intermolecular potentials to 'hard' potentials which are governed by repulsive forces. The non-linearity is especially pronounced in compounds with small packing fractions, caused by small attractive forces (non-aromatic compounds) or bulky cores.

Using thermodynamical arguments, the non-linearity probably arises because of a strong pressure dependence of the transition volume, but a much smaller pressure dependence of the transition entropy. This consideration is the basis of the derivation of a modified Simon-Glatzel equation [12] which reproduces well even strongly non-linear transition lines.

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