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SCANNING DILATOMETRY AND CALORIMETRY OF *p*-ALKYL-*p*′-CYANO-CYCLOHEXYL-CYCLOHEXANES

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ABSTRACT

Thermal expansion coefficient and volume changes accompanying phase transitions of *p*-alkyl-*p*′-cyano-cyclohexyl-cyclohexanes have been determined by a fast scanning dilatometric method. A relation between the percentage changes of volume and the phase involved in the transition is given. A comparison with calorimetric data is also reported. The results confirm that the stability of the smectic phase B for these compounds is enhanced with decreasing molecular length.

INTRODUCTION

Investigations by dilatometry of thermotropic liquid crystals, in order to obtain relations between the molecular structure and mesomorphic properties, have been performed by several scientists [1–7].

The dilatometric technique gives complementary results to calorimetric techniques such as differential scanning calorimetry (DSC) and thermal microscopy (TM). Different devices are used in order to obtain dilatometric measurements. Dilatometers generally consist of a glass body of suitable form to which a straight capillary tube is attached, in which the movement of the meniscus of the liquid phase indicates the change of volume.

The Carlsberg dilatometer [8], according to the method described by Rasper and Kauzmann [9], or a Bekkedahl-type dilatometer as described in ref. 1, are generally used. In each case the temperature fluctuation of thermostatic bath is the critical factor.

A high performance thermostatic bath was reported by Delben [10] in order to minimize temperature fluctuations in "traditional" dilatometric measurements. The measurements are carried out at thermal equilibrium, and a long time is required for each measurement with many measurements being needed for each sample. It therefore takes several working days to obtain an entire dilatometric curve. The fit of the experimental data using

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the Clement and Cohen equation [11], in order to calculate the thermal expansion coefficients, was reported by Stimpfle and coworkers [12]. A more sophisticated device is the differential dilatometer described by Wilkinson and Nagle [13], which has a sensitivity of 2×10^{-5} ml and gives a differential scanning dilatometric curve. This dilatometer was used in the study of phase transitions of phospholipid bilayers. Recently, Grasso [14,15] proposed a new fast dilatometric method for determining phase transitions in liquid crystals. Extensive investigations have already been reported of the structure of nematic and smectic phases of a variety of cyano compounds. In particular, Brownsey and Leadbetter [16] report the structures of liquid crystal phases of three members of the series R–⬡–⬡–CN (R = (a) C_3H_7, (b) C_5H_{11} and (c) C_7H_{15}), and suggest for the two lowest members a bilayer smectic B-type "interdigitated" structure whose stability, unusually, is enhanced with decreasing molecular length. We thought it right to verify this unusual result by our dilatometric method [15], because mixtures of these compounds are used in liquid crystal display and are of considerable technological interest. A thermodynamic study of these compounds by DSC and dilatometric measurements was carried out in order to obtain thermodynamic parameters. The thermodynamic cycles of examined compounds are also reported.

EXPERIMENTAL

Material

The *p*-propyl-*p*′-cyano-cyclohexyl-cyclohexane (compound a), *p*-pentyl-*p*′-cyano-cyclohexyl-cyclohexane (compound b) and the *p*-heptyl-*p*′-cyano-cyclohexyl-cyclohexane (compound c) used in the present study were Merck products and were used without further purification. The weight of each sample was about 0.1 g.

DSC measurements

A Mettler TC 10A processor equipped with a DCS-20 measuring cell, previously calibrated for temperature and energy using indium as standard, was used for the measurements. A IBM personal computer connected to the TC 10A processor was used to store experimental data.

TM measurements

The transition temperatures were obtained using a Galileo polarizing microscope with a 20 × 0.22 objective and a Mettler FP 52 microfurnace for sample-temperature control. The sample was mounted on a glass slide and covered with a glass cover slip.

Dilatometric measurements

A Mettler TC 10A processor equipped with a TMA 40 thermomechanical analyser previously calibrated for temperature and length was used in order to obtain certain measurements as function of temperature at constant pressure.

A quartz cylinder with a tight but freely movable piston was used to measure the length change (ΔL) of the cylindrically shaped sample. Neglecting the radial expansion of the vial (which is comparatively small) the mean volumetric expansion coefficient was calculated using the equation

$$\beta = \Delta V/\Delta T \times \frac{1}{V} \approx \Delta L/\Delta T \times \frac{1}{L}$$

where ΔL is the movement of the piston due to the temperature increase ΔT, and L is the axial thickness of the sample. The error due to neglecting the expansion of the piston and vial was less than 5%. The sensitivity of the apparatus was about 2×10^{-5} ml.

For every measurement a blank curve was obtained and subtracted from the sample curve in order to give accurate values.

A detailed description of the technique used to prepare the sample is reported in ref. 15.

For our measurements, a scan rate of 1°C min^{-1} was chosen to achieve a small temperature gradient within the sample and a short time for the measurements.

RECALL OF THE THERMODYNAMICS OF THE PHASE TRANSITIONS

It is known that there are two types of phase transitions: the first-order and the second-order. The first-order transitions are characterized by a change of the molar volume and are accompanied by a thermal effect (ΔH). So at the transition

$$\Delta V = [\delta\mu(\beta)/\delta p]_T - [\delta\mu(\alpha)/\delta p]_T \neq 0$$

$$\Delta H = T\Delta S = -T[\delta\mu(\beta)/\delta T]_p + [\delta\mu(\alpha)/\delta T]_p \neq 0$$

where α and β indicate two generic phases.

The second-order transitions are characterized not by a change in volume or H, but by a change of the second derivative of the chemical potential.

RESULTS AND DISCUSSION

The combined results of the calorimetric and dilatometric studies are collected in Table 1. The transition temperatures refer to thermal mi-

TABLE 1

Thermodynamic and dilatometric data

Phase [b] transition	T (K)	ΔH (cal)	ΔS (cal K^{-1} mol^{-1})	ΔV (%)	β ($\times 10^{-4}$)	I (°C)
Compound a						
K–K1	302	–		–		
K1						
K1–K2	316	–		–		
K2						
K2–K3	323	–		−0.15		
K3						
K3–N	329.4	7169	21.8	7.98		
N					[a]	
N–I	351.5	231	0.7	0.45		
I					0.4	86
I					24	86
I–N	351.5	205	0.6	−0.5		
N					25	60
N–S1	325.8	1493	4.6	−2.6		
S1					21	40
S1–S2	311.3	514	1.7	n.d.		
S2					19	30
S2–S3	288.2	194	0.7	n.d.		
S3					–	–
S3–K						
Compound b						
K					4.0	55
K–N	338	7568	22.4	7.87		
N					8.4	75
N–I	358.7	277	0.8	0.48		
I					3.8	86
I					8	86
I–N	358.7	318	0.9	−0.5		
N					9	60
N–S1	322.5	1275	4.0	−2.1		
S1					6	36
S1–S2	311	832	2.7	n.d.		
S2					2	27
S2–S3	307.2			−0.9		
S3					–	
S3–K						
Compound c						
K–N	344.2	9136	26.5	8.28		
N					[a]	
N–I	356.4	217	0.6	0.38		
I					2	88
I					5	88
I–N	356.4	373	1.0	−0.5		
N					9	55
N–K	314.1	8325	26.5	−5.6		
K					−17	32

[a] Variable in the nematic range. n.d., not detectable. [b] The notation of Verbit [18] is used.

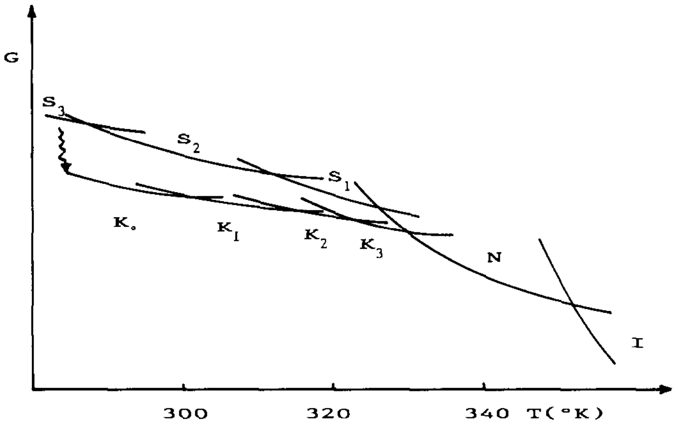

Fig. 1. Compound a: idealized free energy G vs. temperature T diagram. Slopes are exaggerated for clarity.

croscopy measurements unless otherwise specified. In order to obtain data on monotropic transitions, the procedure reported in ref. 17 was followed. From an evaluation of the data reported, the peculiarities of each examined compound will be reported before further discussion.

Compound a

Before the solid–nematic transition that occurs at 56.4° C, as confirmed by calorimetric and microscopic measurements, the dilatogram of this compound shows an interesting polymorphism; in particular, two second-order solid–solid transitions are evident at 29 and 43° C and a first-order solid–solid transition occurs at 50° C with a little contraction of volume. This solid phase K3 shows an unusual linear expansion coefficient decreasing with temperature. The dilatogram provides evidence, moreover, for pretransitional phenomena before the clarification temperature.

On cooling three smectic phases appear at 52.8, 38.8 and 15.2° C after the nematic phase. The last smectic phase so obtained remained in superfusion for many days. In fact, when the sample was heated in a second cycle a thermogram similar to that obtained in the cooling mode was obtained, as confirmed by the respective enthalpies. On cooling to below room temperature, solidification occurred at about 5° C. Figure 1 presents an idealized free energy diagram that describes the phase transitions of compound a. The zigzag arrow from the smectic S3 to solid K indicates that this transition occurs very slowly at room temperature (several days).

Compound b

On heating the phase behaviour of this compound is very simple (Fig. 2). A nematic phase appears stable at 65° C until the isotropic liquid phase

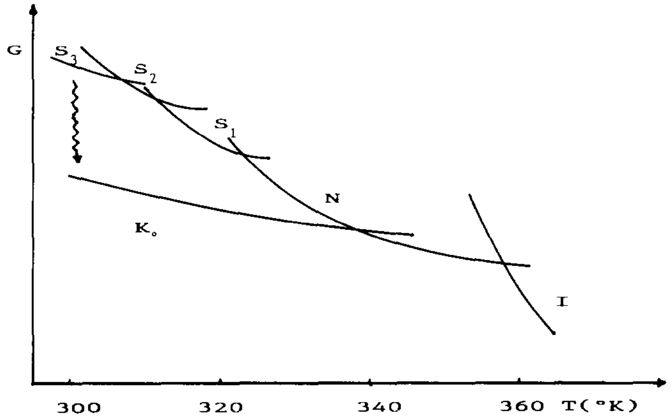

Fig. 2. Compound b: idealized free energy G vs. temperature T diagram. Slopes are exaggerated for clarity.

appears at 85.7 ° C. This result is confirmed by dilatometric measurements. On cooling a very complicated polymorphism appears. After the enantiotropic nematic phase, three monotropic smectic phases appear at 49.5, 38 and 34.2 ° C, and an unresolved solid–solid polymorphism appears at temperatures below 20 ° C. The kinetic of formation of the stable phase K_0 is very slow as is evident from a heating thermogram of this compound, carried out within a few hours. The thermogram that resulted is a sum of two thermograms the first being due to a succession of transitions K–N–I and the second to a succession of S3–S2–S1–N–I transitions. The dilatogram obtained in the cooling mode confirms the three smectic phases and indicates in particular that the volumetric change corresponding to the S1–S2 transition is scarcely detectable. If we assume that smectic phase S1 is of the B-type, as reported in ref. 16, and S3 is of the E-type, S2 could be a tilted B phase. An X-ray analysis should clarify this problem.

Compound c

The phase behaviour of this compound is very simple compared with the previous ones, as shown in Fig. 3. On heating, no smectic phases are present, only a nematic phase that appears at 71.2 ° C and remains stable until the isotropic liquid forms at 83.4 ° C. On cooling, the nematic formed at 83 ° C remains stable until 41.1 ° C when a new phase appears. The DSC thermogram corresponding to this last phase transition shows a single peak, whereas the corresponding dilatogram shows evidence of two transitions very close together, the second of which is a solid–solid transition while the first is probably the formation of a smectic monotropic phase. This ipotetic smectic phase is probably stable over a very small temperature range, less than 1 ° C, and is therefore undetectable by DSC and X-ray diffraction. The

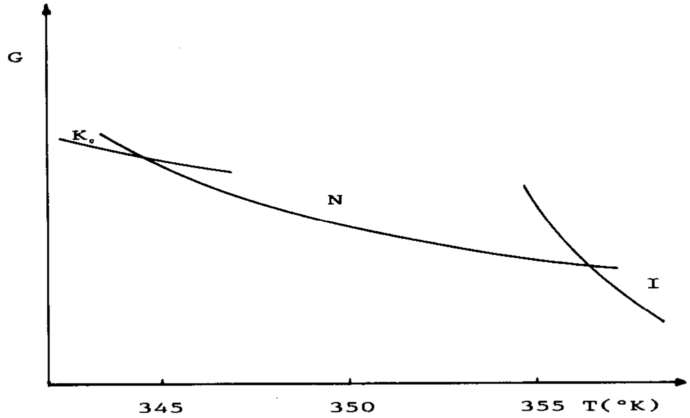

Fig. 3. Compound c: idealized free energy G vs. temperature T diagram. Slopes are exaggerated for clarity.

dilatogram of this compound shows, moreover, a peculiar behaviour on heating. The solid phase undergoes a very remarkable contraction of volume before forming the nematic phase. Several tests were carried out to confirm this result. Moreover, the nematic phase undergoes a remarkable contraction when the temperature increases from 71.2 to 75 °C, probably due to an annealing process.

In Fig. 4 the polymorphic schemes referring to the compounds examined are reported.

In conclusion, calorimetric and dilatometric results confirm that the compounds examined show the highly unusual phase behaviour reported in ref. 16: the stability of smectic phases decreases with the lengthening of alkyl tail. However, our thermodynamic data for compounds b and c, obtained by DSC, TMA and TM techniques, are not coincident with those reported in ref. 16, obtained only by the TM technique. Moreover, the similar trend observed for compounds a and b, with respect to that observed for compound c, confirms that the interdigitation of the CN and alkyl groups occurs only in the first ones. In Fig. 5 the dilatogram referring to

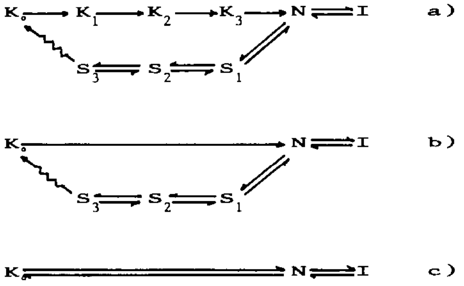

Fig. 4. Polymorphic schemes referring to compounds examined.

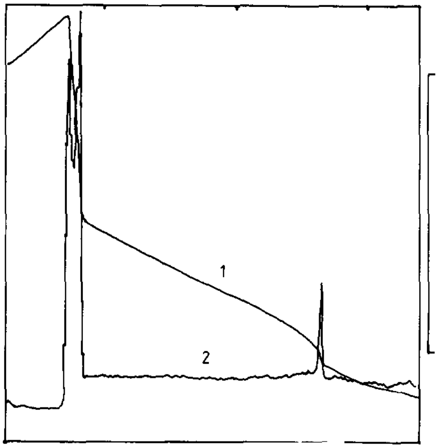

Fig. 5. Sample lengthening as a function of temperature (curve 1). Linear expansion coefficient as a function of temperature (curve 2) for c compound in cooling mode.

compound c in cooling mode is reported. Finally, the dilatometric results (see Table 1) show that each phase transition is characterized by a volume variation that depends upon the phases involved, and which can be used as a further criterion in determining the types of phases when the calorimetric data are ambiguous (e.g. compound c). For the compounds examined, these values (ΔV) are of about 0.4–0.5% for the nematic–isotropic transitions, 7.8–8.2% for the solid–nematic transitions, 2.1–2.6% in the smectic–nematic transitions and 0.3–0.9% for the smectic–smectic transitions.

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REFERENCES

1 D. Guillon and A. Skoulios, Mol. Cryst. Liq. Cryst., 39 (1977) 139.
2 Y. Thiriet, J. Schulz, P. Martinoty and D. Guillon, J. Phys. (Paris), 45 (1984) 323.
3 G. Albertini, E. Fanelli, D. Guillon, S. Melone, G. Poeti, F. Rustichelli and G. Torquati, J. Phys. (Paris), 45 (1984) 341.
4 D. Guillon and A. Skoulios, J. Phys., 3 (1976) 83.
5 G. Poeti, E. Fanelli, G. Torquati and D. Guillon, Nuovo Cimento Soc. Ital. Fis. D, 2 (1983) 1335.
6 S. Denprayoonwong, P. Limcharoen, O. Phaovibul and I.M. Tang, Mol. Cryst. Liq. Cryst., 69 (1981) 313.
7 G.R. van Hecke and L.J. Theodore, J. Phys. Chem., 82 (1978) 1669.
8 K. Linderstrom-Lang and H. Lanz, Comp. Rend. Trav. Lab. Carlsberg, Sez. Chim., 315 (1938) 21.

9 J. Rasper and W. Kauzmann, J. Am. Chem. Soc., 1771 (1962) 84.
10 F. Delben, Chim. Ind. (Milan), 62 (1980) 398.
11 W. Clement and L.H. Cohen, Mol. Cryst. Liq. Cryst., 359 (1974) 27.
12 R.M. Stimpfle, R.A. Orwoll and M.E. Schott, J. Phys. Chem., 83 (1979) 613–617.
13 D.A. Wilkinson and J.F. Nagle, Anal. Biochem., 84 (1978) 263–271.
14 D. Grasso, Chim. Ind. (Milan), 68 (12) (1986) 86.
15 D. Grasso, Liq. Cryst., 2 (1987) 557.
16 G.J. Brownsey and A.J. Leadbetter, J. Phys. Lett., 42 (1981) L–135.
17 D. Grasso, C. Gandolfo, L. Abate, G. Buemi and S. Fasone, Thermochim. Acta, 46 (1981) 71.
18 L. Verbit, Mol. Cryst. Liq. Cryst., 15 (1971) 89.