Thermochimica Acta, 61 (1983) 227–233
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

TRANSITION ENTROPIES AND MESOMORPHIC BEHAVIOUR OF *p-n*-ALKOXYBENZYLIDEN-*p*′-PROPOXYANILINES

DOMENICO GRASSO, LORENZO ABATE, CONCETTA GANDOLFO and SALVATORE FASONE

Istituto Dipartimentale di Chimica e Chimica Industriale, Università di Catania, 95125 Catania (Italy)

(Received 23 July 1982)

ABSTRACT

Calorimetric data on the nematogenic homologous series $H_7C_3{-}O{-}C_6H_4{-}N{=}CH{-}C_6H_4{-}O{-}C_nH_{2n+1}$ are presented. Trends in the nematic–isotropic transition temperatures, enthalpies and entropies are briefly discussed. The importance of the thermal history of the system in relation to its thermal behaviour is evidenced.

INTRODUCTION

A knowledge of both temperatures and heats of transition is necessary for the prediction of the mesophase behaviour. From such information the transition entropy may be calculated, and some information about the type and degree of order present in a mesophasic system can be obtained. The application of differential scanning calorimetry (DSC) and thermal microscopy (TM) has greatly facilitated the determination of the temperatures and heats of transition, and a larger number of thermodynamic data are, at present, available for homologous series of liquid crystal-forming materials.

Previous work by Grasso and co-workers [1–4] has involved the synthesis and characterization of several series of nematogenic compounds of general formula $R{-}O{-}C_6H_4{-}N{=}CH{-}C_6H_4{-}O{-}R'$. The motivation for these studies has been to discern those molecular properties required for the existence of mesophases through systematic variation of terminal substituents of a common central group, the benzyliden-aniline.

The present paper concerns a homologous series of compounds of general formula $H_7C_3{-}O{-}C_6H_4{-}N{=}CH{-}C_6H_4{-}O{-}C_nH_{2n+1}$, with $n = 1, 2, \ldots 8$ for compounds A, B,... H, respectively. The thermodynamic data are presented as supported by Gray and Winsor [5] in K, kcal $mole^{-1}$, and cal $mole^{-1}$ K^{-1} for temperatures T, enthalpies ΔH, and entropies ΔS, respectively.

EXPERIMENTAL

Materials

Commercially available amines and aldehydes were used for the synthesis of the compounds. Equivalent quantities of amine and aldehyde were dissolved in anhydrous benzene and refluxed for several hours. The water of reaction was removed azeotropically and the crude products so obtained were purified by several crystallizations at low temperature from anhydrous ethanol at constant melting point.

Differential scanning calorimetry

A Perkin-Elmer DSC-1B, previously calibrated in terms of temperature and energy, using indium as standard, was used for the measurements. Several DSC scans were carried out for each sample. The measurements were recorded at a scan rate of 4°C min^{-1}.

RESULTS AND DISCUSSION

The temperatures, enthalpies, and entropies relative to the phase transitions for all compounds are collected in Table 1. The corresponding transition diagrams are reported in Fig. 1; those indicated as "cycle I" were obtained using "virgin" products, purified and obtained by crytallization from anhydrous ethanol; those indicated as "cycle II" were obtained using the condensed product obtained by cooling from cycle I as sample unless otherwise stated, the transition temperatures refer to thermal microscopy measurements.

All DSC measurements were carried out by heating or cooling at 4°C min^{-1} and were repeated several times for each compound, using new samples each time. In order to obtain data on monotropic mesophases of compounds, the samples were heated from solid to isotropic liquid, then cooled at the same rate until the mesophase was found, but without formation of the solid phase.

From an evaluation of the data reported in Table 1 and Fig. 1 a different thermal behaviour of compounds is evident, in particular, the following.

Compound A. This is the only one of the series which does not show remarkable differences between the first and the second cycle. It is characterized by a monotropic nematic phase with a large range of thermal stability (369–340 K). This behaviour confirms the results obtained by TM measurements [4]. On cooling, the nematic monotropic gives a solid K_1 thermodynamically less stable with respect to the "virgin" product K_0. In the second cycle, on heating the solid to isotropic liquid, a ΔH value similar

TABLE 1

The temperatures, enthalpies and entropies relative to the phase transitions

Compound	Transition	Cycle I			Cycle II		
		T	ΔH	ΔS	T	ΔH	ΔS
A	K_0–I	392.1	7.80	19.90	392.1	7.73	19.70
	I–N	349.1	0.11	0.29	349.1	0.12	0.33
	N–K_1	340.0	6.37	18.70	340.0	6.42	18.90
B	K_1–K_2				[b]	[b]	[b]
	K_2–K_3				[b]	[b]	[b]
	K_3–I				399.1	6.20	15.40
	K_6–I	400.5	7.70	19.22			
	I–N	398.3	0.17	0.43	398.3	0.18	0.45
	N–K_3	387.1	5.79	14.96	387.1	5.79	14.96
C	K_0–K_1	354.1 [a]	1.68	4.70			
	K_1–I	408.1	9.30	22.80			
	K_2–I				408.1	7.80	19.20
	I–K_2	398.6 [a]	7.90	19.19	398.6 [a]	7.90	19.19
D	K_0–K_1	345.1 [a]	[c]	[c]			
	K_1–K_2	350.1 [a]	1.12	3.25			
	K_2–I	393.6	6.22	15.80	393.6	6.55	16.64
	I–N	387.6	0.19	0.49	387.6	0.19	0.49
	N–K_2	381.1	6.49	17.02	381.1	6.52	17.11
E	K_0–K_1	373.1	6.21	0.57			
	K_1–I	379.3	8.05	21.33			
	K_3–N				377.1	6.16	16.30
	N–I				379.2	0.12	0.32
	I–N	379.2	0.20	0.52	379.2	0.19	0.51
	N–K_3	373.1	6.10	16.35	373.1	6.10	16.35
F	K_0–N	372.1	8.54	22.90			
	K_1–N				372.1	6.31	16.94
	N–K_1	365.1	6.05	16.55	365.1	6.05	16.55
	N–I	383.6	0.17	0.43	383.6	0.16	0.42
	I–N	383.6	0.25	0.65	383.6	0.24	0.64
G	K_0–N	375.1	10.95	29.19			
	K_1–N				375.1	9.35	24.92
	N–K_1	371.1	8.31	22.39	371.1	8.15	21.96
	N–I	380.3	0.15	0.39	380.3	0.15	0.39
	I–N	380.1	0.22	0.58	380.3	0.22	0.58
H	K_0–N	372.7	11.15	29.91			
	K_1–N				372.7	9.87	26.47
	N–K_1	363.4	8.20	22.56	363.4	8.20	22.56
	N–I	382.1	0.21	0.55	382.1	0.21	0.55
	I–N	382.0	0.30	0.79	382.0	0.31	0.81

---

[a] Temperature obtained by DSC measurements.

[b] Transition occurred at non-reproducible temperatures.

[c] Data not evaluable.

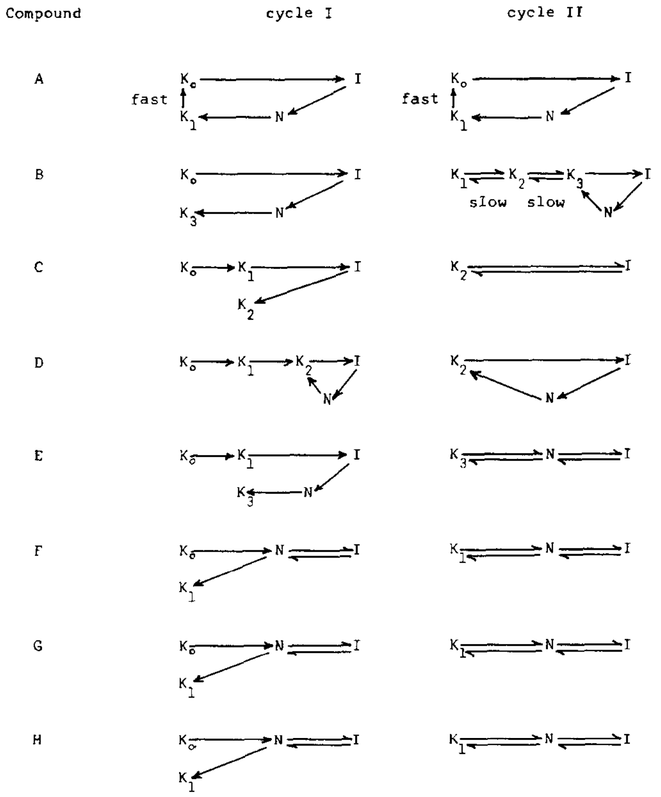

Fig. 1. Transition diagrams. K, solids; N, nematic; I, isotropic liquid.

to that of the first transition K_0–I is obtained. A rapid conversion, experimentally not detectable, of K_1 just formed to K_0 can therefore be supposed.

Compound B. In this compound the two cycles (I and II) are very different; the first is very similar to the cycles of compound 1 and presents a monotropic nematic phase, which yet on cooling gives a new solid phase K_3 thermodynamically less stable (≈ 4 e.u.) with respect to the "virgin" starting sample. On heating the solid phase K_3 just formed, the isotropic liquid is again obtained. On the contrary, if K_3 is left at room temperature for about 1 h, on further heating two solid–solid transitions appear before the melting to give the isotropic liquid. The quantitative data relative to the last K–K transitions are not reproducible and consequently are not reported. These data confirm, in part, those obtained by thermal microscopy [4], where, however, only one K–K transition is evident. The different behaviour in relation to annealing time suggests the existence of an equilibrium between two solid phases that occurs slowly in time. There exists a remarkable thermal hysteresis between the two cycles.

Compound C. In this compound the two cycles are very different. On heating the "virgin" product, a solid–solid transition occurs before the melting to isotropic liquid; on cooling, a new K_2 solid phase, thermodynamically less stable (≈ 3.5 e.u.) with respect to the "virgin" sample, is formed. In the second and consecutive cycles, K_2 gives the anisotropic liquid and vice versa. In spite of several measurements by DSC this compound did not show any mesomorphic phase either on heating or cooling, contrary to literature data [6]; only the melting temperature is confirmed. This unexpected result confirms our previous results obtained by thermal microscopy on different samples [4]. To remove every doubt, several tests were carried out on different samples obtained by different syntheses, and purified with particular care.

Compound D. Remarkable phenomena of thermal hysteresis between the first and second cycle are not evident; the only difference is that the first presents two solid–solid transitions, of which only the second is quantitatively appreciable and detectable by TM. On cooling, a monotropic nematic phase appears, as in compounds A and B.

Compound E. The thermal behaviour of this compound is very unusual. The two cycles are very different. On heating the "virgin" product there is a solid–solid transition followed by a solid–isotropic liquid transition; on cooling the isotropic liquid, a monotropic nematic phase appears that on further cooling gives a new solid phase K_3. On heating in the second cycle this new phase is able to give a stable nematic phase. This result suggests that the molecular arrangement of K_3 is influenced by the preceding nematic phase (monotropic); that is, K_3 "remembers" the order of appearance of the nematic phase. This "memory effect" confirms the great importance of the knowledge of the preceding phase in the study of thermodynamic properties of liquid crystals.

Compounds F, G, H. These present a similar behaviour and show stable nematic phases in both cycles. The data are in agreement with those obtained by TM. A remarkable thermal hysteresis is evident in each case.

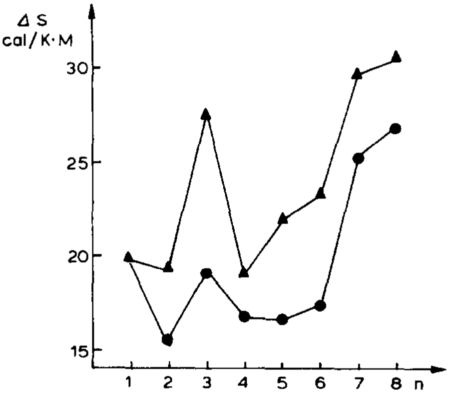

Fig. 2. Effect of alkyl chain length on the total transition entropy. ▲, Cycle I; ●, cycle II.

Figure 2 reports the trend of the total transition entropy referring to the first and second cycles (upper and lower curves, respectively). Their differences give an immediate idea of the thermal hysteresis of this class of compounds.

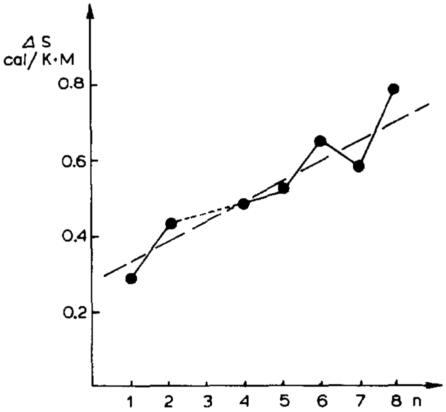

Fig. 3. Effect of alkyl chain length on the entropy of the liquid isotropic nematic transition.

Apart from compound C, the general trend of these curves is very similar to that obtained for the *p*-*n*-alkoxybenzylidene-*p*′-ethoxyanilines [2] and for the *p*-*n*-alkoxybenzoic acids [7]. In the present case, as in those previously cited, a minimum of entropy corresponds to the buthoxy derivative (cycle I); that suggests for these compounds a lower molecular order in the solid stable phase with respect to the other compounds of the same series. Likewise the high entropy values of compounds G and H suggest higher molecular order in the solid stable phase with respect to the other compounds. On the other hand, this result is expected because the molecular order increases with molecular length.

Figure 3 reports the trend of ΔS for the transition isotropic liquid–nematic. Besides an evident even–odd effect, the increasing trend with the lengthening of the chain suggests that in the nematic phase also, the molecular order increases with the length of the terminal substituents. On the whole, the results suggest that a critical molecular length exists, under the same conditions, necessary to make stable the nematic mesophase. Under this critical length (compound E in the present series) only a monotropic nematic phase exists, with the exception of compound C that does not show any mesomorphic behaviour. Moreover, the remarkable thermal hysteresis shown by the examined compounds, the influence of the "annealing time" (compound B), and the preceding thermal history of the system (compound E), emphasize the importance of these factors in the determination of the thermodynamic parameters of the mesogenic compounds.

REFERENCES

1 D. Grasso, L. Abate, S. Fasone, C. Gandolfo and G. Siracusa, Thermochim. Acta, 43 (1981) 107.
2 D. Grasso, C. Gandolfo, L. Abate, G. Buemi and S. Fasone, Thermochim. Acta, 46 (1981) 71.
3 D. Grasso, Mol. Cryst. Liq. Cryst., 78 (1981) 217.
4 C. Gandolfo and D. Grasso, Thermochim. Acta, 56 (1982) 59.
5 G.W. Gray and P.A. Winsor, Liquid Crystals and Plastic Crystals, Ellis-Horwood, Chichester, 1974.
6 K. Murase, Bull. Chem. Soc. Jpn., 45 (1972) 1772.
7 A.J. Herbert, Trans. Faraday Soc., 63 (1967) 555.
8 L. Verbit, Mol. Cryst. Liq. Cryst., 15 (1971) 89.