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THERMAL PARAMETERS OF SOME LIQUID CRYSTALS

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Although transition temperatures for many liquid crystal materials have been reported in the literature, latent heat data have been much less readily available. Barrall and Johnson[1] and Marzotko and Demus[2] have recently reviewed the calorimetric situation. The present paper reports transition temperatures and latent heats (enthalpies) for twenty-eight liquid crystalline materials. Most of the materials studied possess a single mesophase--the nematic. A few also possess at least one smectic phase.

The temperatures and latent heats for all observable phase transitions were determined by means of a Perkin-Elmer DSC-2 Differential Scanning Calorimeter. For a number of materials the nature of the phases and transition temperatures were verified by thermal microscopy (TM) of samples heated between crossed polarizers.[3] The results are given in Table I (for compounds found to have only stable nematic mesophases) and Table II (for compounds having stable smectic or monotropic nematic mesophases). In the Tables M is molecular weight, and T_{KN} and T_{NI} indicate crystal-nematic and nematic-isotropic transition temperatures (°C); L_{KN} and L_{NI} are the corresponding latent heats (KJ/mol). In Table II are given transition temperatures and latent heats for crystal-smectic (KS), smectic-nematic (SN), and nematic-isotropic (NI) phase changes. Temperatures and latent heats for monotropic phases are enclosed in brackets.

The materials were obtained from various organic chemical suppliers and were studied without further purification. However, estimates of sample purity from both DSC peak shape and examination of the sharpness of phase transitions by thermal microscopy indicated that most of the materials were of reasonable purity (nominally 99 percent or greater). (If a substance was found from DSC and/or TM to be of low purity, data for that material were not included in this report.

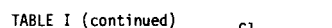
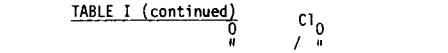
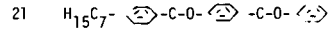
TABLE I. Thermal parameters for compounds having only stable nematic mesophases, †

ID	Chemical Formula	M	Transition Temperatures (°C) T_{KN}	T_{NI}	Latent Heats (KJ/mol) L_{KN}	L_{NI}	References to Other Work
1	H_9C_4-⟨⟩-N=N-⟨⟩-C_4H_9	310.4	19.6	32.5	13.4 ± 0.2	0.35 ± 0.02	a
2	$H_{11}C_5$-⟨⟩-N=N-⟨⟩-C_5H_{11}	338.5	26.6	67.9	15.7 ± 0.08	0.95 ± 0.05	a
3	$H_{13}C_6$-⟨⟩-N=N-⟨⟩-C_6H_{13}	366.6	25.5	54.3	17.2 ± 0.25	0.69 ± 0.04	a
4	$H_{11}C_5O$-⟨⟩-N=N-⟨⟩-OC_5H_{11}	370.5	77 (K_1N) 67.5 (K_2K_1)	122	15.4 22.8 ± 1.0	1.10 ± 0.05	b
5	$H_{11}C_5CO$-⟨⟩-NN-⟨⟩-OC_2H_5	340.4	74.6 67.4*	130.4	35.9 ± 0.46 35.5 ± 0.84*	1.29 ± 0.01	-
6	$H_{13}C_6CO$-⟨⟩-NN-⟨⟩-OC_2H_5	354.5	65.6 62.0*	118.6	21.7 ± 0.2 38.4 ± 0.5*	1.21 ± 0.09	-
7	$H_2C{:}C_9H_{17}CO$-⟨⟩-NN-⟨⟩-OC_2H_5	408.5	63.5 61.5*	109.0	44.8 41.2 ± 1.0*	1.63 ± 0.08	-
8	H_4C_2=CHCO-⟨⟩-NN-⟨⟩-OC_2H_5	310.4	109.7	196.7	23.6 ± 0.17	1.92 ± 0.06	-
9	H_7C_3-⟨⟩-CHN-⟨⟩-CN	248.3	63.0 60.0*	71.4	19.5 ± 1.3 18.6 ± 0.96*	0.569 ± 0.01	-
10	H_9C_4O-⟨⟩-CHN-⟨⟩-CN	278.4	64.5	106.2	25.7 ± 0.7	0.578 ± 0.02	c

TABLE I (continued)

11	$H_{11}C_5O$-⟨⟩-CHN-⟨⟩CN	292.4	62.7	88.2	24.4 ± 0.96	0.452 ± 0.01	c
12	$H_{13}C_6O$-⟨⟩CHN-⟨⟩-CN	306.4	56.5	102.2	25.8 ± 0.17	0.641 ± 0.004	c
13	$H_{15}C_7O$-⟨⟩CHN-⟨⟩CN	320.4	67.4 58.0*	96.5	34.3 22.9*	0.708 ± 0.02	c
14	$H_{17}C_8O$-⟨⟩CHN-⟨⟩CN	334.4	79.9	93.4	37.6 ± 0.17	0.829 ± 0.016	-
15	$H_{13}C_6\overset{O}{\overset{\|}{C}}O$-⟨⟩CHN-⟨⟩-CN	334.4	55.4	95.5	30.1 ± 0.5	0.632 ± 0.029	-
16	H_3CO-⟨⟩CHN⟨⟩$O\overset{O}{\overset{\|}{C}}CH_3$	269.3	84.9 82.0*	109.5	23.6 ± 0.08 20.9 ± 0.33*	0.645 ± 0.02	-
17	H_3CO-⟨⟩CHN-⟨⟩$O\overset{O}{\overset{\|}{C}}C_3H_7$	297.4	50.5 50.3*	111.8	23.3 ± 0.13 17.1 ± 0.50*	0.603 ± 0.01	-
18	$H_9C_4\overset{O}{\overset{\|}{C}}O$-⟨⟩CHN-⟨⟩$O\overset{O}{\overset{\|}{C}}OC_5H_{11}$	411.5	48.5 47.3*	96.0	25.8 22.2*	0.77 ± 0.04	-
19	$H_{15}C_7$-⟨⟩$\overset{O}{\overset{\|}{C}}$-O-⟨⟩-CN	321.4	42.5 26.5*	54.7	31.5 21.2 ± 0.08*	1.00 ± 0.05	
20	$H_{11}C_5$⟨⟩$\overset{O}{\overset{\|}{C}}$O-⟨⟩$\overset{Cl}{\overset{\|}{C}}\overset{O}{\overset{\|}{O}}$-⟨⟩$C_5H_{11}$	493.0	39.6 37.8*	123.0	23.8 ± 0.25 21.3 ± 0.38*	1.18 ± 0.06	d

TABLE I (continued)

21	$H_{15}C_7$- C_8H_{17}	563.1	39.7	102.8	30.4 ± 0.2	1.03 ± 0.02	d
22	H_3CO-  OCH_3	344.4	225.1	~341	45.4		e
23	$H_{17}C_8O$-  OC_8H_{17}	575.2	58.7 57.4*	180.4	49.5 ± 0.9 37.6 ± 1.8*	1.68 ± 0.08	f
24	$H_{11}C_5$-  -CN	325.4	131(K_1N) 115(K_2K_1) ~80(K_3K_2)	240.0	9.00 ± 0.17 6.61 ± 0.84 0.79	0.933 ± 0.05	g

†K = crystal (subscript indicates more than 1 phase); N = nematic; I = isotropic liquid.

*Indicates a transition from a metastable crystal (or monotropic smectic) phase to the nematic phase.

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a. J. van der Veen, W.H. de Jeu, M.W.M. Wanninkhof, and C.A.M. Tienhoven, J. Phys. Chem., 77, 2153 (1973) report transition temperatures in reasonable agreement with those given here. Their latent heats (determined by DTA) are 7 percent to 32 percent lower than the present values. Unfortunately, Marzotko and Demus (Ref. 2) have misquoted the van der Veen values of L_{NI} for these materials (as Kcal/mol instead of KJ/mol).

b. H. Arnold, Z. Phys. Chem., 226, 146 (1964). The present data are in reasonable agreement with those of Arnold.

c. C. Maze, private communication. For the most part the present data are in fairly good agreement with those of Maze (Maze does not report L_{NI} values). For compound 11 Maze reports a T_{NI} value 10° higher than that in Table I. For compound 13 Maze's T_{KN} and L_{KN} values seem to correspond to the transition involving the metastable crystal.

d. J.P. Van Meter and B.H. Klanderman, Mol. Cryst. Liq. Cryst., 22, 285 (1973) report transition temperatures only. Agreement with present work is good.

e. G.W. Gray, J.B. Hartley, A. Ibbotson, and B. Jones, J. Chem. Soc., 4359 (1955) report transition temperatures only, in nominal agreement with present work.

f. S.L. Arora, J.L. Fergason, and A. Saupe, Mol. Cryst. Liq. Cryst., 10, 243 (1970). Temperature values only. Agreement is good.

g. G.W. Gray, K.J. Harrison, and J.A. Nash, Pramana Suppl. No.1, 381 (1975). No value of L_{NI}. Agreement is good.

TABLE II. Thermal parameters for materials with smectic or monotropic nematic phases.†

ID	Chemical Formula	M	°C			KJ/mol			Reference to Other Work
			T_1	T_2	T_3	L_1	L_2	L_3	
25	$H_{17}C_8$-⟨⟩-⟨⟩CN	291.4	24(KS)	34(SN)	42.6(NI)	25.3 ± 0.1	0.13	0.971 ± 0.08	a,b
26	$H_{21}C_{10}O$-⟨⟩CHN-⟨Cl⟩⟨⟩NCH-⟨⟩$OC_{10}H_{21}$	631.4	66(KS) 64 (K'S)*	114(SN)	168.4(NI)	61.1 45.8 ± 0.2*	0.808 ± 0.01	1.58 ± 0.05	-
27	H_9C_4-⟨⟩CO-⟨⟩CN	279.4	68(KI) 52.5(K'I)*	[38.6KN]		28.2 ± 0.40 21.8 ± 0.2*	[0.532 ± 0.01]		a
28	$H_{11}C_5O$-⟨⟩CO-⟨⟩-CN	309.4	84.5(KI)	[74.1KN]		37.0 ± 0.4	[0.494]		a

†KS = crystal-smectic, SN = smectic-nematic, NI = nematic-isotropic; [ ] = monotropic transition.

*Transition from metastable phase.

a. C. Maze, private communication, does not report SN transition for compound 25. Otherwise agreement for this material is good. Maze data for compound 27 seems to correspond to transition involving metastable crystal. Agreement for compound 28 is good. Maze reports no L_{NI} values.

b. D. S. Hulme, E. P. Raynes, and K. J. Harrison, J.C.S. Chem. Comm., 98 (1974). Agreement is good. L_{NI} not reported.

Barrall and Johnson[1] discuss the effects of sample purity).

For most compounds the KN transition temperatures and enthalpies were determined from two or three DSC runs. Data for only a few materials were based on a single experiment; on the other hand, one material was run eight times. Nematic-isotropic (and other mesophase transition) data were based on an average of four runs (a minimum of two and a maximum of 15). It is seen from the error ranges cited in the tables that reproducibility of the latent heat data is reasonable. All data were derived from DSC spectra taken at scan rates of 5°C/min. Oppenheim[4] and Brennan[5] have discussed the influence of scan rate on measured latent heats. The latent heat data of the present report are, for the most part, in reasonable agreement with the limited number of results available from other sources, indicating that the scan rate used was acceptable.

REFERENCES

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3. G.W. Smith and Z.G. Gardlund, J. Chem. Phys., 59, 3214 (1973).

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5. W.P. Brennan, ibid, paper B1-20.