Thermal Parameters For Crystal-Mesophase And Crystal-Crystal Transitions Of Some Benzylideneanilines

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THERMAL PARAMETERS FOR CRYSTAL-MESOPHASE AND CRYSTAL-CRYSTAL TRANSITIONS OF SOME BENZYLIDENEANILINES

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In previous publications[1,2] temperatures, enthalpies (latent heats) and entropies for liquid crystalline phase transitions of 35 N-(p-alkoxybenzylidene)-p-n-alkylaniline compounds, $C_nH_{2n+1}O-\phi-CHN-\phi-C_mH_{2m+1}$ (abbreviated nO·m), have been reported. The present note completes that study by summarizing thermal parameters for transitions involving crystalline phases of these same materials.

The transition temperatures were determined (as previously by thermal microscopy (TM)[2] and differential scanning calorimetry (DSC).[3] The phases were identified by TM. Transition enthalpies (latent heats) were measured by DSC. Since the precision of DSC measurements is known to be lower than that of adiabatic calorimetry,[4] the present results must be regarded as preliminary. However, at present most thermal data for liquid crystals have been determined by DSC, adiabatic calorimetry having been applied in only a few cases.

The existence of a multiplicity[5,6] of low temperature crystalline states (some of which may be metastable)[5,7] or of glassy phases[8] may have influenced our DSC measurements, in some cases resulting in low transition enthalpies. Although multiplicity and metastability of solid or glassy phases have been noted in some of the nO·m compounds, a detailed investigation of these factors was beyond the scope of this work.

Enthalpies (ΔH) and entropies (ΔS) of transitions involving crystalline phases are given in Table I for compounds with n=1 to 7 and m=4 to 8. In addition, the transitions and their temperatures are identified by the line

TABLE I. Enthalpies (KJ/mol), Entropies (J/mol-deg), for Certain Crystal-Crystal and Crystal-Mesophase Transitions of nO·m Compounds*

n	m=4	m=5	m=6	m=7	m=8
1	13.8,46.9(K20.9N)	22.7,72.4(K39.7N)	27.5,89.2(K35.3N)	18.1,60.3 (K$_2$27N); 33.7,109 (K$_1$35N)	30.9,95.9(K49.3N)
2	17.2,55.7(K35.3N)	24.6,73.3(K63.3N)	25.9,82.9(K39.6N)	26.3,80.8(K52.5N)	31.0,96.7(K47.6N)
3	27.3,86.7(K41.1N)	19.0,62.4(K32.7N)	27.2,86.7(K40.7N)	29.2,96.2(K30.6N)	3.4,11.2(K$_5$29K$_4$); 1.9, 9.5(K$_4$32K$_3$); 16.5,53.3(K$_3$36K$_2$); 10.3,33.2(K$_2$38K$_1$); 6.6,21.1(K$_1$38.9N)
4	1.7, 6.1(K$_2$8K$_1$); 1.9, 6.8(K$_1$12S$_3$)	4.2,14.1(K28S$_2$)	4.2,15.0(K$_3$7K$_2$); 0.2, 0.8(K$_2$22K$_1$); 8.9,30.0(K$_1$26S$_2$)	6.6,22.6(K20S$_3$)	37.2,121.0(K33S$_2$)
5	8.4,29.4(K12S$_2$)	7.1,23.7(K29S$_4$)	23.1,74.7(K36S$_5$)	7.3,25.5(K$_4$12K$_3$); 5.8,19.8(K$_3$19K$_2$); 1.0, 3.5(K$_2$25K$_1$); 2.7, 8.8(K$_1$29.5S$_4$)	35.7,113.0(K43.2S$_2$)
6	1.1, 4.0(K1OS$_3$)	9.7,30.9(K40S$_3$)	11.9,41.4(K15S$_3$)	10.3,34.2(K27S$_2$)	6.4,23.9(K$_2$-5K$_1$); 26.6,87.9(K$_1$29S$_2$)
7	30.2,98.8(K32.2S$_3$)	13.5,45.9(K23S$_4$)	36.6,116.7(K40.4S$_3$)	1.9, 6.2(K$_2$28K$_1$); 16.8,54.8(K$_1$33S$_4$)	40.7,126.9(K48.1S$_2$)

*Data are cited in form ΔH, ΔS(XT$_t$Y) where, ΔH is enthalpy (KJ/mol), ΔS entropy (J/mol-deg), X the low temperature phase, T$_t$ the transition temperature (°C), and Y the high temperature phase.

notation of Verbit[9] using the symbols K (crystal), S (smectic), and N (nematic) with appropriate subscripts where a multiplicity of phases is found. The nature of the smectic phases is discussed in Refs. 1 and 2.

For the most part the crystal-mesophase transition enthalpies of Table I lie within the range of values found for almost 400 other compounds:[10] 7.1 to 117 KJ/mol (1.7 to 28 Kcal/mol). Four compounds (40.4, 40.5, 50.7, and 60.4) exhibit rather low transition enthalpies, suggesting the desirability of further studies on the existence of low temperature solid phases in these materials. Few data for crystal-mesophase transition enthalpies of nO·m compounds have been published. For the crystal-nematic transition of compound 10.4 (MBBA) Barrall, et al.[11] report $\Delta H = 13.6$ KJ/mol, in good agreement with the value of Table I. However, Mayer, et al.[5] using adiabatic calorimetry, found two crystalline phases for 10.4, measuring $\Delta H = 14.7$ KJ/mol for the transition from the metastable crystalline phase to the nematic and $\Delta H = 18.0$ KJ/mol for the transition from the stable crystal. The existence of stable and metastable phases for 20.4 (EBBA) has also been pointed out.[7,11] For the stable KN transition Barrall, et al.[11] have found $\Delta H = 26.8$ KJ/mol, in rather poor agreement with the value of Table I. The disagreement emphasizes the need for further work.

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