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Note

TRANSITION ENTROPIES AND MESOMORPHIC BEHAVIOUR OF *p-n*-ALKOXY-BENZYLIDEN-*p'*-ETHOXYANILINES

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A knowledge of both temperature and heat of transition is necessary for prediction of the mesophase behaviour. From this 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) has greatly facilitated the determination of the temperatures and heats of transition, and a larger number of thermodynamic data are at present available for homogenous series of liquid crystal-forming materials.

As reported in a previous note [1] we have begun a systematic study of the thermodynamic parameters of compounds of general formula $R—C_6H_4—X—C_6H_4—R'$. The present paper concerns a homologous series of compounds of general formula $H_5C_2—O—C_6H_4—N=CH—C_6H_4—O—C_nH_{2n+1}$ with $n = 1, 2, \ldots 8$ (for compounds A, B, ... H, respectively).

The thermodynamic data are reported as supported by Gray and Winsor [2] 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 4--5 h. The water of reaction was removed azeotropically and the product yield was about 80%. In every case the crude products were purified by several crystallizations at low temperature from anhydrous ethanol at constant melting point. The purity of the compounds was tested by GC.

Thermal microscopy (TM)

The transition temperatures were observed using a Galileo polarizing microscope with a 20 × 0.22 objective, and a Mettler FP 52 microfurnace for sample temperature control. Samples were mounted on a glass slide and covered with a glass cover slip. Several measurements were carried out for each compound.

Differential scanning calorimetry (DSC)

A Perkin-Elmer DSC-IB, previously calibrated in terms of temperature and energy using indium as standard, was used for the measurements. Four DSC scans were carried out for each sample. The measurements were recorded at a scan rate of 2°C min^{-1}.

RESULTS AND DISCUSSION

It is well known that the effect of the purity on the heat and temperature transition is very large [3]; therefore attention was paid to purification of the compounds, and the measurements already reported [1] were repeated. Looking at the two sets of measurements, the one involving the larger energy change was assumed to be more correct. A way of minimizing the error of the pre-transition effect included in the measured transition heat was used [4,5].

The temperature T, as well as the ΔH and ΔS values relative to the transition phases on heating the examined compounds are collected in Table 1.

Since the temperature accuracy of TM is greater than that of DSC measurements, the transition temperatures of Table 1 refer to TM measurements, where not otherwise specified. The trend of the transition temperatures for the studied compounds is reported in Fig. 1.

In order to obtain data on monotropic mesophases of compounds, the treatment described below was carried out. The samples were heated from solid to isotropic liquid at 2°C min^{-1}. The isotropic liquid was then cooled at 2°C min^{-1} until the mesophase was formed, but the solid phase had not formed. The mesophases so obtained were reheated under the same experimental conditions to the isotropic liquid. These measurements were repeated four times for each compound. The sample was then cooled to room temperature where the solid phase reformed. The relative transition diagrams are reported below.

On heating, compounds A, B and C melt to give an isotropic liquid, while on cooling they show a monotropic nematic phase detectable in both DSC and TM measurements. In this last situation the nematic phase remains in a supercooled state at room temperature. In this case the reported temperature values refer to DSC measurements.

Compounds D, G, and H show a stable nematic phase before being trasformed to an isotropic liquid.

Compound E shows two intermediate phases; besides a nematic phase

TABLE 1

Transition temperatures T, ΔH and ΔS for each transition phase of the investigated compounds

Compound	Transition *	Temp. transition (K)	ΔH (kcal mole^{-1})	ΔS (cal mole^{-1} K^{-1})
A	K/I	401.8	7.27	18.1
	N/I ←	394.5	≃0.6	1.5
B	K/I	421.6	8.08	19.2
	N/I ←	417.9	≃0.8	2.0
C	K/I	399.1	7.14	17.9
	N/I ←	397.5	≃0.9	2.3
D	K/N	378.3	5.63	14.9
	N/I	403.2	0.37	0.92
E	K_I/K_{II}	356.6	0.66	1.84
	K_{II}/N	374.6	6.06	16.17
	N/I	393.2	0.17	0.43
F	K_I/N	370.2	7.24	19.5
	N/I	395.8	0.32	0.8
	K_{II}/N ← **	≃362		
G	K/N	374.7	9.99	26.6
	N/I	393.3	0.67	1.7
H	K/N	371.6	9.88	26.6
	N/I	392.2	0.36	0.9

* K/I, Solid/isotropic liquid transition; K/N, solid/nematic transition; N/I, nematic/isotropic liquid transition; K_I/K_{II}, solid/solid transition.

** Temperature obtained from DSC thermogram.

← Monotropic transition.

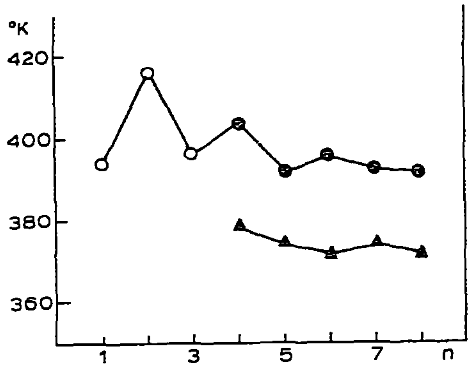
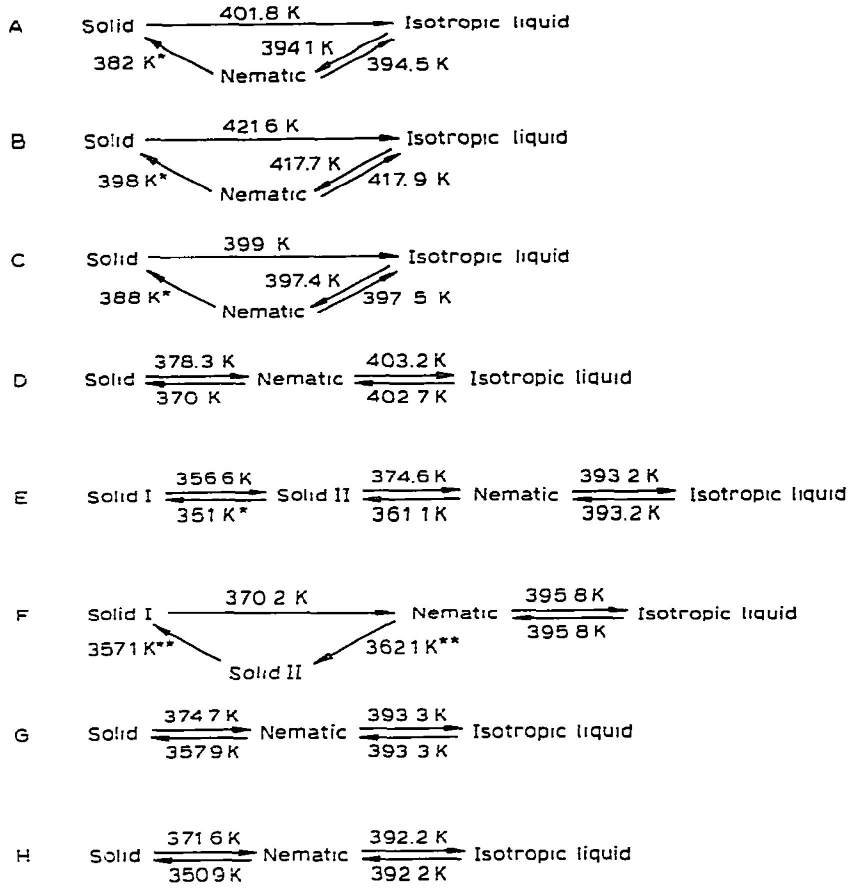


Fig. 1. Effect of alkyl chain length on the transition temperatures: ●, nematic → isotropic liquid; ○, nematic → isotropic liquid (monotropic); ▲, solid → nematic (n = number of carbon atoms in the alkyl chain).

Transition diagrams



* Temperature obtained from DSC measurement

** Transition evident in DSC thermogram only

stable in the 374.6—393.2 K temperature range, a phase stable in the 356.6—374.6 K temperature range already attributed to a smectic structure [1] is shown. Nevertheless, the small ΔS value of this last transition and the fact that compounds G and H with R′ chains longer than that of the E compound do not show smectic phases, led us to believe that this can be a solid—solid transition. An analogous result was reported for the *p-p′*-butyl-azoxy-benzene [7].

On heating, compound F shows only a nematic stable phase while on cooling, an additional solid phase, stable in the 362.1—357.1 K temperature range appears. For this compound the same considerations as for compound E can be made, the difference in this case being that the new phase is a monotropic one, revealing the nematic phase only on cooling.

From an evaluation of the data reported, the characteristic even—odd effect of the clearing temperatures T_c is evident. As expected for molecules of this kind [8], the terminal intermolecular interaction is considered to be stronger in molecules containing odd-numbered chains because the terminal C—C bonds lie in the same direction as the preferred axis of the molecules.

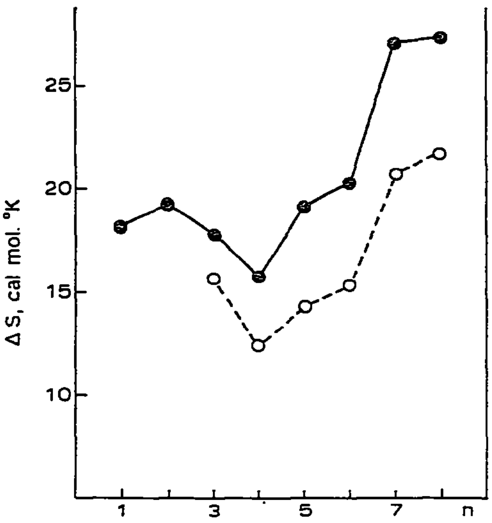


Fig. 2. Effect of the alkyl chain length on the total entropy of transition for: ●, *p*-*n*-alkoxy-benzylidene-*p*′-ethoxy-aniline; ○, *p*-*n*-alkoxy-benzoic acids.

Therefore, the T_c values of the "odd" compounds are always higher than those of the "even" ones.

An evaluation of the total transition entropy (see Fig. 2) shows a different behaviour of compounds G and H with respect to the others. The first, in fact, presents a value of about 27 cal mole^{-1} K^{-1}, while the remaining ones have values close to 18 cal mole^{-1} K^{-1}, which seems to indicate a slight effect of the extension of the alkoxylic chain on the molecular order in the first six members of the series of the considered compounds. Similar behaviour has been reported for the series of *p*-*n*-alkoxy-benzoic acids [6] (dashed line in Fig. 2). In particular, in both cases a minimum of entropy corresponds to butoxy derivatives.

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