Thermochimica Acta, 43 (1981) 107—110
Elsevier Scientific Publishing Company, Amsterdam — Printed in Belgium

Note

LIQUID CRYSTALLINE PROPERTIES OF SOME BENZYLIDENANILINE DERIVATIVES

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(Received 23 June 1980)

Since the discovery of the liquid-crystalline or mesomorphic state [1] much attention has been paid to the correlation of molecular structure with thermal behaviour; in particular, the influence of the nature of various terminal groups on the transition temperature has been extensively investigated in compounds of general formula $R—C_6H_4—X—C_6H_4—R'$, were X is —N=N—, —NO=N—, —CH=N—, —CH=CH, —COO— and R, R′ are generally *para* alkyl or alkoxy groups.

There have been many papers dealing with this problem, some of which are reported in ref. 2; nevertheless, only some of them concern thermodynamic data and moreover, the reported thermal data often refer to work carried out many years ago. Therefore, we have begun a systematic study of the thermodynamic parameters of several classes of mesomorphic com-

TABLE 1

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

Compound	Transition *	Temp. (°C)	Temp. (°C) from lit. data	ΔH (cal mole^{-1})	ΔS (cal mole^{-1} deg^{-1})
A	K/I	125	122	7190	18.06
B	K/I	149.5	143	7580	18.17
	N/I ←	145.7 ←			
C	K/I	126.5	124	7405	18.65
	N/I ←	125.9 ←			
D	K/N	106	106	7475	19.71
	N/I	131	130	306	0.75
E	K/S	83.5		1208	3.38
	S/N	99.5	102	7125	19.12
	N/I	120	119	190	0.48

* K/I = Solid/isotropic liquid transition; K/N = solid/nematic transition; K/S = solid/smectic transition; S/N = smectic/nematic transition; N/I = nematic/isotropic liquid transition; ← = on cooling.

pounds of this kind. The data in this paper concern five molecules of general formula R—O—C_6H_4—CH=N—C_6H_4—O—R′ were R is alternately p-OCH_3 (A), p-OC_2H_5 (B), p-OC_3H_7 (C), p-OC_4H_9 (D), p-OC_5H_{11} (E) and R′ is p-OC_2H_5. The available literature data [3,4] are reported in Table 1.

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 H_2O 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.

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. Special care was taken to ensure clear observation.

Differential scanning calorimetry (DSC)

A Perkin-Elmer DSC model 1B, 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}.

Since the temperature accuracy of TM is greater than that of DSC measurements, the transition temperatures of Table 1 refer to TM measurements.

RESULTS AND DISCUSSION

The temperatures, T, ΔH and ΔS values for each transition phase on heating the investigated compounds are collected in Table 1. In Fig. 1 the DSC thermal behaviour of the E compound is given as an example.

From an evaluation of the results it can be seen that for the A, B and C compounds the ΔH and ΔS values of the solid—isotropic liquid transition (K/I) are comparable within experimental approximation; for the D compound, which shows a nematic phase in the temperature range 106—131°C, ΔH and ΔS values relative to the solid—nematic transition (K/N) are about 25 times greater than those of the nematic—isotropic liquid transition. An analogous result was found for the E compound which exhibits a stable smectic phase in the 83.5—99.5°C temperature range.

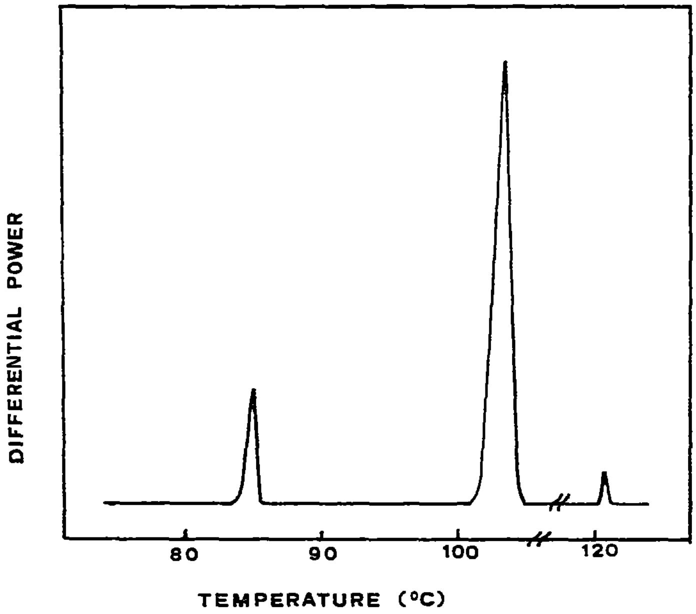

Fig. 1. DSC curve of *p*-pentyloxy-benzilidene-*p*-ethoxy-aniline.

On cooling, the DSC curves of B and C compounds show a new metastable nematic phase which dissappears with the solidification.

Assuming the clearing temperature T_c to be a criterion of the thermal stability of the mesomorphic state, we can correlate its general trend in a homologous series of compounds with changes in the anisotropy of the polarizability, at a first approximation determined by the geometrical anisotropy. The compounds examined here have the essential requirements for mesomorphic behaviour: they are relatively rigid, polar and rod-shaped, and their molecules tend to be oriented with their long axes parallel due to mutual attractive forces. While the presence of a permanent dipole moment does not play a decisive role (many compounds without a permanent dipole moment show, in fact, mesomorphic properties) [5], the mutual interaction, and thus the polarizability of the molecules play a determining role. Therefore, the presence of an alkoxy group as *para*-substituent in molecules of the kind examined increases the polarizability along the long axis more than an alkyl group, increasing the thermal stability, i.e. T_c. Moreover, when the terminal attraction decreases and the lateral one becomes relatively predominant, as in the E compound, the existence of a smectic phase becomes possible. The even—odd effect can also be explained by the mutual interaction, particularly by considering the direction of the polarizability of terminal groups, as suggested by Gray [5]. The terminal intermolecular attraction is therefore considered to be stronger in molecules containing odd-numbered terminal chains, because the terminal C—C bonds are in the same direction as the preferred axis of the molecule, while in the even-numbered chains they make an angle with this axis.

In conclusion, it is evident that for the examined compounds, the determining effect of the chain length on the mesomorphic behaviour and the characteristic even—odd effect is as expected for molecules of this kind.

REFERENCES

1 F. Reinitzer, Monatsh. Chem., 9 (1888) 421.
2 W H. De Jeu and J. Van der Veen, Philips Res. Rep., 27 (1972) 172.
J.P. Van Meter and B.H. Klanderman, Mol. Cryst., 22 (1973) 271.
3 R. Gabler, dissertation, Leipzig, 1939.
4 C. Weigand and R. Gabler, J. Prakt. Chem., 155 (1940) 332.
5 G.W. Gray, Molecular Structure and Properties of Liquid Crystals, Academic Press, New York, 1962.