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CALORIMETRY OF HOMOLOGOUS *p-n*-ALKOXYBENZYLIDEN-*p′*-*n*-PENTYLOXYANILINES

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ABSTRACT

Calorimetric data are presented for the homologous *p-n*-alkoxybenzyliden-*p′*-*n*-pentyloxyanilines. The solid-state polymorphism is discussed in terms of free energy–temperature diagrams.

Trends in the nematic–isotropic liquid transition temperatures, enthalpies and entropies are discussed briefly.

INTRODUCTION

Few systematic calorimetric studies of homologous mesomorphic compounds have been reported [1,2]. With the view of providing such calorimetric data, some time ago we began to study the homologous *p-n*-alkoxybenzyliden-*p′*-*n*-alkoxyanilines. The aim of these studies is to identify the molecular properties required for the existence of mesophases, trough systematic variations of terminal substituents of the common central group $-\underset{|}{C}{=}N-$. Data concerning the compounds have been reported extensively [3–8]. Previous papers [9–11] report the thermodynamic data of the series ethoxy-, propoxy-, and butoxybenzyliden-alkoxyanilines, respectively.

The present paper reports data of the series $H_{11}C_5O{-}C_6H_4{-}N{=}CH{-}C_6H_4{-}OC_nH_{2n+1}$ ($n = 1$–8) for compounds A–H, respectively. The thermodynamic data are presented as supported by Gray and Winsor [12] in K, cal mol^{-1}, and cal mol^{-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 (DSC)

A Mettler TA processor equipped with a DSC-20 cell, 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.

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.

RESULT AND DISCUSSION

The combined results of the microscopic and calorimetric studies are presented in Table 1. The data reported as cycle I were obtained using samples purified and crystallized from anhydrous ethanol; those indicated as cycle II were obtained using as sample the condensed product obtained by cooling from cycle I. The transition temperatures refer to thermal microscopy measurements [13], unless otherwise specified. The DSC measurements were carried out on heating, or on cooling at 4 K min^{-1}, unless otherwise specified. In order to obtain data on monotropic transitions, the procedure reported in ref. 10 was followed.

From an evaluation of the data reported, the peculiarities of each homologue will be delineated, before further discussion of general trends. Figure 1 presents an idealized free energy diagram capable of describing the many phases observed in these compounds.

Compound A. This compound presents a remarkable thermal hysteresis. At a scan rate of 4 K min^{-1} (standard conditions) this compound presents, on heating, only a solid–isotropic liquid transition, with a melting point much lower with respect to the other homologues.

The corresponding ΔH of the first cycle is much greater than the corresponding value of the second and following cycles. On cooling, this compound exhibits, at thermal microscopy, a nematic phase, but the phase is so unstable that only fleeting studies could be performed. The only way to achieve the nematic phase was to cool the sample quickly from isotropic to temperatures lower than ~ 59°C.

TABLE 1

Thermodynamic data for compounds A–H

Compound	Transition	Cycle I			Cycle II		
		T (K)	ΔH (cal mol^{-1})	ΔS (cal mol^{-1} K^{-1})	T (K)	ΔH (cal mol^{-1})	ΔS (cal mol^{-1} K^{-1})
A	$K-I$	341.9	7123	20.8	341.9	4919	14.4
	$I-K$	336.5[a]	4767	14.2	336.5[a]	4873	14.5
B	$K-N$	367.4	7494	20.4	367.4	5354	14.6
	$N-I$	394.0	181	0.46	394.0	186	0.47
	$I-N$	393.9	232	0.59	393.9	208	0.52
	$N-K$	365.0	5228	14.3	365.0	5257	14.4
C	$K-N$	380.3[a]	6401	16.8	380.3[a]	6039	15.9
	$N-I$						
	$I-N$	379.9	168	0.44	379.9	124	0.33
	$N-K$	377.1	5751	15.3	377.1	5663	15.0
D	K^0-I	388.8	6422	16.5	388.8	5924	15.2
	$I-N$	387.8	207	0.53	387.8	220	0.6
	$N-K'''$	386.6	6208	16.1	384.8	1260	3.3
	$K'''-K''$				384.0	4400	11.42
	$K''-K'$				388.8	325	0.9
E	K^0-K'	353.3[a]	580	1.6	353.3[a]	570	1.6
	$K'-I$	386.3	7015	18.2	386.3	7022	1.2
	$I-K'$	382.8[a]	6340	16.6	383.7[a]	6340	16.5
	$K'-K''$	381.2[a]	650	1.7	382.4[a]	550	1.4
	$K''-K'''$	351.0[a]	700	2.0	351.0[a]	700	2.0
F	$K-N$	376.7	5722	15.2	376.7	5550	14.7
	$N-I$	385.6	270	0.70	385.6	250	0.65
	$I-N$	385.3	330	0.86	385.3	290	0.75
	$N-K$	373.2	5675	15.2	373.2	5730	15.4
G	$K-N$	370.7	7740	20.9	370.7	7200	19.4
	$N-I$	382.7	370	0.97	382.7	410	1.07
	$I-N$	382.6	366	0.96	382.6	356	0.93
	$N-S$	371.4	723	1.97	371.4	785	2.11
	$S-K'$	366.6	4013	11.0	365.6	3929	10.8
	$K'-K''$	364.1[a]			364.0[a]		
	$K''-K'''$	353.1[a]	1230	3.5	353.1[a]	1210	3.5
H	K^0-S_1	362.3	8340	23.0	362.3	5627	15.5
	S_1-N	374.9	454	1.2	374.9	414	1.1
	$N-I$	383.9	354	0.9	383.9	320	0.83
	$I-N$	383.7	400	1.0	383.7	400	1.0
	$N-S_1$	374.9	420	1.12	374.9	421	1.12
	S_1-S_2	362.3	429	1.19	362.3	440	1.21
	S_2-S_3	355.1	100	0.3	355.1		
	S_3-K'	352.2	4800	13.7	352.2	4930	14.0
	$K'-K''$	351.1[a]			351.1[a]		

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[a] Temperatures obtained from DSC thermograms.

The nematic phase could be readily discerned as crystallization proceeded rapidly. It was not possible to establish a nematic–isotropic equilibrium temperature. Further, the nematic phase could not be observed with DSC techniques. A similar behaviour was reported for 4-ethoxy-4′-cyclodecanecarbonyloxyazobenzene [14]. The phase behaviour of compound A is presented in Fig. 1a which shows a monotropic-nematic phase and an enantiotropic crystal form.

Compound B. This compound, like compound A, presents a remarkable thermal hysteresis. On heating the virgin product, a solid–nematic transition

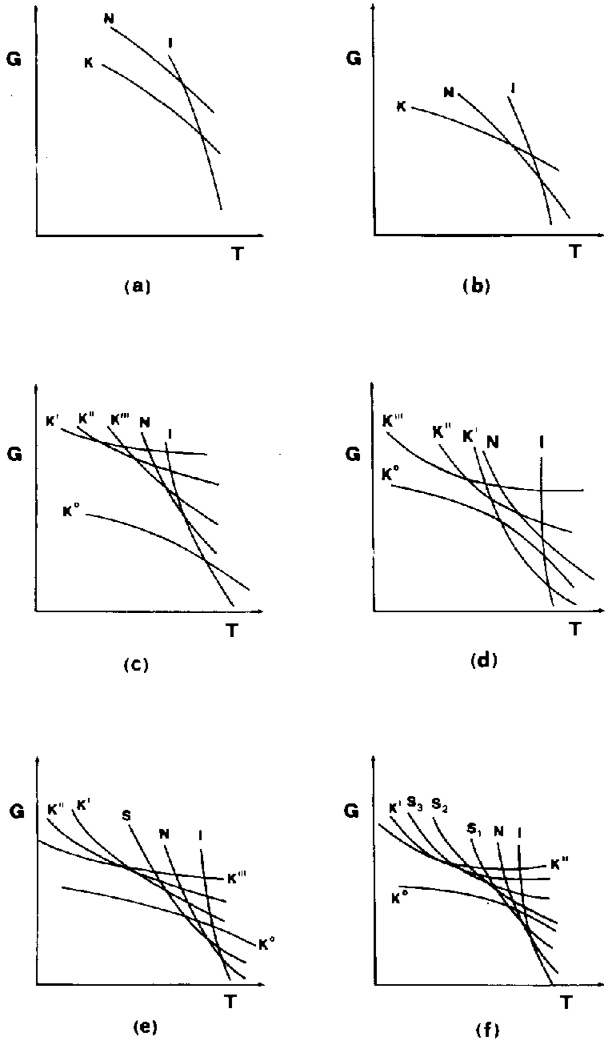

Fig. 1. Idealized free energy, G, vs. temperature, T, diagrams. Slopes are exaggerated for clarity. The temperature scales are not respected. The notation of Verbit [16] is used. (a) Compound A; (b) compounds B, C and F; (c) compound D; (d) compound E; (e) compound G; (f) compound H.

with a ΔH value of about 7500 cal mol^{-1} occurs before clarification. In the following cycles on heating the corresponding ΔH is about 5350 cal mol^{-1}. On cooling, all cycles are coincident within experimental error. Besides a stable nematic phase, a crystal form appears. Figure 1b shows the simple phase behaviour of this compound.

Compound C. This compound presents a moderate thermal hysteresis between first and second cycles, on heating. On cooling, the cycles are coincident within experimental error.

Whilst by thermal microscopy a stable nematic phase appears with a range of thermal stability of about one degree [13], by DSC techniques this nematic phase is neither observed on heating at standard conditions, nor at 0.2 K min^{-1}. The phase behaviour of this compound is again represented by Fig. 1b.

Compound D. This compound presents a moderate thermal hysteresis like compound C, and a thermal cycle like compound A. In this case, however, the monotropic-nematic phase is more stable, and appears in all the DSC thermograms. Moreover, on cooling, this compound exhibits a remarkable polymorphism, showing three crystalline modifications. Figure 1c presents the phase diagram for this compound.

Compound E. As for compound A, the DSC measurements of this compound are not in agreement with those obtained by TM. In fact, no nematic phase is evident in the DSC thermograms, carried out either on heating or on cooling. The only way to achieve the nematic phase was to cool the sample quickly from isotropic to temperatures lower than 108°C. The nematic phase could be readily discerned as crystallization proceeded rapidly. Moreover, in the DSC thermograms monotropic and enantiotropic crystal phases are evident. Figure 1d presents its pertinent phase diagram. Any appreciable hysteresis is presented from this compound.

Compound F. This compound shows a very simple thermal behaviour, which presents a stable nematic phase and no appreciable thermal hysteresis. Its phase behaviour is presented in Fig. 1b.

Compound G. With this homologue, a stable smectic phase appears as well as the stable nematic and isotropic liquid phases. Moreover, a considerable polymorphism is observed on cooling: three crystalline modifications are shown. The crystal smectic transition evident at the TM is unresolved in the DSC thermograms. A moderate thermal hysteresis is present in this compound. The phase behaviour of compound G is presented in Fig. 1e.

Compound H. The *p*-octyloxybenzyliden-*p*′-pentyloxyaniline exhibits a remarkable polymorphism. On heating, a stable smectic and a nematic phase appears as well as the isotropic liquid phase. On cooling, after the nematic and smectic phases, two new smectic monotropic phases appear before two solid–solid monotropic transitions; this last one is not detectable by TM measurements.

Figure 1f presents the phase diagram for this compound. A large thermal hysteresis concerning the crystal–smectic transition which has a ΔH of about 8350 cal mol^{-1} at the first cycle and a value of 5600 cal mol^{-1} in the following cycle. The transitions and the thermal cycle for this molecule are in agreement with those obtained by a spectroscopic method [15]. Figure 1f presents the pertinent diagram. Figure 2 presents the trend of the total transition entropy with respect to the first and second cycles (upper and lower curves, respectively). Although the lower curve shows even–odd alternation, the data referring to the upper curve are scattered, probably due to the solid phase polymorphism which, in the range of temperature investigated, is evident for several of the compounds examined. In considering the entropy of the solid–isotropic liquid transition of other homologous series a similar behaviour is found for the first terms. In every case the present values are lower with respect to those reported for the *p*-*n*-alkoxybenzyliden-*p*′-butoxyaniline [11]. This is in agreement with the conclusion of ref. 13. On the grounds of the schematic molecular arrangement reported in ref. 13, in the present series of compounds the molecular interaction is smaller with respect to the series of the *p*-*n*-alkoxybenzyliden-*p*′-butoxyaniline, and so a smaller average value for the solid–isotropic liquid transition entropy is obtained. Although it seems unreasonable to assume that an alkyl-chain adopts a regular extended zig-zag conformation in the fluid nematic phase, the alternation in the transition entropy can only be explained if some preference for such an extended conformation in fact occurs.

Figure 3 reports the trend for the isotropic liquid–nematic transition, referring to the first thermal cycle. The increasing trend with the lengthening

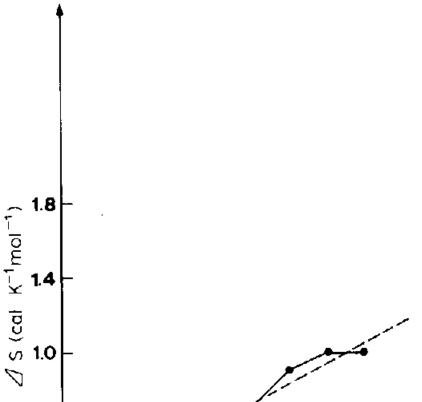

Fig. 2. Effect of alkyl chain length, *n*, on the total transition entropy, ΔS.

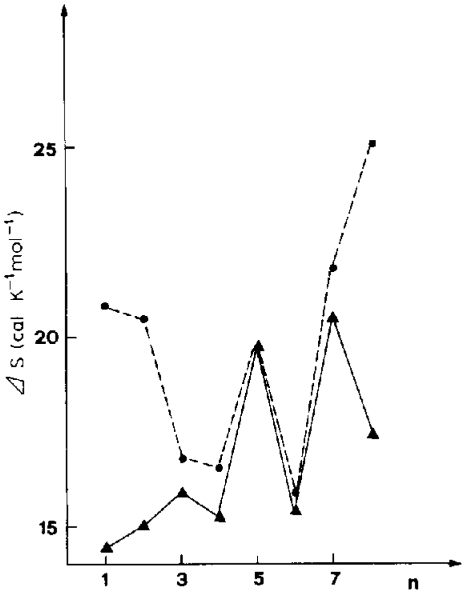

Fig. 3. Effect of alkyl chain length, *n*, on the entropy, ΔS, of the liquid isotropic nematic transition: (●) cycle I; (▲) cycle II.

of the chain suggests that in the nematic phase also, the molecular order increases with the length of the terminal substituents. The increment of $\Delta S_{NI} \simeq 0.1$ kcal mol^{-1} K^{-1} with chain length is much less than the R ln 3 predicted on the basis of a single conformation in the nematic and an infinite number of conformations in the isotropic phase [17]. This suggests that the terminal groups in the nematic phase cannot be restricted to a single elongated conformation. Similar results have been reported for other homologous series [18,19].

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