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CALORIMETRY OF HOMOLOGOUS *p-n*-ALKOXYBENZYLIDEN-*p*′-HEXYLOXY-ANILINES

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ABSTRACT

Transition temperatures, calorimetric data and solid-state polymorphism for the homologous *p-n*-alkoxybenzyliden-*p*′-*n*-hexyloxy-anilines are discussed briefly using experimental data obtained by TM, DSC and free energy-temperature diagrams.

INTRODUCTION

In previous papers [1–5] we have reported the synthesis and the thermodynamic characterization of several series of mesogenic compounds of *p-p*′-dialkoxy-benzyliden-aniline. This paper reports the thermodynamic data for compounds of the general formula $H_{13}C_6O-C_6H_4-N=CH-C_6H_4-O-C_nH_{(2n+1)}$ where $n = 1-8$ (compounds A–H).

Transition temperatures T, enthalpies ΔH and entropies ΔS are reported in units of K, cal mol^{-1} and cal mol^{-1} K^{-1} respectively. The aim of the present work is to study how the systematic lengthening of the terminal chains influences the thermodynamic properties and consequently the mesophase stability for the above compounds.

EXPERIMENTAL

Materials

Commercially available amines and aldehydes were used for 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.

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Differential scanning calorimetry (DSC)

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

RESULTS AND DISCUSSION

Data obtained by TM and DSC for the compounds examined are listed in Table 1. The transition temperatures refer to thermal microscopy measurements, unless otherwise specified. The trend of the transition temperatures was discussed in ref. 6 in relation to the molecular conformation of alkoxy-chains and is consistent with previous reports [7].

The DSC measurements were carried out on heating, or on cooling at 4 K min^{-1}. Data reported as cycle I were obtained using samples purified and crystallized from anhydrous ethanol; those indicated as cycle II were obtained using the condensed product obtained by cycle I.

Figure 1 reports the effect of alkyl chain length on the entropy for the nematic–isotropic liquid transition. It is evident that there is a remarkable increase of the values of ΔS with chain lengthening especially for compounds G and H. This trend can be explained if it is assumed that the molecular order in the nematic phase increases with the molecular length as reported for other series of similar compounds [1,2,5,6].

Figure 2 reports the effect of alkyl chain length on the total entropy ΔS for cycles I and II. It is evident that for most compounds the entropy values for the first cycle are remarkably higher than the values for the second and following cycles. This behaviour can be explained if it is supposed that the original solid phase is different in the two cases. Thus when the melt obtained at the first cycle is condensed, the solid phase so obtained is higher energetically than the "virgin product", and this "metastable" state can be maintained for a long time (weeks or months). More interesting is the general trend that shows a remarkable and progressive decrease of the total entropy passing from compunds A to E, followed by a considerable quasilinear increase on passing from compounds E to H. This clear trend can be explained if it is supposed that the lengthening of the alkoxy chain for the

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^0–K'	364.6 [a]	602	1.7	365.2	305	0.8
	K'–I	378.2 [a]	7639	20.2	378.2	7616	20.1
	I–N	376.3	181	0.5	376.3	147	0.4
	N–K'	354.2	7068	19.9	354.2	7073	19.9
B	K^0–K'	–	–	–	–	–	–
	K'–N	375.4	7675	20.4	375.4	6813	18.2
	N–I	396.6	307	0.8	396.6	285	0.7
	I–N	396.5	242	0.6	396.5	303	0.7
	N–K'	363.0	6986	19.2	363.0	6986	19.2
C	K^0–K'	374.9	7464	19.9	–	–	–
	K'–N	376.1			376.2	6781	18.0
	N–I	382.9	199	0.5	383.2	221	0.6
	I–N	382.7	236	0.6	382.6	234	0.6
	N–K'	368.8	6740	18.3	368.8	6741	18.3
D	K^0–N	376.7	7310	19.4	376.7	6382	16.9
	N–I	390.9	273	0.7	390.9	344	0.6
	I–N	390.6	331	0.8	390.9	291	0.7
	N–K'	374.2 [a]	4740	12.7	374.2	4680	12.5
	K'–K''	364.9 [a]	980	2.7	364.9	980	2.7
E	K^0–N	377.9	5544	14.6	377.9	5237	13.9
	N–I	384.9	272	0.7	384.9	220	0.6
	I–N	384.7	334	0.9	384.7	2636	0.7
	N–K^0	375.2	5667	15.1	375.2	5667	15.1
F	K–N	380.2	6351	16.7	380.2	6308	16.6
	N–I	389.2	304	0.8	389.2	303	0.8
	I–N	388.4	366	0.9	388.4	340	0.9
	N–K	378.7	6464	17.1	378.7	6446	17.1
G	K^0–S	374.2	7444	19.8	374.2	6642	17.7
	S–N	376.0			376.0		
	N–I	386.5	400	1.0	386.5	306	0.8
	I–N	385.6	477	1.2	385.6	408	1.1
	N–S	375.7	644	1.7	375.7	581	1.5
	S–K^0	370.7	6224	16.8	370.7	6224	16.8
H	K^0–S_1	366.9	7907	21.6	366.9	7628	20.8
	S_1–N	380.5	515	1.4	380.5	558	1.5
	N–I	388.0	565	1.5	388.0	480	1.2
	I–N	387.7	639	1.6	387.7	509	1.3
	N–S_1	380.5	451	1.2	380.5	499	1.3
	S_1–S_2	364.2	524	1.4	364.2	431	1.2
	S_2–K^0	359.2 [a]	6351	17.7	359.2	6345	17.7

[a] Temperatures obtained from DSC thermograms.

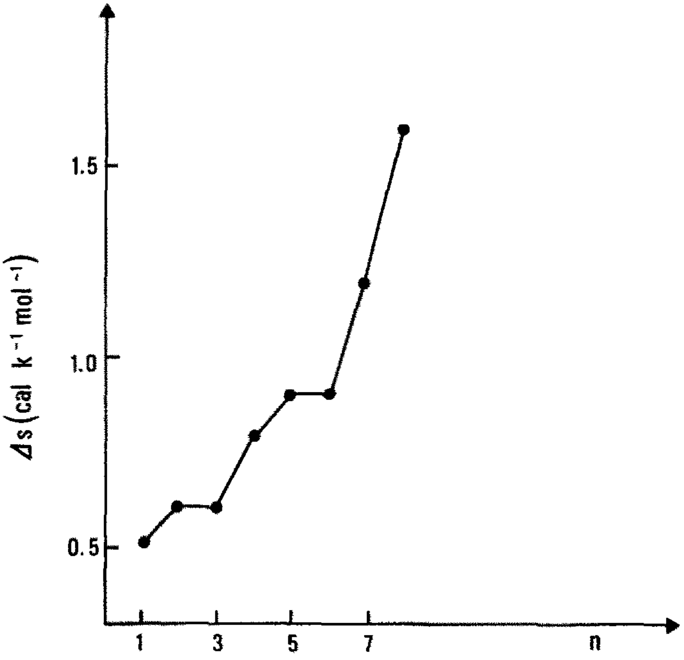


Fig. 1. Effect of alkyl chain length on the entropy of the liquid isotropic nematic transition.

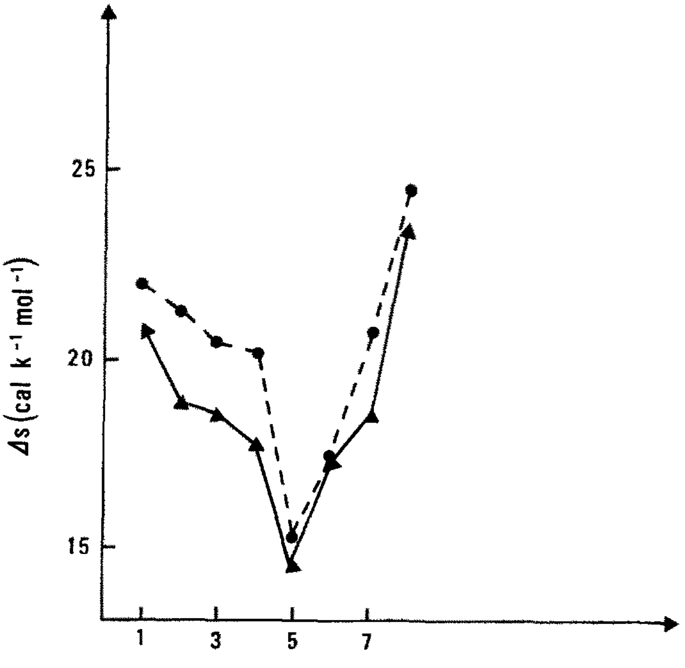
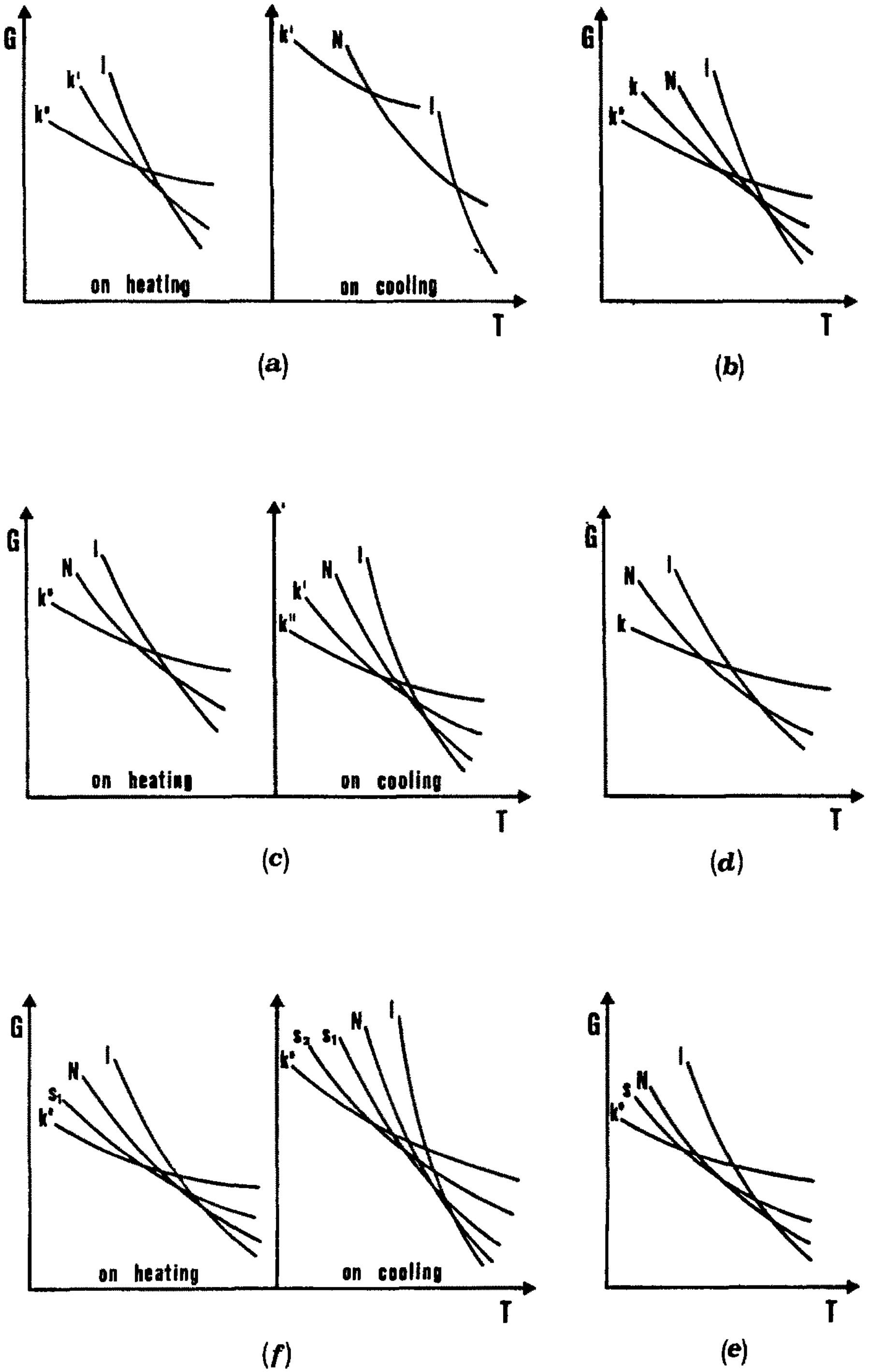


Fig. 2. Effect of alkyl chain length on the total transition entropy: (●) cycle I, (▲) cycle II.



(*a*) (*b*)

(c) (*d*)

(*f*) (e)

Fig. 3. Idealized free energy (G) vs. temperature (T) diagrams. Slopes are exaggerated for clarity. The temperature scales are not respected. The notation of Verbit [8] is used. (a) Compound A; (b) compounds B, C; (c) compound D; (d) compounds E, F; (e) compound G; (f) compound H.

first four terms of the series introduces a progressive disorder in the molecular arrangement due to the possibility of the existence of "non-linear" conformations of the alkyl chain. If the chains are short it can be reasonably supposed that the chain–chain intermolecular interactions do not prevail and a "curl" conformation of the chain is possible. This phenomenon reaches a maximum for a critical length (compound E). For the following compounds, the progressive lengthening of the chain over this critical length gives molecular arrangements more and more ordered due to the increase of the chain–chain interactions.

Figure 3 reports the idealized free energy diagrams capable of describing the many phases observed in above compounds. The peculiarities of each homologue are described below.

Compound A

This compound, on heating, presents no appreciable thermal hysteresis between the first and second cycle. On cooling all cycles are coincident within experimental error. A solid–solid transition is shown by DSC on heating at a scan rate of 4 K min^{-1} (standard conditions) which is not visible at thermal microscopy, whereas on cooling a monotropic nematic phase can be observed before the solidification. The phase behaviour is reported in Fig. 3(a).

Compound B

This compound is shown by thermal microscopy to possess two solid phases at room temperature, undetectable by DSC, and a stable nematic phase. On cooling the solid–solid transition can be observed by DSC only at a scan rate of 0.5 K min^{-1}. A remarkable thermal hysteresis concerns the solid–nematic transition between the two cycles on heating. Figure 3(b) presents the phase diagram for this compound.

Compound C

As with compound B, this product shows a remarkable thermal hysteresis. The DSC thermogram from heating the virgin product shows a solid–solid transition before the stable nematic phase. This solid–solid transition is not shown in the following cycles. On cooling the cycles are coincident. The phase behaviour of this compound is shown in Fig. 3(b).

Compound D

A considerable thermal hysteresis characterizes this product which reveals a stable nematic phase as well as the isotropic liquid phase on heating. On cooling DSC shows another crystalline modification not visible to thermal microscopy. Its phase behaviour is shown in Fig. 3(c).

Compound E

This compound shows very simple thermal behaviour with a stable nematic and a isotropic liquid phase. A little thermal hysteresis only is noted on heating. Fig. 3(d) shows the phase diagram.

Compound F

This compound exhibits a thermal cycle similar to compound E, but with no thermal hysteresis. The phase diagram is shown in Fig. 3(d).

Compound G

As in the previous series [4] this homologue presents a smectic as well as a stable nematic and isotropic liquid phase. This smectic phase, very visible at thermal microscopy is shown by DSC only at a scan rate of 0.5 K min^{-1}. A considerable thermal hysteresis is observed for this compound on heating, whereas on cooling the cycles are coincident. The phase behaviour is reported in Fig. 3(e).

Compound H

A stable smectic and nematic phase on heating characterizes this compound which presents no appreciable thermal hysteresis. On cooling another smectic monotropic phase appears besides the enantiotropic phases mentioned above. Figure 3(f) shows the phase behaviour for this compound.

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