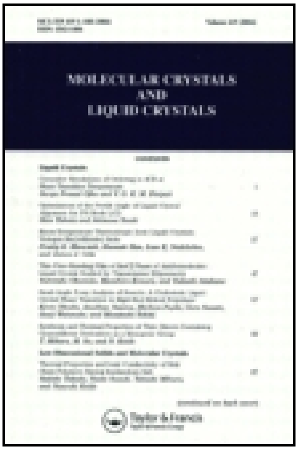

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HOMOLOGOUS 4-ACETYL-4'-N-ALKANOYLOXY AZOBENZENES. CALORIMETRY.

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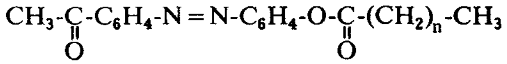
ABSTRACT: *DSC calorimetric measurements on the homologous 4-acetyl-4'-n-alkanoyloxy azobenzenes have been performed. Enthalpy and entropy values trends are presented and discussed.*

INTRODUCTION

In a previous paper[1] we reported on the preparation, thermal behaviour and transition temperatures of a new series of mesomorphic compounds of the general formula



$$CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}C_6H_4\text{-}N=N\text{-}C_6H_4\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}(CH_2)_n\text{-}CH_3$$

with n ranging from zero to sixteen.

In this paper we report the transition energies of each compound as measured from the DSC thermograms obtained with a Perkin-Elmer DSC 1B calorimeter calibrated with Gallium and Indium metal samples (purity 5N). A Mettler type M5 balance (± 0.002 mg) was employed for sample weighing. Peak areas were determined by means of a Salmoiraghi Mod. 308 planimeter (accuracy: 1‰ of the area to be measured). For each compound eight samples, sealed in Aluminum pans, have been examined at least three times. The results are summarized in TABLE 1.

As far as the solid-solid transition enthalpies are concerned only the relevant values for the homologs with n ranging from 7 to 16 are quoted. For n ranging from 0 to 6 no solid-solid transition energy could be measured. The cases, for which special procedures have been applied because of poor separated peaks or poor reproducibility of the DSC curves, are described in some details below.

TABLE 1 Measured transition temperatures, enthalpies and derived entropies for 4-acetyl-4'-n-alkanoyloxy azobenzenes.

n	Transition	Temperature°K	Δ H/R	Δ S/R
0	K_3 I	403.0	3873 ± 45	9.61
1	K_3 K_1	358	---	---
	K_1 S_B	386.5	1923 ± 64	4.98
	S_B S_A	390.0	1186 ± 29	3.04
	S_A N	392.0	704 ± 18	1.80
	N I	399.0	28 ± 2	0.07
2	K_3 K_1	369	---	---
	$K_2^m S_A$	381.5	2430 ± 65	6.37
	N S_A^m	383.0	433 ± 9	1.13
	K_1 N	384.0	3233 ± 33	8.42
	N I	395.0	34 ± 2	0.09
3	K_3 K_1	338	---	---
	K_1 S_A	381.5	2877 ± 50	7.54
	S_A N	384.5	533 ± 14	1.39
	N I	388.0	30 ± 1	0.08
4	K_3 K_1	362	---	---
	$K_2^m S_A$	373.0	2979 ± 55	7.99
	K_1 S_A	379.0	3102 ± 46	8.18
	S_A N	383.0	386 ± 10	1.01
	N I	391.0	40 ± 1	0.10
5	K_3 K_1	333	---	---
	K_1 S_A	373.5	3179 ± 44	8.51
	S_A N	387.0	614 ± 12	1.58
	N I	388.0		
6	K_3 K_2	326	---	---
	K_2 K_1	341	---	---
	K_1 S_A	375.5	3430 ± 50	9.13
	S_A N	389.5	602 ± 13	1.54
	N I	390.0		

TABLE 1 (continued)

7	K_3 K_1	350.0	718 ± 70	2.05
	K_1 S_A	375.5	3610 ± 74	9.61
	S_A I	390.5	680 ± 16	1.74
8	K_3 K_1	349.0	797 ± 65	2.28
	K_1 S_A	378.0	3776 ± 56	9.99
	S_A I	392.5	690 ± 25	1.76
9	K_3 K_1	362.0	1100 ± 55	3.04
	K_1 S_A	377.0	4031 ± 83	10.69
	S_A I	392.0	726 ± 16	1.85
10	K_3 K_1	360.0	1374 ± 80	3.82
	K_1 S_A	379.0	4372 ± 76	11.53
	S_A I	392.0	747 ± 16	1.91
11	K_3 K_1	370.0	1631 ± 52	4.41
	K_1 S_A	379.0	4609 ± 95	12.16
	S_A I	391.5	761 ± 17	1.94
12	K_3 K_1	368.0	1732 ± 56	4.71
	K_1 S_A	380.0	4777 ± 87	12.57
	S_A I	391.0	782 ± 17	2.00
13	K_3 K_1	375.0	2052 ± 87	5.47
	K_1 S_A	381.0	5080 ± 95	13.33
	S_A I	390.5	795 ± 31	2.03
14	K_3 K_1	374.0	1993 ± 34	5.33
	K_1 S_A	381.5	5477 ± 161	14.36
	S_A I	390.0	832 ± 26	2.13
15	K_3 K_1	380.0	2205 ± 124	5.80
	K_1 S_A	382.5	5765 ± 86	15.07
	S_A I	389.0	803 ± 25	2.06
16	K_3 K_1	378.0	1894 ± 86	5.01
	K_1 S_A	384.0	6406 ± 105	16.68
	S_A I	388.5	881 ± 20	2.27

n = 1 (Propanoate)

The thermal behaviour of this compound may be summarized as[1]:

$$\begin{tikzcd}
K_3 \arrow[r, "\sim 358"] & K_1 \arrow[r, leftrightarrows, "386.5"] & S_B \arrow[r, leftrightarrows, "390"] & S_A \arrow[r, leftrightarrows, "392"] & N \arrow[r, leftrightarrows, "399"] & I
\end{tikzcd}$$

The relevant values concerning transition energy for the steps K_1-S_B and S_B-S_A have been obtained from the difference between the measured total energy K_1-N and the contributions S_B-S_A-N and S_A-N.

n = 2 (Butanoate)

Multiplicity and metastability of solid or glassy phases have been noted for this compound for which the proposed thermal behaviour was schematized as[1]:

$$\begin{tikzcd}
K_3 \arrow[r, "\sim 369"] & K_1 \arrow[r, "384"] & N \arrow[r, leftrightarrows, "395"] \arrow[d, leftrightarrows, "383"] & I \\
 & K_2 \arrow[u] \arrow[r, leftrightarrows, "381.5"] & S_A &
\end{tikzcd}$$

The peak areas during the first heating cycle are not reproducible probably because of the existence of the two solids K_3 and K_1. For this reason the transition entropy K_1-N has been measured using samples premelted and successively cooled and left at room temperature for 7 months. The value for the transition K_2-S_A has been computed as explained before, taking the difference K_2-S_A-N and S_A-N.

n = 5,6 (Heptanoate, Octanoate)

For these two compounds only the total energy changes S_A-N-I are quoted because the peaks are too close.

n = 15 (Heptadecanoate)

The enthalpy of the K_3-K_1 transition has been computed, as in the case of the homolog n = 1, by taking the difference between the total K_3-K_1-S_A and K_1-S_A transition energies.

DISCUSSION

FIGURE 1 shows plots of the entropies of each compound (as deduced from TABLE 1) vs the number of $-CH_2$ in the terminal chain.

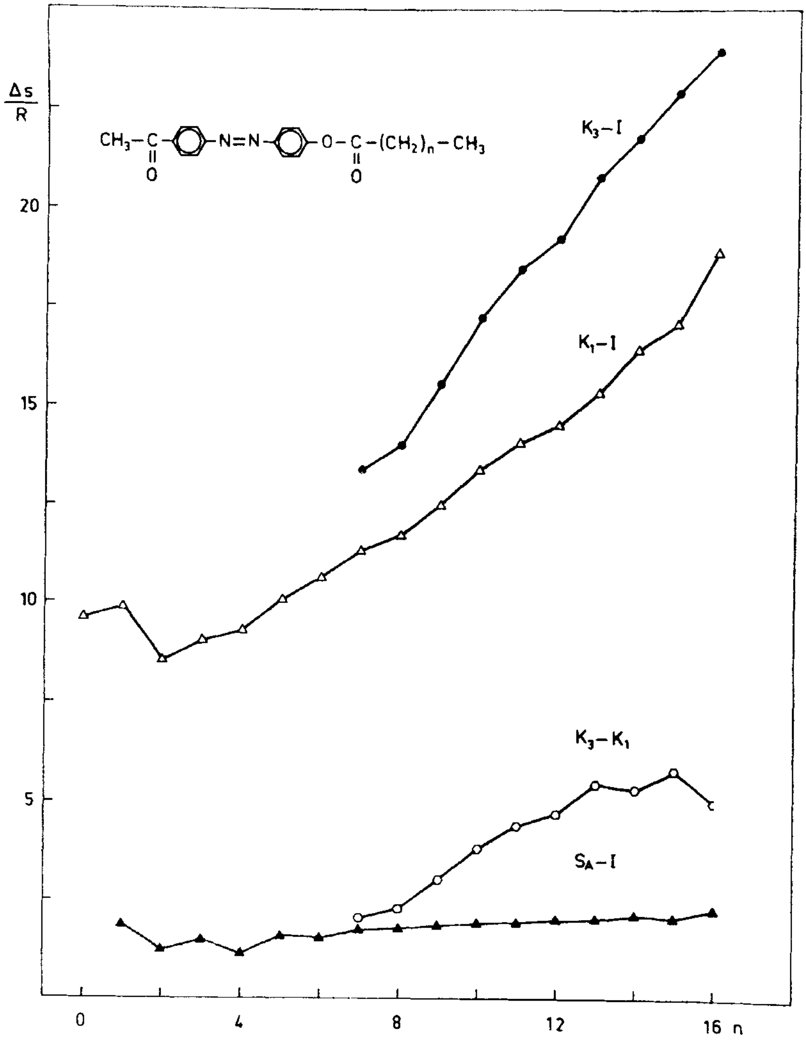


FIGURE 1 Plot of Δ S/R vs n for 4-acetyl-4'-n-alkanoyloxy azobenzenes.

Also if facile arguments cannot always be used in rationalizing fusion entropy changes observed, it may be seen that both enthalpies and entropies relative to either the solid-solid transition or the sum of all the transitions and fusion (K_1-I) increases rather regularly with increasing n.

On the contrary, the entropies for the transitions S_A-I are rather constant even if it is evident for the first homologs the even-odd behaviour observed in other cases[2-4]. This lack of sufficient increments of change in the entropy for each increase in chain length may be tentatively explained as an indication that the terminal alkyl chains do not exist in a single elongated conformation in the S_A and in the nematic state[5].

The monotonous gain in entropy with increasing in the curve K_1-I in FIGURE 1 and the relative high values for the lower homologs ($n = 0$ and $n = 1$) may, on the contrary, tentatively be explained following Bondi[6]. This author reports that alkyl chain segments of long chain molecules may undergo torsional oscillations in the crystal and hindered rotations relative to each other in the liquid. This justifies the rapid rise in ΔS with increasing n and the relatively high values for $n = 0$ and $n = 1$ while, starting with $n = 2$, the rotation begins to be hindered.

The least square slope of the straight line obtained by interpolation of the points of the curve K_3-I is 1.21, very close to the one reported by Bondi[6] for different normal alkyl compounds with orthorombic crystal structure. However, no independent evidences, such as X rays data, are at present available to support the hypothesis of an orthorombic crystal structure.

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