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Giovanni Poeti [a] , Enzo Fanelli [a] & Mario Braghetti [a]
[a] Istituto Chimico della Università di Camerino, Via S. Agostino, 62032, Camerino, Italy
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Liquid Crystalline Phases in 4-Acetyl-4′-*n*-Alkanoyloxy-Azobenzenes

GIOVANNI POETI, ENZO FANELLI and MARIO BRAGHETTI

Istituto Chimico della Università di Camerino,
Via S. Agostino, 62032, Camerino, Italy

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The preparation and melting behaviour of the homologous series of 4-acetyl-4′-*n*-alkanoyloxy-azobenzenes, $CH_3—CO—C_6H_4—N=N—C_6H_4—O—CO—(CH_2)_n—CH_3$, (with *n* ranging from zero to 16) is reported. The melting behaviour has been investigated by means of thermal microscopy and differential scanning calorimetry. The experimental results indicate for almost all the compounds the presence of solid state polymorphism and a type A smectic; for one compound a type B smectic phase is also present. Some homologs present, in addition, a nematic phase.

INTRODUCTION

Compounds of the type $X—C_6H_4—N=N—C_6H_4—Y$, where X and Y are —R, —O—R or —COOR groups, are known to form liquid crystalline phases and have been studied by many authors.

This paper is concerned with the preparation and the melting behaviour of a new series of homologs of general formula

$$CH_3—CO—C_6H_4—N=N—C_6H_4—O—CO(CH_2)_n—CH_3$$

with *n* ranging from zero to sixteen. All the homologs, but the first,[1] show liquid crystalline behaviour and polymorphism in the solid state.

Smectic phases are formed by all the compounds; in addition the first six members (*n* from 1 to 6) present a nematic phase. This one is present only in a few cases with the texture characteristic of a nematic phase. Normally it is yellow black under polarized light, it flashes when pressure is applied on the cover slip and its transition to the isotropic liquid occurs through the fast formation of a schlieren texture.

For the homologs forming the nematic phase, the experimental results suggest the existence of two or three solid phases with very slow crystal-crystal conversion rates. Beginning with $n = 7$ the solid-solid transitions are, on the contrary, relatively fast when the sample is molten for the first time. For the homologs with $n > 10$ the same transitions are present and well defined also in samples repeatedly molten and solidified.

EXPERIMENTAL

Preparation of 4-acetyl-4'-*n*-alkanoyloxyazobenzenes

The homologs with *n* from zero to two were prepared using a modification of the procedure suggested by Chattoway.[2,3] The remaining compounds were prepared by reacting 4-(4'-Acetylphenylazo) phenol with the corresponding acyl chloride. 4-(4'-Acetylphenylazo) phenol was obtained from phenol and the corresponding diazonium salt prepared from 4-aminoacetophenone (Fluka).

The final products were crystallized from ethanol until the mesophase-isotropic transitions were constant. All the compounds were dried under vacuum before use and checked by elemental analysis and NMR spectroscopy.

Differential scanning calorimetry

The DSC traces were obtained with a Perkin Elmer DSC-1B instrument. The samples, (4 to 9 mg), were encapsulated in hermetically sealed aluminum sample pans in a nitrogen filled dry-box.

Heating and cooling rates were between 0.5 and 8°K/min.

Thermal microscopy

A Reichert hot stage Polarizing Microscope (mod. Neopan) equipped with a Asahi Pentax K2 photographic camera, was used for texture observations and transition temperature determinations. The temperature scale was calibrated using dried Reichert standards.

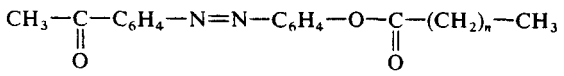
The reproducibility of the transition temperatures was within ± 0.5°K.

RESULTS AND DISCUSSION

Table I summarizes the results of the DSC measurements and of the microscopic observations; the temperatures quoted in the table are those measured with the microscope. The behaviour of the first six homologs will be described

TABLE I

Transition temperatures for



n	Transition		Temperature °K
0	K_3	I	403
1	K_3	K_1	358[a]
	K_1	S_B	386.5
	S_B	S_A	390
	S_A	N	392
	N	I	399
2	K_3	K_1	369[a]
	K_2	S_A	381.5
	S_A	N	383
	K_1	N	384
	N	I	395
3	K_3	K_1	338[a]
	K_1	S_A	381.5
	S_A	N	384.5
	N	I	388
4	K_3	K_1	362[a]
	K_2	S_A	373
	K_1	S_A	379
	S_A	N	383
	N	I	391
5	K_3	K_1	333[a]
	K_1	S_A	373.5
	S_A	N	387
	N	I	388
6	K_3	K_2	326[a]
	K_2	K_1	341[a]
	K_1	S_A	375.5
	S_A	N	389.5
	N	I	390
7	K_3	K_1	350
	K_1	S_A	375.5
	S_A	I	390.5
8	K_3	K_1	349
	K_1	S_A	378
	S_A	I	392.5
9	K_3	K_1	362
	K_1	S_A	377
	S_A	I	392
10	K_3	K_1	360
	K_1	S_A	379
	S_A	I	392

TABLE I (continued)

n	Transition		Temperature °K
	K_3	K_1	370
11	K_1	S_A	379
	S_A	I	391.5
	K_3	K_1	368
12	K_1	S_A	380
	S_A	I	391
	K_3	K_1	375
13	K_1	S_A	381
	S_A	I	390.5
	K_3	K_1	374
14	K_1	S_A	381.5
	S_A	I	390
	K_3	K_1	380
15	K_1	S_A	382.5
	S_A	I	389
	K_3	K_1	378
16	K_1	S_A	384
	S_A	I	388.5

[a] Approximate values read with the microscope.

in some details because of its complexity. The other homologs present a very similar behaviour and only nonanoate will be described as an example.

The different solid phases are named following the notation of Verbit.[4] Identification and classification of the different mesophases were made from texture observations under the polarizing microscope and comparison with the literature criteria.[5–10]

$n = 0$ (*Etanoate*)† As already reported in the literature[1] the compound melts giving an isotropic liquid. The melting temperature (403°K) is in agreement with the reported value.

$n = 1$ (*Propanoate*) Four transitions are clearly seen at 386.5, 390, 392 and 399°K; a fifth one may be located around 358°K when the crystals change color.

In order of increasing temperature the four transitions correspond to the formation of a type B smectic, a type A smectic, a nematic phase and the isotropic liquid.

† The individual homologs are named by their parent acid.

The DSC curves show, during heating, four transitions; during the reverse process the solidification is very slow and occurs with considerable supercooling.

Exothermic peaks are sometimes observed during the heating of previously solidified samples indicating partial crystallization.

$n = 2$ (*Butanoate*) The behaviour of butanoate is complex because of the existence of solid modifications with very slow interconversion rates. This results in a strong dependence of the DSC curves on the thermal history of the sample and on the heating and cooling rates.

In Figures 1 and 2 are shown some DSC curves obtained by heating different samples at 0.5 and 2°K/min respectively. The first curve in each figure refers to a sample crystallized from ethanol and the following ones to the same sample after solidification and different times at rest at room temperature. As may be seen, at low heating rate (Figure 1a), the melting peak at 384°K is preceeded by an endothermic-exothermic peak that is not seen at a higher heating rate (Figure 2a).

A common feature in both cases is the transition to the isotropic liquid (395°K) that is present also in the cooling curves (Figures 1–2f) and whose position does not depend on the thermal history of the sample or on the heating rate.

The other heating curves are similar to the first one only if they are performed after comparable times at rest. The initial curve (1a) may in fact be reproduced, at least in its more important features, only when the samples are left at rest at room temperature for several months.

If the sample is heated immediately after the first solidification, the peak at 384°K is not present any more and two new transitions appear at 381.5 and 383°K.

The peak at 383°K is always smaller than the one at 381.5°K and both decrease with increasing time at rest with the simultaneous reappearance of the peak at 384°K. This one grows until it becomes the only transition present when the time at rest is of the order of some months.

If the DSC curve is recorded during cooling (Figures 1–2f) only three exothermic transitions are always present. When the heating rate is greater than 0.5°K/min a broad endothermic peak preceeds the melting process, (Figure 2a, shaded area). Such a transition is not seen under any other circumstance unless the sample is recrystallized from ethanol. This behaviour may be explained by supposing the existence of monotropic phase S_A and of three crystal modifications: K_3–K_2–K_1.

Three different crystal forms may be seen from Figure 3. These have been obtained at the microscope by using the same heating rate of the DSC study.

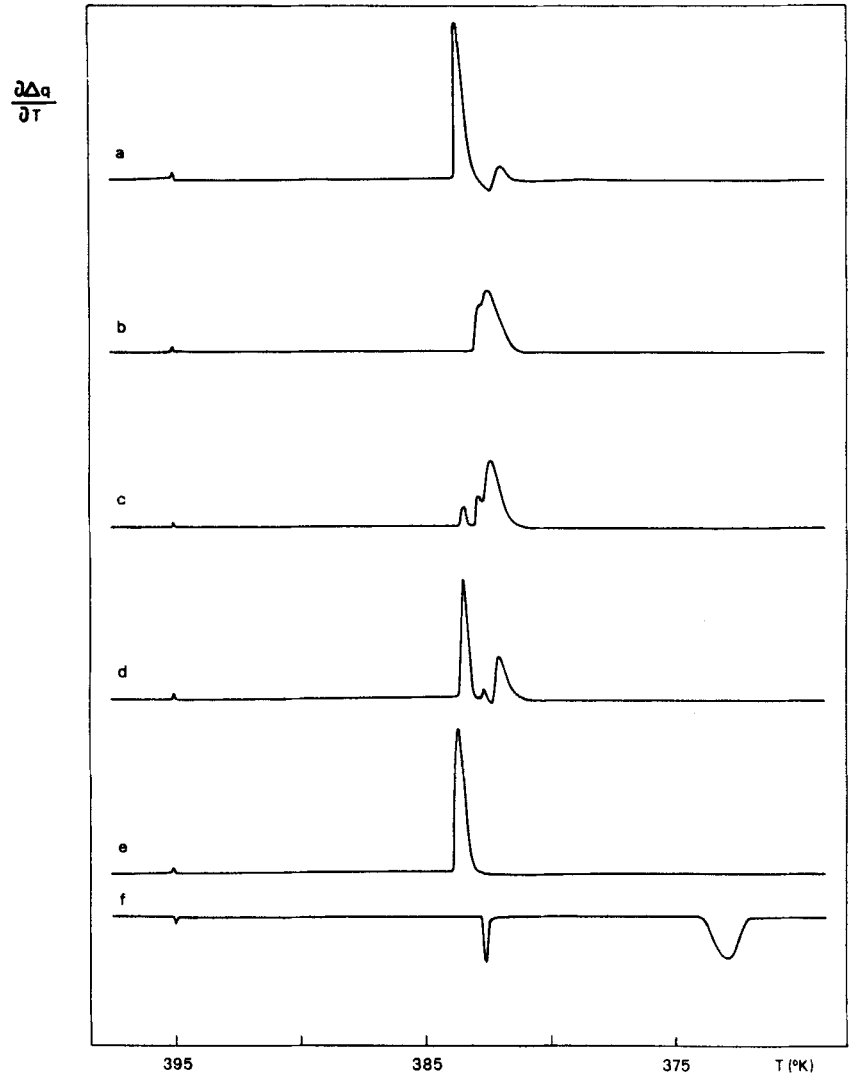


FIGURE 1 Thermograms of 4-Acetyl-4′-*n*-Butanoyloxy azobenzene ($n = 2$), taken on samples of similar weight at the same sensitivity range and chart speed. Scan speed 0.5°K/min. (a) first heating curve. (b) sample heated immediately after solidification. (c) sample heated after 30 minutes. (d) sample heated after 90 minutes. (e) sample heated after 60 days at rest at room temperature. (f) cooling thermogram.

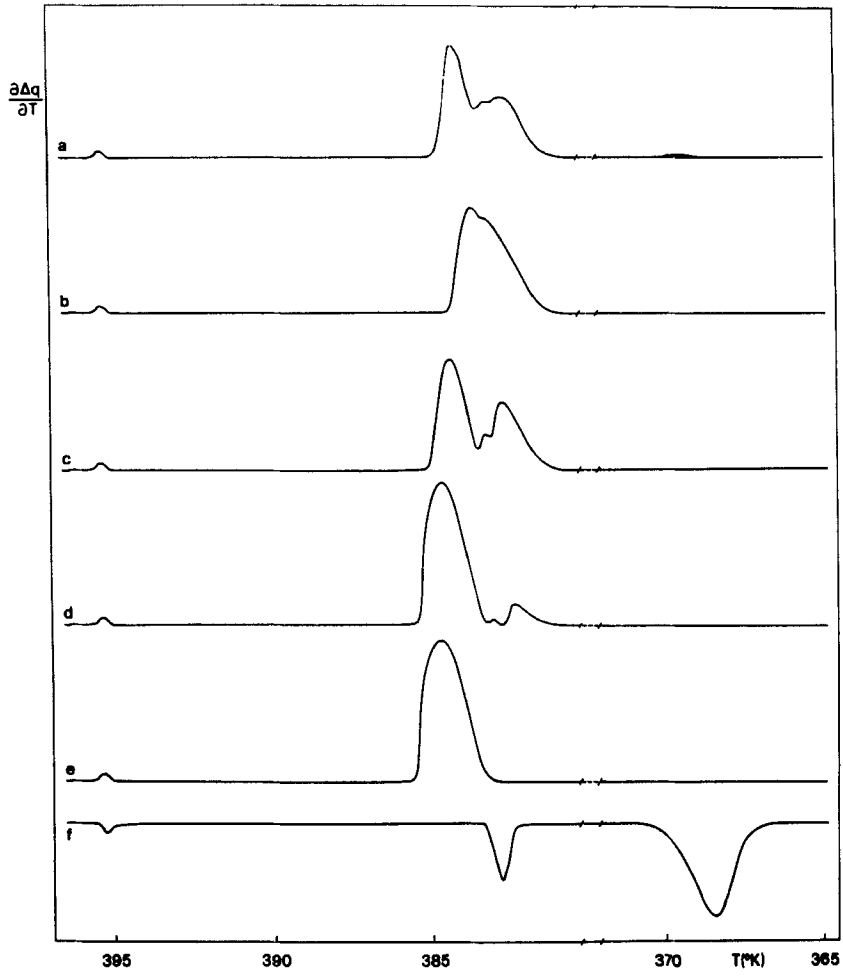
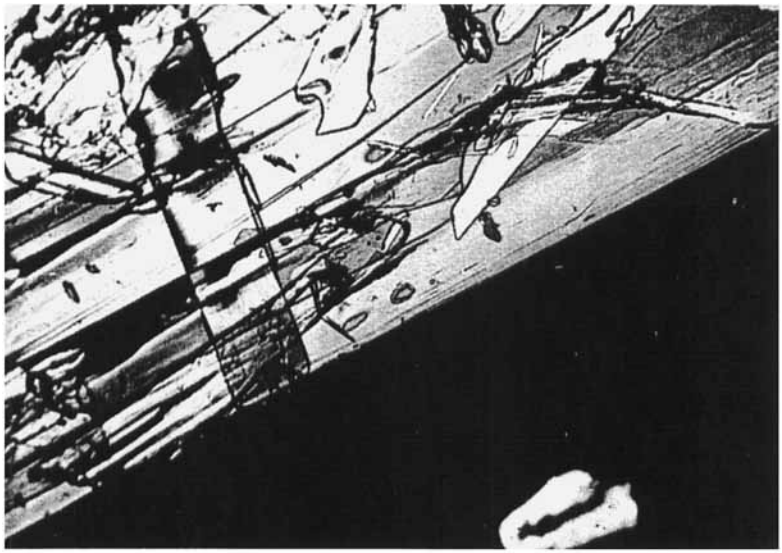
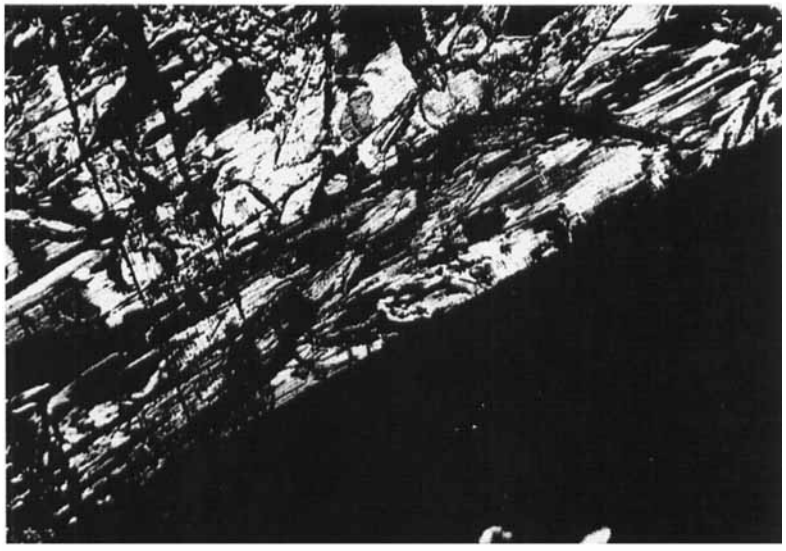


FIGURE 2 Thermograms of 4-Acetyl-4′-*n*-Butanoyloxy azobenzene ($n = 2$), taken on samples of similar weight at the same sensitivity range and chart speed. Scan speed 2°K/min. (a) first heating curve. (b) sample heated immediately after solidification. (c) sample heated after 180 minutes. (d) sample heated after 300 minutes. (e) sample heated after 60 days at rest at room temperature. (f) cooling thermogram.



(a)



(b)

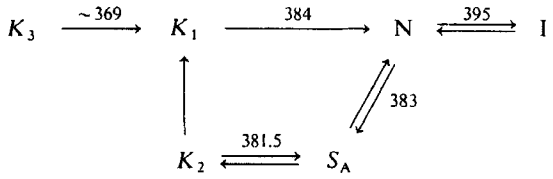
FIGURE 3 Photomicrographs taken on the same sample of 4-Acetyl-4′-*n*-butanoyloxy-azobenzene ($n = 2$) between glass slides, crossed polarizers, magnification ca. 70×. (a) crystal form obtained from ehtanol at room temperature. (b) the sample as seen at 376°K during the slow transition $K_3 \rightarrow K_1$.

(c)

(d)

FIGURE 3 Photomicrographs taken on the same sample of 4-Acetyl-4′-*n*-butanoyloxy-azobenzene ($n = 2$) between glass slides, crossed polarizers, magnification ca. 70 ×. (c) K_1 phase obtained after superheating, melting of K_3 and recrystallization. (d) formation of K_2 phase from smectic A while cooling.

The possible transitions are schematized in the following diagram:



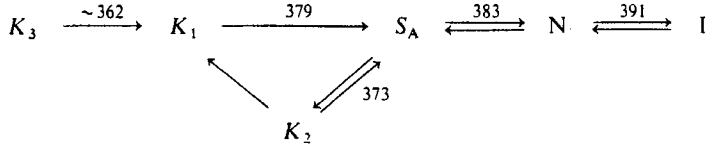
K_3, the crystal form obtained from ethanol, (Figure 3a) is slowly transformed (Figure 3b) in K_1 that, at 384°K, gives the nematic phase. If the heating rate is too high, K_3 may superheat, melt and recrystallize to give K_1 (Figure 3c).

During the cooling process the isotropic liquid gives the smectic A and the metastable solid K_2 (Figure 3d) that is slowly transformed at room temperature into thermodynamically stable solid modification K_1.

$n = 3$ (*Pentanoate*) The experimental data seem to indicate also for pentanoate the existence of two crystal modifications K_3 and K_1 (Table I), where K_3 is the product crystallized from ethanol. The transition K_3–K_1 is very broad and may be seen only in the first DSC curve.

K_1 melts at 381.5°K giving a type A smectic and a nematic phase at 384.5°K. The transition N–I is at 388°K. As was the case for propanoate, exothermic peaks are observed during heating of samples previously molten and solidified indicating partial crystallization. The microscopic observations are consistent with the calorimetric data.

$n = 4$ (*Hexanoate*) Also for this homolog the behaviour depends on the thermal history of the sample as it may be seen from Figure 4 and Figure 5. The microscopic observations and the DSC curves may be rationalized using the diagram



where three crystal forms are postulated.

K_3, obtained from ethanol, gives K_1 with a very slow and broad transition. The transformation can be easily seen at the microscope because K_3 is coloured and becomes grey between 353 and 363°K.

The other endothermic events observed, in order of increasing temperature, are K_1–S_A, S_A–N, N–I (Figure 4a). If the DSC curve is recorded during cooling (Figure 4e), the transitions observed, in order of decreasing temperature, are I–N, N–S_A, S_A–K_2. The solid–solid transition from the metastable

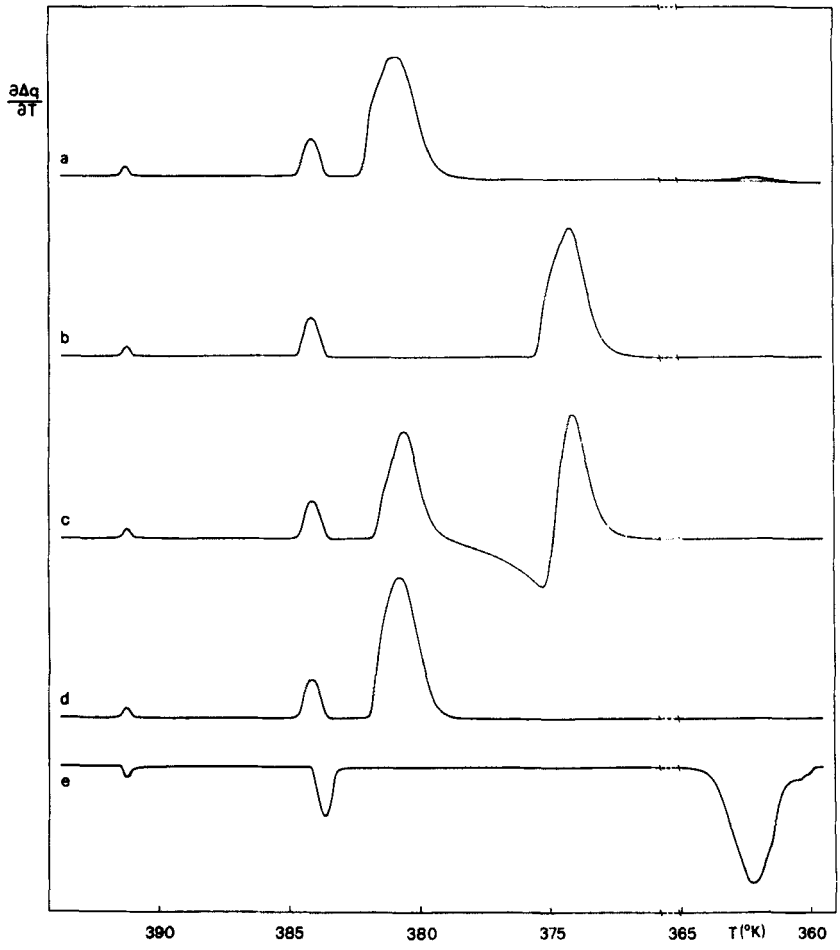
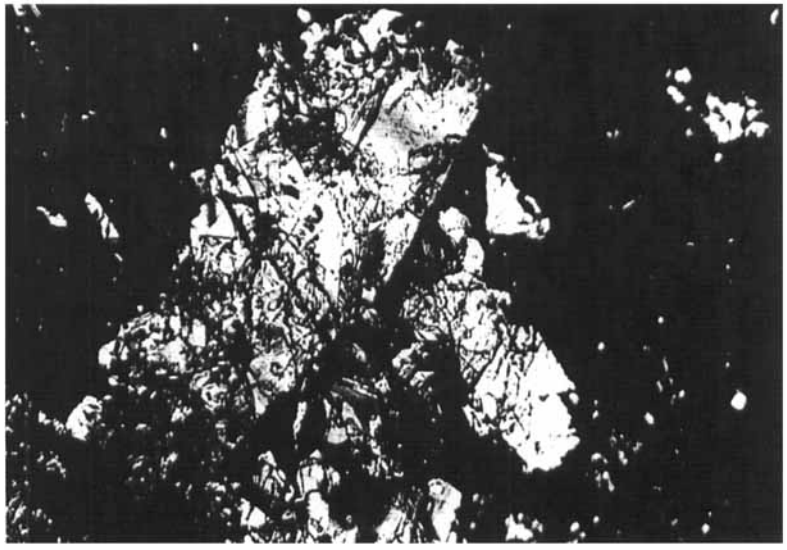


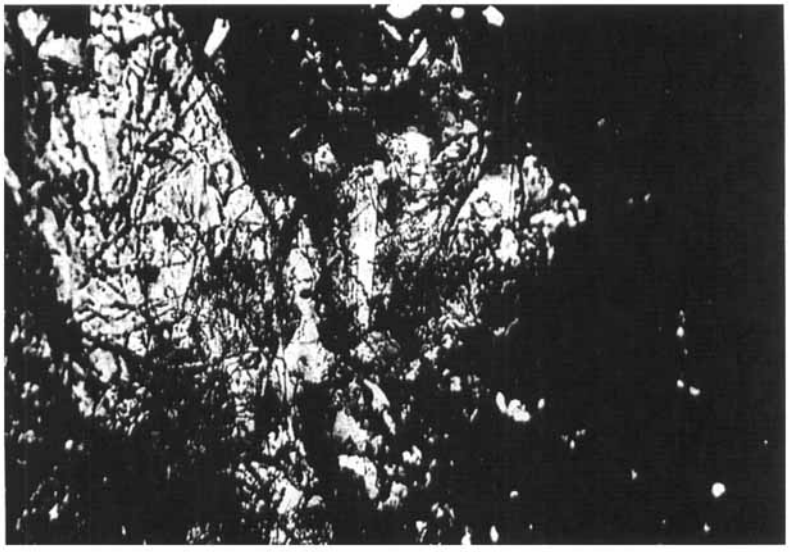
FIGURE 4 Thermograms of 4-Acetyl-4′-*n*-Hexanoyloxy azobenzene ($n = 4$) taken on samples of similar weight at the same sensitivity range and chart speed. Scan speed 2°K/min. (a) first heating curve. (b) sample heated immediately after solidification. (c) sample heated after 50 minutes. (d) sample heated after 60 days at rest at room temperature. (e) cooling thermogram.

phase K_2 to K_1 is very slow as it may be seen from the DSC curves obtained by heating the solidified samples after some time at rest.

For intermediate times the solid is a mixture of K_1 and K_2 and the melting of K_2 is followed by crystallization on the preexisting K_1 crystals and by the transition K_1–S_A (Figure 4c). The transition K_2–S_A (Figure 4b) is the only transition present in samples heated immediately after the solidification. If the time at rest is very long (Figure 4d) only the transition K_1–S_A is seen. A

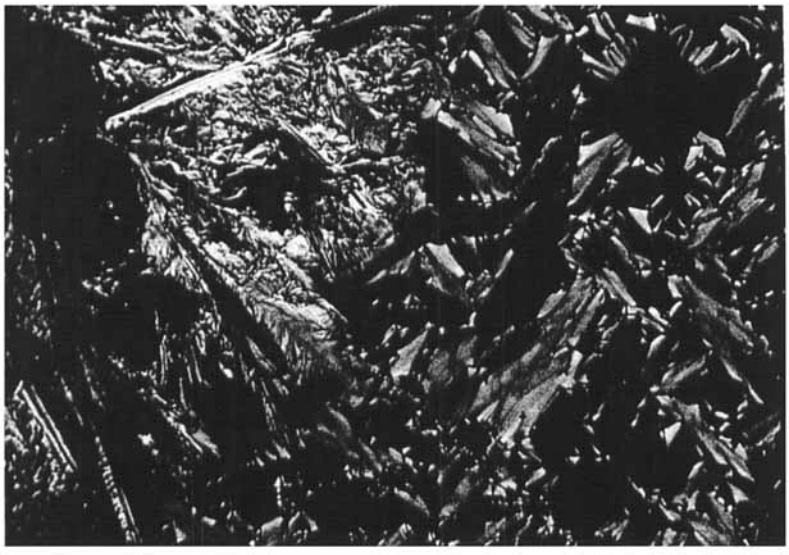


(a)



(b)

FIGURE 5 Photomicrographs taken on the same sample of 4-Acetyl-4′-*n*-Hexanoyloxy-azobenzene ($n = 4$) between glass slides, crossed polarizers, magnification ca 70×. (a) crystal form obtained from ethanol at room temperature. (b) the sample as seen at 364°K during the slow transition $K_3 \rightarrow K_1$.



(c)

(d)

FIGURE 5 Photomicrographs taken on the same sample of 4-Acetyl-4'-*n*-Hexanoyloxy-azobenzene ($n = 4$) between glass slides, crossed polarizers, magnification ca. 70 ×. (c) formation of K_2 phase from smectic A, while cooling. (d) K_1 phase.

similar behaviour was reported by several authors[11,12] for some nematogenic azobenzene derivatives.

$n = 5$ (*Heptanoate*) The transitions presented by this compound are, in order of increasing temperature, K_3–K_1, K_1–S_A, S_A–N and N–I. The solid–solid transition K_3–K_1 is very slow, as was the case for $n = 3$, and is seen at the microscope as a change in color of the crystals.

For this reason the transition temperature can be determined only approximately.

$n = 6$ (*Octanoate*) Three crystal modifications are characteristic of this compound, but the transitions K_3–K_2 and K_2–K_1 are, as before, slow and broad and the temperatures are difficult to determine.

K_1 is seen as a grey crystal that melts at 375.5°K giving a type A smectic. The transition S_A–N and N–I are very close together and cannot be resolved at all in the DSC curve also at very low heating rate. The same behaviour, except for the K_3–K_2, is seen in the cooling curves.

$n = 7$ (*Nonanoate*) K_3, the form obtained from ethanol, gives K_1 at 350°K. The other transitions are K_1–S_A, S_A–I at 375.5°K and 390.5°K respectively. The same transitions are seen during a cooling process with the exception of the first.

The remaining homologs present a behaviour similar to the one described for $n = 7$ and will not be described in detail. The relevant data are summarized in Table I.

CONCLUSIONS

Characteristic features of this series of homologs are polymorphism in the solid state and formation of smectic mesophases. As is the case for other series of homologs based on a terminal hydrocarbon chain, a rather drastic change in behaviour occurs in correspondence of the homolog with $n = 6$. Figure 6 shows a plot of the transition temperatures as a function of the number of carbon atoms in the hydrocarbon chain. For $n = 6$ the trend of the transition temperature changes, the N phase is no longer present and the transition temperatures for the homologs with n even and odd come closer and closer.

In the case of the K–K transitions, for values of n less than 6, even terms have higher transition temperatures, while the reverse is true for the homologs with n greater than 6. A similar behaviour is, at present, unexplained and only a detailed X-ray study may probably clarify the problem. By

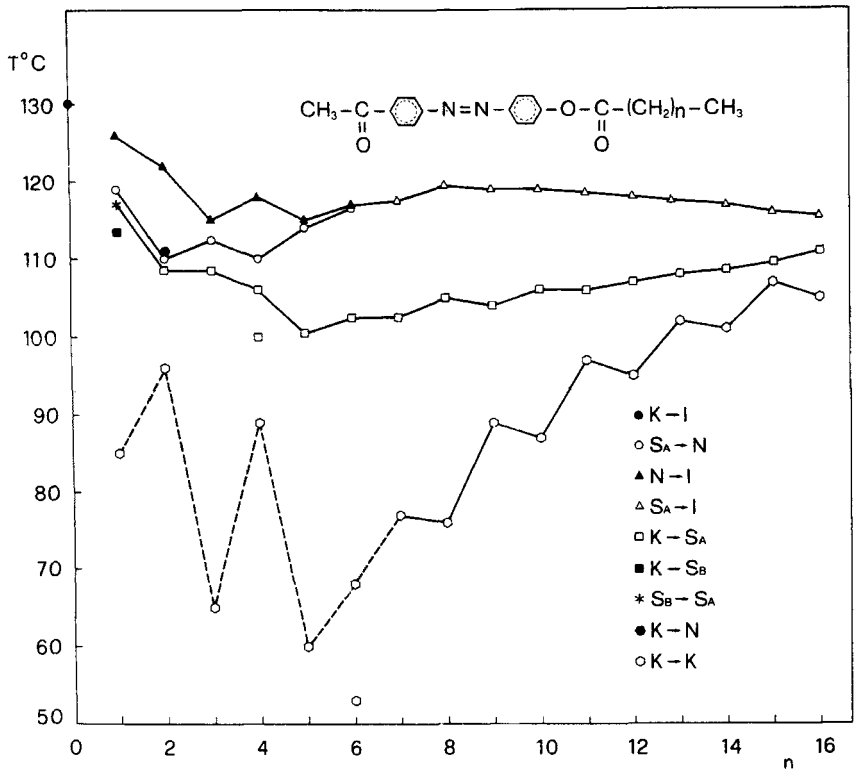


FIGURE 6 Effect of chain length on the transition temperatures for 4-Acetyl-4'-*n*-Alkanoyloxy azobenzenes.

comparing the present results with other regarding 4-alkoxy-4'-acyloxyazobenzenes[11–13] it may be observed that the introduction of an acetyl group in place of an alkoxy gives products with higher melting points and also provide the molecules with sufficient lateral attractive forces to cause smectic formation.

The first homolog of the series does not have any mesophase because of its high melting point, while at the level of $n = 7$ the terminal interactions are so weak that the only mesophase present is the smectic one.

A paper concerning the quantitative thermodynamic data on the same series of homologs is in preparation.

Acknowledgements

We are indebted to Mr. Lucio Amici for his collaboration in solving some technical problems.

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