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Mesomorphic Behavior of Some 4-*n*-Butyryl-4′-*n*-alkanoyloxy Azobenzenes. A New Series of Liquid Crystal Compounds.

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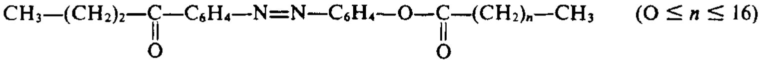
New esters of the type



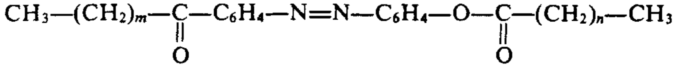
$$CH_3-(CH_2)_2-\underset{\underset{O}{\|}}{C}-C_6H_4-N{=}N-C_6H_4-O-\underset{\underset{O}{\|}}{C}-(CH_2)_n-CH_3 \qquad (0 \leq n \leq 16)$$

have been synthetized and their mesomorphic behavior studied by optical methods, X-ray diffraction and differential scanning calorimetry. Smectic and/or nematic phases have been observed for all the homologs. A complex polymorphism has been found for the smectic phases in some cases.

INTRODUCTION

The preparation and characterization of new liquid crystals is an important step in the understanding of the properties relating molecular structure and mesogenic behavior.

The present paper is concerned with the preparation and the thermal characterization of compounds of general structure:



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

with $m = 2$ and n ranging from 0 to 16. Previous work was concerned with similar compounds with $m = 0$[1,2] $m = 1$.[3] The thermal behavior of each homolog has been characterized by DSC, optical measurements and X-ray diffraction.

EXPERIMENTAL

Synthesis

The 4-*n*-butyryl-4′-*n*-alkanoyloxy azobenzenes have been prepared using 4-aminobutyrophenone (Kodak) and following the procedure previously described.[3]

Each compound has been crystallized from ethanol, redissolved in the same solvent, treated with activated carbon and further crystallized until the transition to the isotropic liquid was found constant.

Structure and/or purities of the products were checked by IR, NMR, HPLC and elemental analysis.

As already reported for the other series[3] the results obtained with HPLC have shown the existence of a cis-trans equilibrium in solution.

PHYSICAL MEASUREMENTS

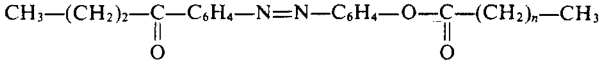
Transition temperatures and phases identification have been made using a Reichert polarizing microscope in conjunction with a Mettler FP 52 heated stage and control unit. The thermal behavior has been studied using a differential scanning calorimeter (Perkin-Elmer DSC-1B). The transition temperatures listed in the Results Section have been determined, unless otherwise indicated, with the microscope with a precision of ±0.5°K. The X-ray diffraction measurements were performed by using a conventional X-ray powder diffractometer with a hot stage controlling the temperature to ±0.1°K. The details of the technique can be found in Ref. 4 and 5. Moreover the photographic techniques associated to a Searle Camera for X-ray small angle scattering were used.

RESULTS AND DISCUSSION

Table I reports the transition temperatures of the compounds studied. The same data are shown in graphical form in Figure 1 where the temperature stability range of each compound is plotted vs. the

TABLE I

Transition temperatures for



$CH_3—(CH_2)_2—\underset{\underset{O}{\|}}{C}—C_6H_4—N{=}N—C_6H_4—O—\underset{\underset{O}{\|}}{C}—(CH_2)_n—CH_3$

n	Transition		Temperature °K
0	K	I	398.0
	I	N^m	390.5
	N^m	K	*385.5
1	K	N	397.0
	N	I	398.0
	N	S_A^m	393.5
	S_A^m	K	*388.5
2	K_1	S_A	383.0
	S_A	N	392.5
	N	I	396.5
	S_A	S_1^m	379.5
	S_1^m	S_2^m	372.5
	S_2^m	K_1	*360.5
3	K	S_1	363.0
	S_1	S_A	377.0
	S_A	I	392.5
	S_1	K	—
4	K	S_A	373.0
	S_A	N	391.5
	N	I	392.5
	S_A	S_1^m	367.0
	S_1^m	K	*348.5
5	K_1	S_A	368.0
	S_A	I	392.5
	S_A	S_1^m	361.5
	S_1^m	S_2^m	353.0
	S_2^m	K_1	*349.5
6	K	S_A	368.5
	S_A	I	395.0
	S_A	S_1^m	357.0
	S_1^m	K	*353.0
7	K	S_A	367.5
	S_A	I	396.0
	S_A	S_1^m	356.5
	S_1^m	K	*355.0
8	K	S_A	369.5
	S_A	I	397.0
	S_A	S_1^m	359.0
	S_1^m	K	*358.5

TABLE I (*continued*)

n	Transition		Temperature °K
9	K	S_A	371.0
	S_A	I	397.0
	S_A	K	*357.0
10	K	S_A	372.0
	S_A	I	397.0
	S_A	K	*359.5
11	K	S_A	373.5
	S_A	I	396.0
	S_A	K	*366.0
12	K	S_A	374.5
	S_A	I	395.0
	S_A	K	*364.0
13	K	S_A	376.5
	S_A	I	394.0
	S_A	K	*370.5
14	K	S_A	377.5
	S_A	I	393.0
	S_A	K	*369.0
15	K	S_A	379.5
	S_A	I	391.5
	S_A	K	*374.0
16	K	S_A	379.5
	S_A	I	390.5
	S_A	K	*374.0

m = monotropic phase
* = values deduced from DSC curves

number of CH_2 (n) in the terminal chain. Unidentified solid and smectic phases are indicated with K or S followed by a comma with the highest temperature transition receiving the lowest number.[6]

The properties of the first eight homologs are presented in some details because of the complexity involved. The others show only one smectic A phase which melts directly giving isotropic liquid.

$n = 0$ (Ethanoate)

This compound has the higher melting point and melts directly giving isotropic liquid. The cooling process shows the existence of a mono-

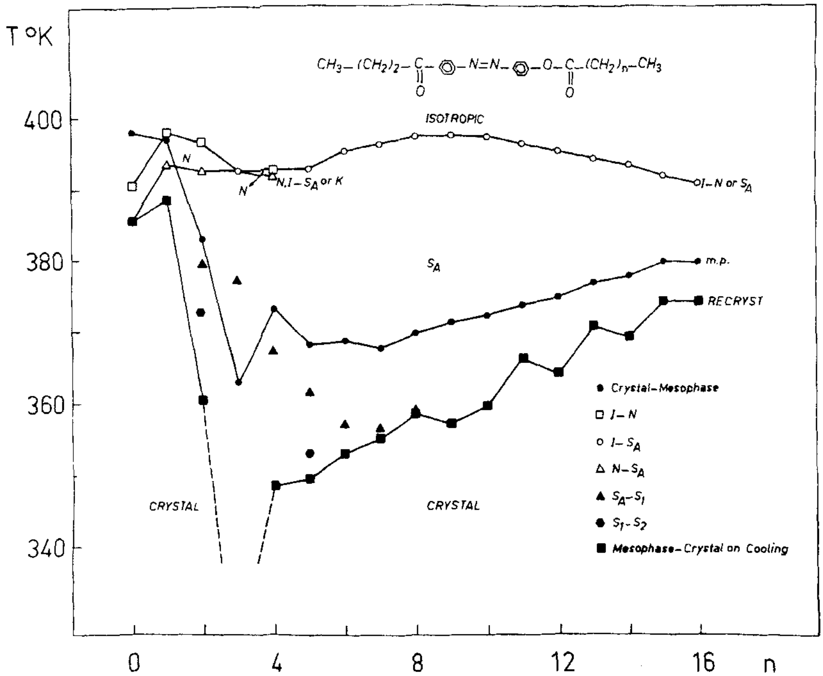


FIGURE 1 Plot of transition temperatures vs. number of methylene groups (*n*) in the ester alkyl chain for 4-*n*-butyryl-4'-*n*-alkanoyloxy azobenzenes.

tropic nematic phase. The following scheme may summarize the thermal behavior.

$$\begin{tikzcd}
K \arrow[rr, "398"] & & I \arrow[dl, shift left, "390.5"] \\
& N \arrow[ul, "{*385.5}"] \arrow[ur, shift left] &
\end{tikzcd}$$

$n = 1$ (Propanoate)

As it may be seen from the following scheme

$$\begin{tikzcd}
K \arrow[rr, "397"] & & N \arrow[r, shift left, "398"] \arrow[dl, shift left] & I \arrow[l, shift left] \\
& S_A \arrow[ul, "{*388.5}"] \arrow[ur, shift left, "393.5"] & &
\end{tikzcd}$$

the slight decrease of the melting temperature in this homolog allows the formation of a nematic phase stable over a very narrow temperature range. The nematic phase gives the monotropic phase S_A during the cooling process and recrystallization occurs without a marked undercooling as it is the case for other compounds (see below).

n = 2 (Butanoate)

The thermal analysis showed different results for a "virgin sample" defined as a freshly recrystallized sample from the ethanol solvent, and a "non virgin sample" defined as a sample submitted at least to the transition to S_A phase. In fact the virgin sample during the first heating can show one of the two different behaviors, reported as (a) and (b) in Figure 2.

The three peaks appearing both in (a) and in (b) refer to the transitions from the solid phase K_1 to the S_A, from the S_A to N and from N to I. Of the remaining three peaks appearing in (a), the one at the lowest temperature could correspond to the transition from the superheated solid K_3 to K_1 via a previous melting to the metastable smectic phase S_2. Similar behaviors were already observed in Ref. 1. The two remaining peaks could correspond to the transition $S_2 \rightarrow S_1$ (lower temperature) and to the transition $S_1 \rightarrow S_A$ (higher temperature) of a small part of sample which was not able to undergo the transition to K_1. The X-ray diffraction always shows the transitions $K_3 \rightarrow K_1$, $K_1 \rightarrow S_A$, $S_A \rightarrow N$ and $N \rightarrow I$, during the heating process.

The non virgin sample always produces the thermogram of Figure 2b, with exception of a previous very rapid cooling from S_A. In this last case a new metastable solid phase K_2 appears. The X-ray diffraction confirms the three transitions appearing in Figure 2f.

The thermograms (c) and (d) refer to the cooling till the formation of the S_2 phase and successive heating, respectively. The reversibility of the appearance of both monotropic phase S_1 and S_2 is observed. The thermogram (e) refers to a cooling till room temperature. The peak at the lowest temperature corresponds to the $S_2 \rightarrow K_1$ crystallization: the small bump near to this peak could correspond to the formation of K_2. The X-ray diffraction confirms all the transitions appearing in (e), with exception of the transition $S_1 \rightarrow S_2$. This last fact could be due to a high degree of metastability of the S_2 phase.

The main features of the behavior of this compound can be summarized in the following scheme

$$\begin{tikzcd}
K_3 \arrow[r] \arrow[dr, dashed] & K_1 \arrow[r, "383"] & S_A \arrow[r, shift left, "392.5"] \arrow[d, shift left, "379.5"] & N \arrow[l, shift left] \arrow[r, shift left, "396.5"] & I \arrow[l, shift left] \\
 & S_2 \arrow[u, "\bullet 360.5"'] \arrow[r, shift left] & S_1 \arrow[u, shift left] \arrow[l, shift left, "372.5"] & &
\end{tikzcd}$$

Figure 3 shows typical textures for S_A, S_1, S_2 phases and the $S_2 \rightarrow K_1$ transition as obtained from microscopic observation. From this figure and X-ray diffraction the S_1 and S_2 phases appear as ordered smectic phases, whose exact nature will be object of further investigations.

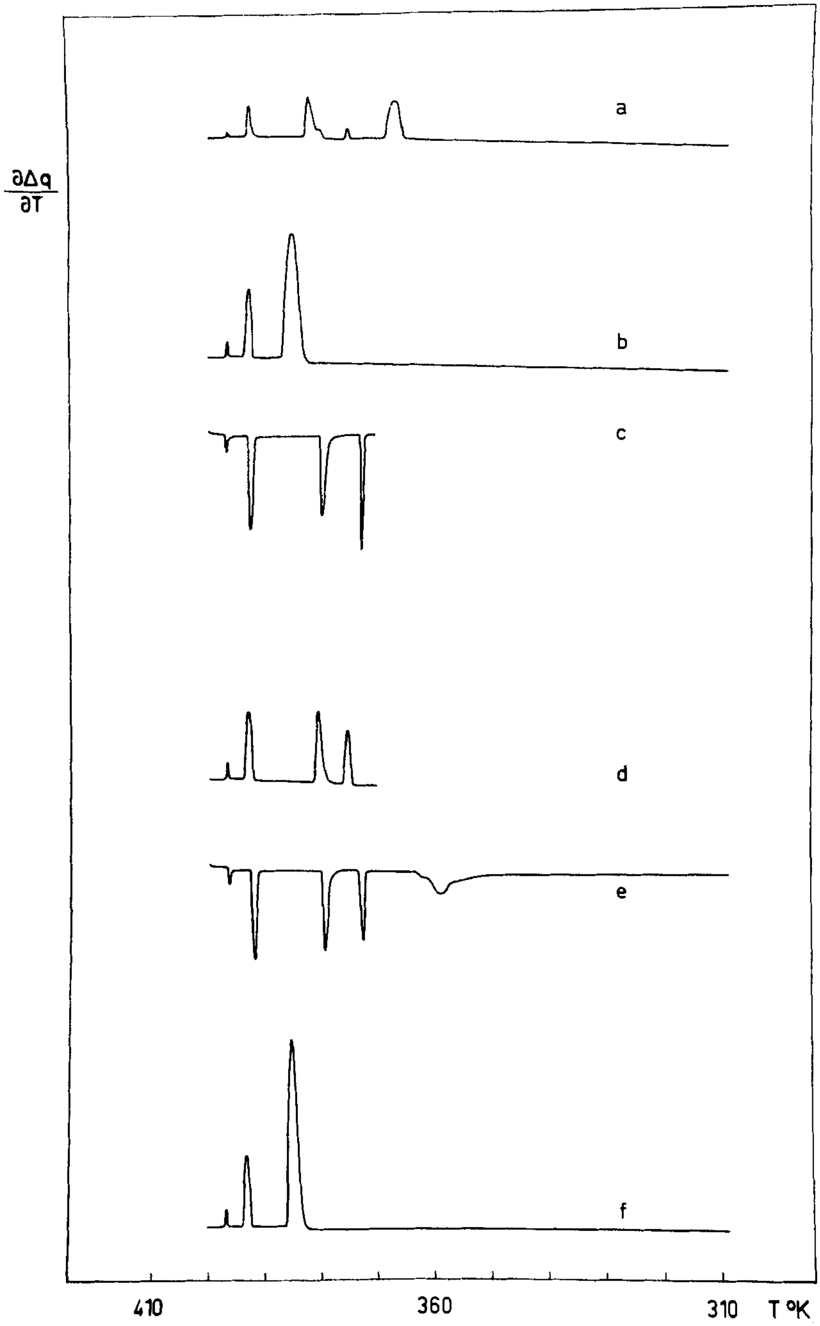
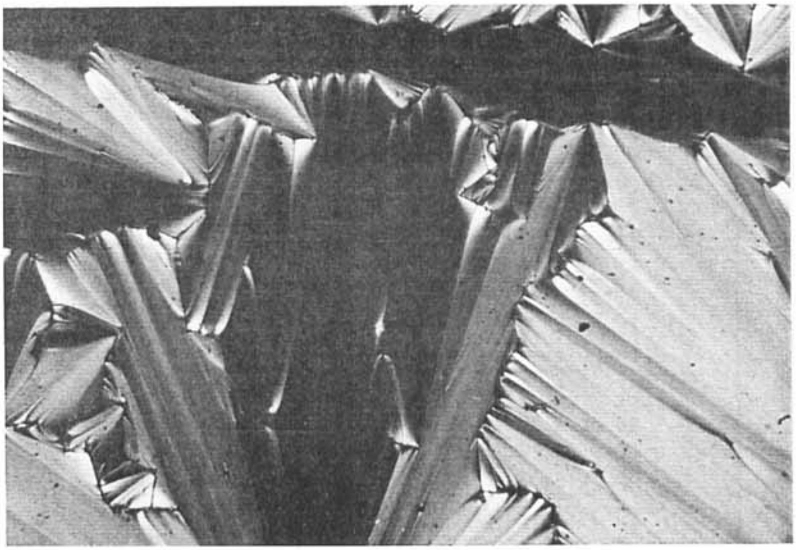
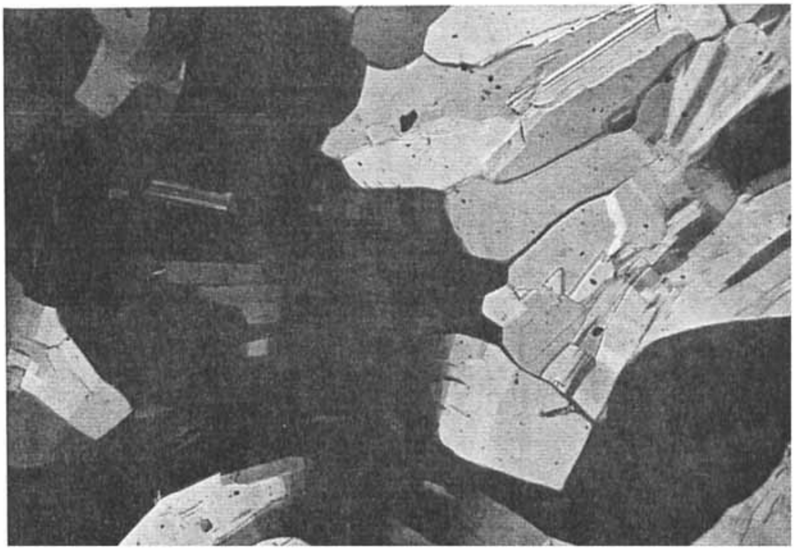


FIGURE 2 DSC thermograms for 4-*n*-butyryl-4′-*n*-butanoyloxy azobenzene ($n = 2$) taken on the same sensitivity range and chart speed. Scan rate 2°K/minute. (a) and (b) First heating curves. (c) Cooling curve down to 368°K. (d) Heating curve obtained immediately after c. (e) Cooling curve down to room temperature. (f) Heating curve obtained after ten months at room temperature.

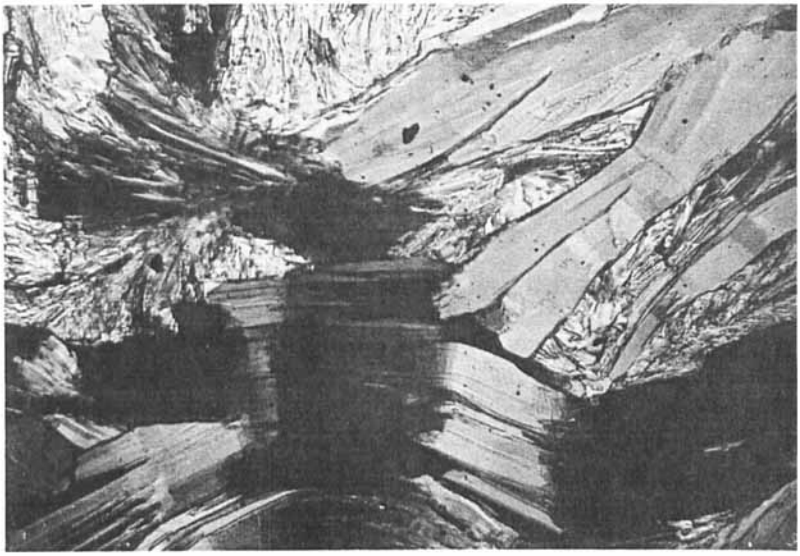


(a)

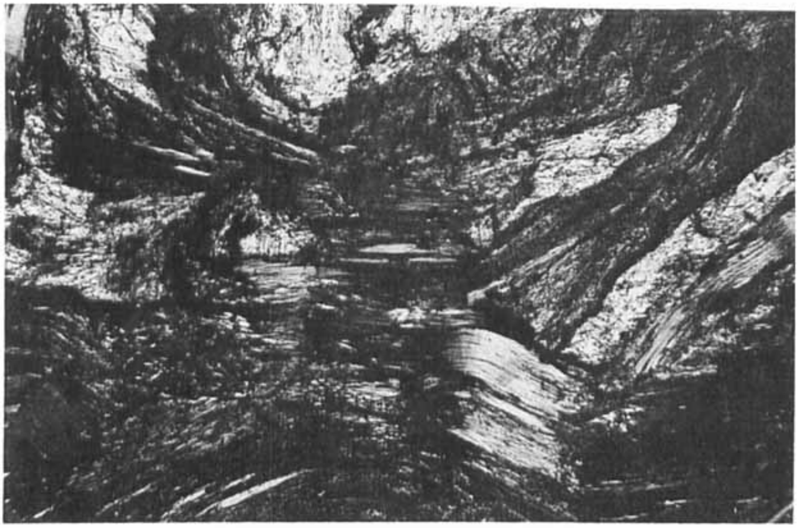


(b)

FIGURE 3 Photomicrographs taken on the same sample of 4-*n*-butyryl-4'-*n*-butanoyloxy azobenzene ($n = 2$). Cooling cycle. Film between glass slides; crossed polarizers; magnification ca 80X. (a) Smectic A fan texture. (b) Monotropic phase S_1 at 378°K. (c) Monotropic phase S_2 at 376°K. (d) Formation of K_1 phase.



(c)



(d)

n = 3 (Pentanoate)

As may be seen from Figure 1, this compound presents a behavior which is rather anomalous with respect to the others. No nematic phase appears and the smectic A melts directly to give the isotropic liquid. The phase indicated as S_1, which precedes formation of S_A, as it is seen in the scheme

$$K \overset{363}{\rightleftarrows} S_1 \overset{377}{\rightleftarrows} S_A \overset{392.5}{\rightleftarrows} I$$

is very viscous and this may explain the absence of any monotropic phase and the impossibility of determining recrystallization temperature even when the sample is cooled down to 263°K. The initial solid is obtained only after that the molten sample is left at room temperature for several days. Figure 4 (a,b,c,d) shows typical textures for the different phases. Figures 4b and 4c show two typical textures for the S_1 phase, which appears to be an ordered smectic phase also under X-ray conditions. The typical textures of S_1 during cooling cycle is shown in Figure 4b. The mosaic in Figure 4c is formed very slowly when the sample is maintained at a temperature close to 376°K for about one hour during heating cycle.

n = 4 (Hexanoate)

The thermal behavior of this compound may be summarized by the scheme

$$\begin{tikzcd}
K \arrow[rr, "373"] & & S_A \arrow[r, shift left, "391.5"] \arrow[dl, shift left, "367"] & N \arrow[l, shift left] \arrow[r, shift left, "392.5"] & I \arrow[l, shift left] \\
& S_1 \arrow[ul, "{*348.5}"] \arrow[ur, shift left] & & &
\end{tikzcd}$$

from which it is apparent that to the increase in the melting temperature corresponds a decrease of the degree of undercooling, the presence of a nematic phase stable over a very narrow temperature range and the existence of the monotropic phase S_1 during the cooling cycle. As before, it was not possible to identify completely the phase S_1 (see Figure 5) which appears to be an ordered smectic phase. The influence of the cooling rate on the overall thermal behavior is very similar to the one described for the case of *n* = 2.

n = 5 (Heptanoate)

The thermal behavior may be described by the scheme

$$\begin{tikzcd}
& K_1 \arrow[r, "368"] & S_A \arrow[r, shift left, "392.5"] \arrow[d, shift left, "361.5"] & I \arrow[l, shift left] \\
K_2 \arrow[ur, dashed] & & & \\
& S_2 \arrow[ul, dashed] \arrow[uu, "{*349.5}"'] \arrow[r, shift left] & S_1 \arrow[l, shift left, "353"] \arrow[u, shift left] &
\end{tikzcd}$$

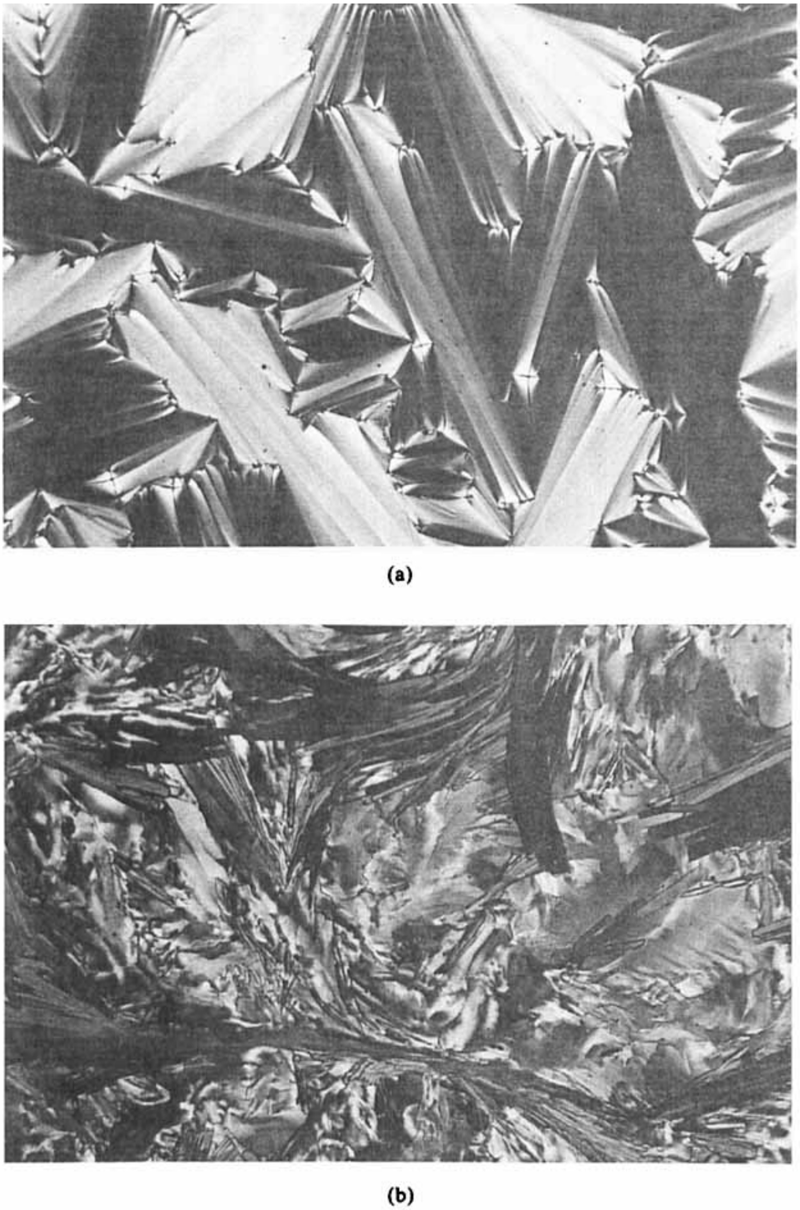
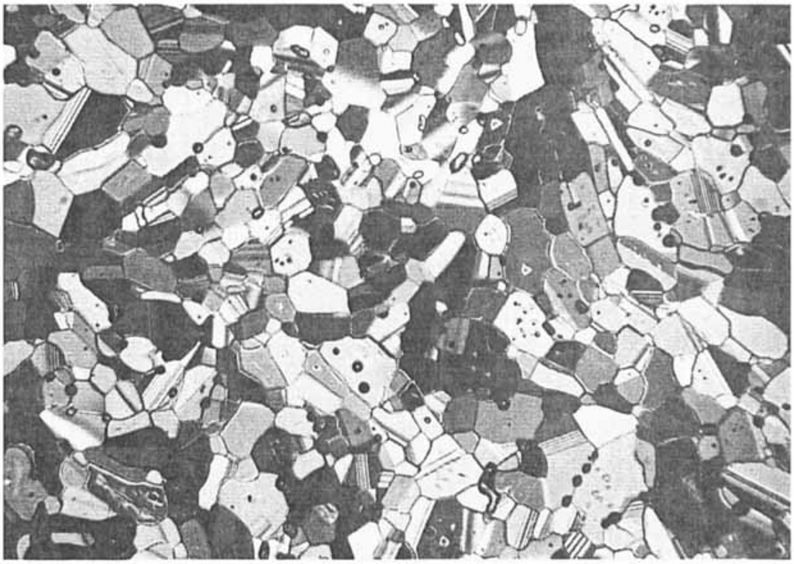
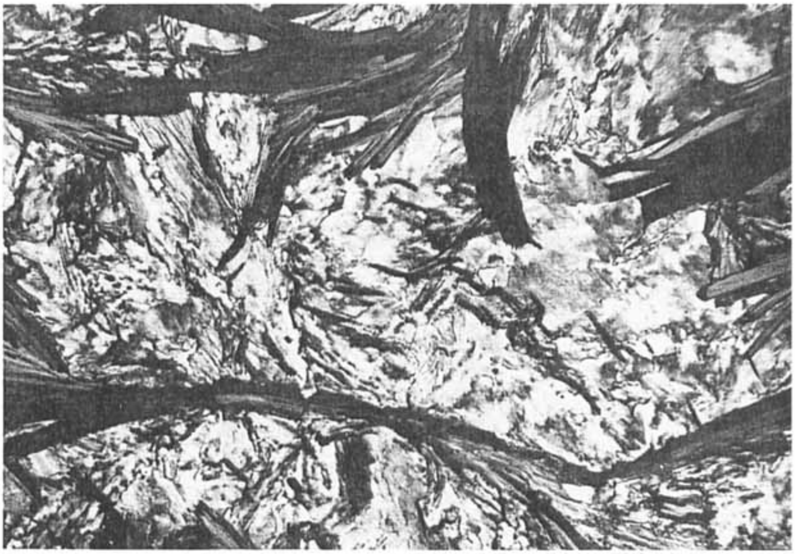


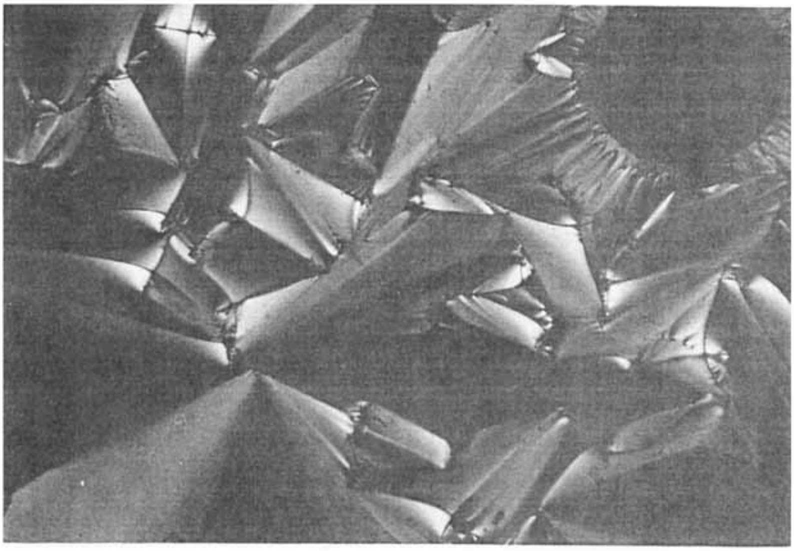
FIGURE 4 Photomicrographs taken on the same sample of 4-*n*-butyryl-4′-*n*-pentanoyloxy azobenzene ($n = 3$). Cooling cycle. Film between glass slides; crossed polarizers; magnification ca 80X. (a) Smectic A fan texture. (b) S_I phase at 375°K. (c) S_I phase after 60 minutes at rest at 376°K. (d) Supercooled S_I phase after 15 hours at rest at room temperature.



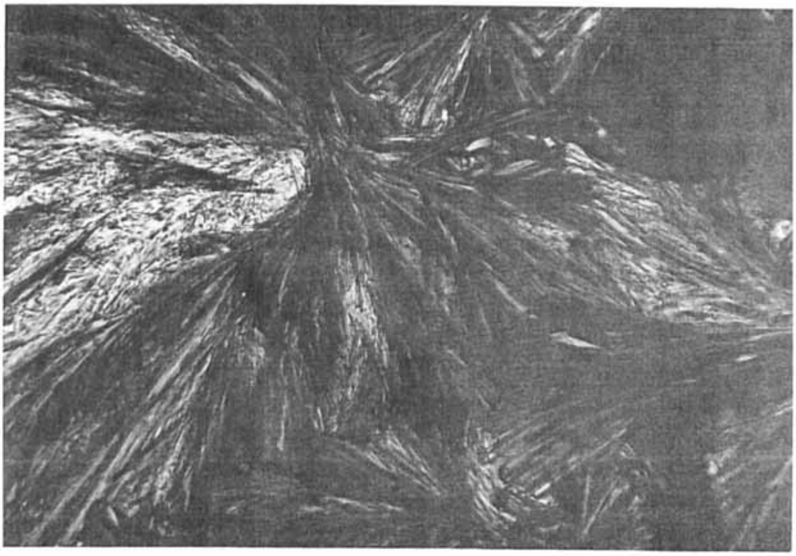
(c)



(d)

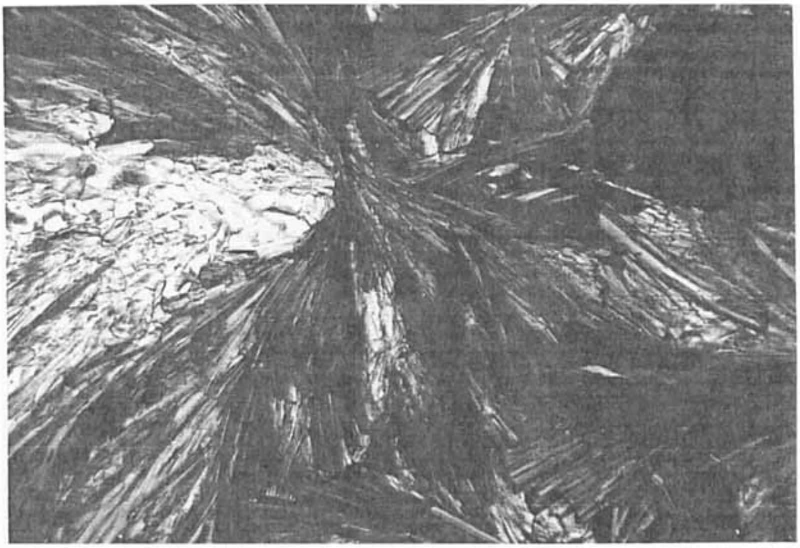


(a)



(b)

FIGURE 5 Photomicrographs taken on the same sample of 4-*n*-butyryl-4'-*n*-hexanoyloxy azobenzene ($n = 4$). Cooling cycle. Film between glass slides; crossed polarizers; magnification ca 80X. (a) Smectic A fan texture. (b) Monotropic phase S_I at 367°K. (c) Monotropic phase S_I after 360 minutes at rest at 367°K.



(c)

from which it is apparent that the increased thermal stability of the smectic A seems to inhibit the existence of a nematic phase. Two monotropic ordered smectic phases S_2 and S_1 are always formed very close to the recrystallization temperature. The typical textures are shown in Figure 6.

The behavior of samples obtained from those previously cooled and melt is rather complex and depends on thermal history. Samples cooled and left at room temperature for a long time behave as during the first heating process (Figure 7e) irregardless of cooling rate. The same is true if the cooling rate is 2°K/minute (Figure 7d). The typical shape of heating curves obtained after a short time from a rapid cooling is shown in Figures 7b and 7c, where it is evident a endothermic-exothermic behavior (Figure 7b) and a double peak (Figure 7c).

A possible interpretation of these experimental results is the existence of a metastable phase K_2 which slowly gives the initial solid phase K_1. If the transition $K_2 \rightarrow K_1$ is not completed, the melting of K_2 is followed by recrystallization of K_1 thus justifying the shape of the thermograms in Figures 7b and 7c.

This behavior seems to be characteristic of homologs with $n = 5$ as it has been found in different series.[3,7,8,9]

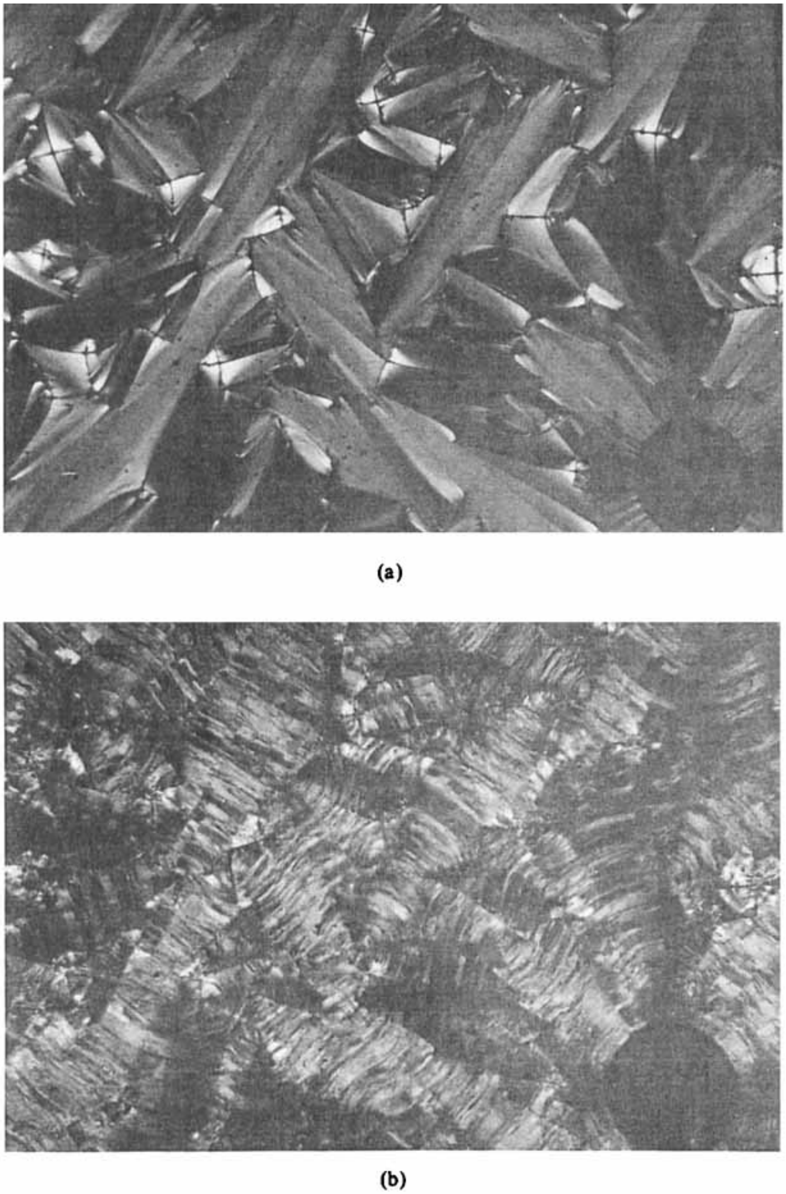
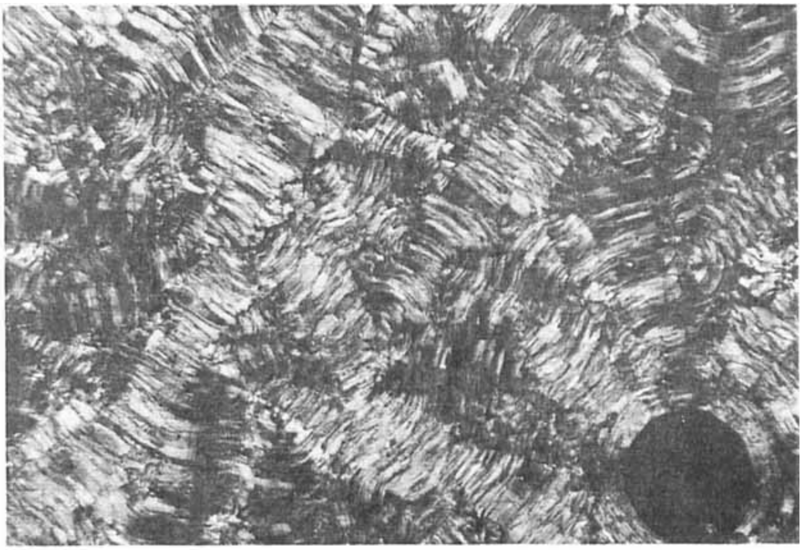


FIGURE 6 Photomicrographs taken on the same sample of 4-*n*-butyryl-4′-*n*-heptanoyloxy azobenzene ($n = 5$). Cooling cycle. Film between glass slides; crossed polarizers; magnification ca 80X. (a) Smectic A fan texture. (b) Monotropic phase S_1 at 358°K. (c) Monotropic phase S_2 at 353°K.



(c)

$n = 6, 7, 8$

This three homologs present the same thermal behavior as schematized by the scheme

$$\begin{tikzcd}
K \arrow[rr] & & S_A \arrow[r, shift left] \arrow[dl, shift left] & I \arrow[l, shift left] \\
& S_I \arrow[ul] \arrow[ur, shift left] & &
\end{tikzcd}$$

With increasing n the transition temperature $S_A \rightarrow S_I$ (see Table I) comes closer and closer to the recrystallization temperature. For $n = 8$ only at higher cooling rate (32°K/minute) it is possible to see S_I. When cooling rate is lower the recrystallization always occurs before formation of the monotropic phase

$n = 9, 10, \ldots 16$

All these compounds present a behavior which may be schematized as

$$K \rightleftarrows S_A \rightleftarrows I$$

The melting and recrystallization temperature (Table I and Figure 1) assumes the odd-even trend[1,3] which is more pronounced for the second parameter.

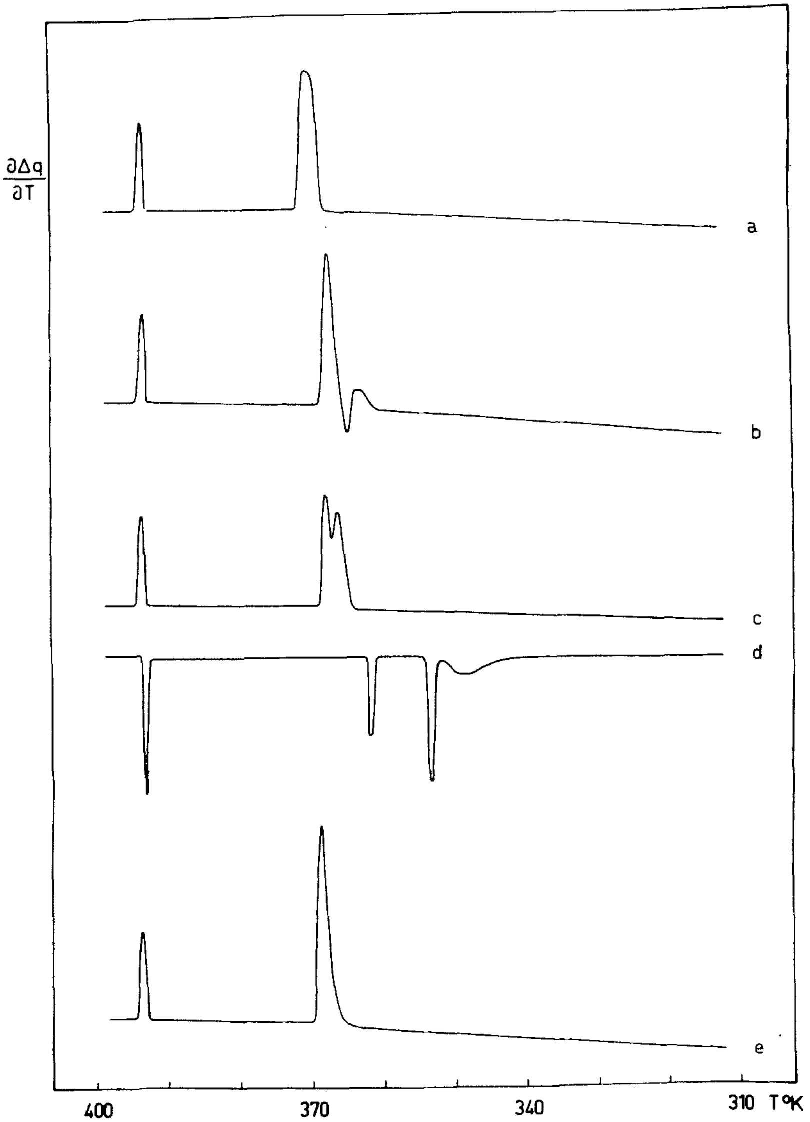


FIGURE 7 DSC thermograms for 4-*n*-butyryl-4′-*n*-heptanoyloxy azobenzene ($n = 5$) taken on the same sample sensitivity range and chart speed. Scan rate 2°K/minute. (a) First heating curve. (b) and (c) Heating curves of a sample cooled rapidly, obtained immediately (b) or after one day (c). (d) Cooling thermogram at 2°K/minute. (e) Heating curve after several months or immediately after d.

CONCLUSIONS

It is apparent from the data that the investigated series is characterized for the homologs between zero and eight (with exception of $n = 3$) by monotropic phases, some of them appear as ordered smectics when observed by X-ray diffraction. The investigation was made sometimes difficult by the metastable character of some phases. Further studies are in progress, to obtain a more safe classification of the phases indicated by S_1, S_2. These studies in conjunction with the future investigations on the same kind of homologs (with $m = 3, 4, 5$) under preparation will allow the derivation of some correlations between the molecular structure and the liquid crystal behavior of this kind of homologous azocompounds. Now it is already possible to derive some common features of the three series investigated ($m = 0, 1, 2$).

When changing from $m = 0$ to $m = 1$ it was observed a general increasing of the existence range of the mesophases, with particular reference to nematic and smectic A phases. This behavior is originated more by the increasing of transition temperatures from mesophases to isotropic liquid rather than by the decreasing of transition temperatures from solid to mesophases.

For the series $m = 2$ the temperature of transition from solid to mesophases remains almost unchanged with respect to the corresponding homologs of the series $m = 1$. On the other hand the transition temperatures towards the isotropic liquid becomes similar to the corresponding ones of the series $m = 0$.

Another common characteristic is the existence of a critical length for the alyphatic chain, such as for higher values of the length the molecules appear to be rather insensitive to the addition of a methylene group. Such a critical length corresponds to the length of the alyphatic chain of the homolog $n = 6$ belonging to the series $m = 0$ and in the homolog $n = 8$ for the series $m = 1$ and $m = 2$.

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References

1. G. Poeti, E. Fanelli and M. Braghetti, *Mol. Cryst. Liq. Cryst.*, **45**, 145–160 (1978).
2. E. Fanelli, G. Poeti and M. Braghetti, *Mol. Cryst. Liq. Cryst. (Letters)*, **64**, 199–204 (1981).

3. G. Poeti, E. Fanelli and M. Braghetti, *Mol. Cryst. Liq. Cryst.*, **61**, 163–184 (1980).
4. G. Albertini, B. Dubini, S. Melone, M. G. Ponzi-Bossi, F. Rustichelli and G. Torquati, *J. Physique*, **C3**, 384 (1979).
5. G. Albertini, B. Dubini, S. Melone, M. G. Ponzi-Bossi, P. Puliti and F. Rustichelli, *Il Nuovo Cimento*, **56B**, 157 (1980).
6. L. Verbit, *Mol. Cryst. Liq. Cryst.*, **15**, 89 (1971).
7. V. D. Neff, M. K. Chang and D. L. Fishel, *Mol. Cryst. Liq. Cryst.*, **17**, 369–374 (1972).
8. C. L. Hillemann, G. R. Van Hecke *et al.*, *J. Phys. Chem.*, **79**(**15**), 1566 (1975).
9. J. W. Goodby and G. W. Gray, *J. Physique Colloq.*, **C3-17**, 37 (1976).