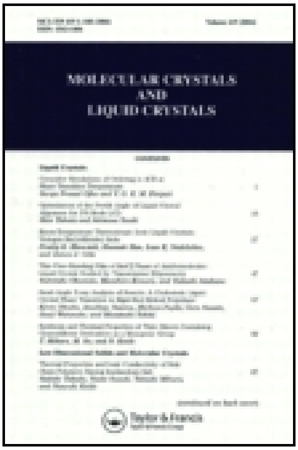

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Liquid Crystalline Phases in 4-Propionyl-4′ -n-Alkanoyloxyazobenzenes

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Liquid Crystalline Phases in 4-Propionyl-4′-*n*-Alkanoyloxyazobenzenes

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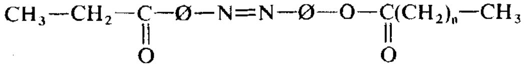
The series of homologues of 4-propionyl-4′-n-alkanoyloxyazobenzenes



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

with *n* ranging from zero to sixteen has been prepared.

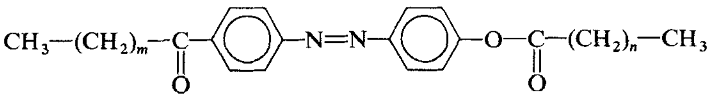
Optical microscopy and differential scanning calorimetry have been used to study the mesomorphic behaviour of these compounds.

All the homologues are liquid crystals with nematic as well as smectic phases.

The presence of smectic polymorphism and of monotropic phases may be considered as the most important characteristics of these compounds.

INTRODUCTION

This paper is a part of continuing series[1] concerned with the preparation and the study of the melting behaviour of new series of homologues having the following general formula:



The results obtained show the liquid crystal phases and transitions of the compounds with $m = 1$ and n ranging from zero to 16.

All the compounds examined are liquid crystals and the series is characterized by marked smectic polymorphism and by the formation of monotropic phases.

Some difficulties have been found in the identification of the smectic phases because it was not always easy to categorise typical microscopic textures and, in a few cases, little change was observed on passing from one phase to another. For the above reasons and where the identification is uncertain, the phases are indicated simply as S_1, S_2 and S_3, following the notation proposed by Verbit.[2]

As the number of different transitions is high, in order to exclude any possible problem caused by impurities, great care has been taken in the purification of the different compounds.

However, some of the experimental results (see below) suggest the possibility of cis-trans isomeric equilibrium.

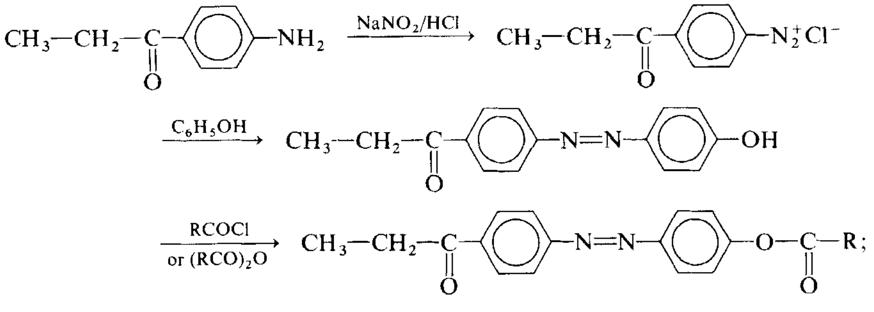
At present the only available data relating to this type of azocompound are limited to the series we are dealing with and to the one having $m = 0$.[1]

From a comparison of the properties of the two series and in agreement with Goodby and Gray,[3] we may only deduce that the length of the terminal alkyl chains markedly affects the smectic polymorphism.

EXPERIMENTAL

Preparation of 4-propionyl-4'-n-alkanoyloxyazobenzenes

All the homologues have been prepared by following the sequence:



$R = CH_3—(CH_2)_n—$.

The starting chemical was 4'-aminopropiophenone (Kodak). The final products were obtained using pyridine as solvent; the esterification of the intermediary compound was carried out by using anhydrides (Merck-Schuchardt) for the homologues with $n = 0, 1, 2$ and acid chlorides (obtained by reaction of the acid with $SOCl_2$) for the other compounds.

The purification of final products was performed as follows: first crystallization from ethanol; redissolution in the same solvent; treatment with activated carbon; hot filtration and final recrystallization. The crystallization was repeated at least three times.

Standard characterization of each compound included NMR, elemental analysis and liquid chromatography.

PHYSICAL MEASUREMENTS

A Reichert microscope equipped with a microfurnace Mettler FP 52, and Asahi Pentax K2 camera and a temperature programmer Mettler FP 1 has been used to observe and identify the different phases. To improve the observation of the thermal behaviour, the programmer has been modified to control the temperature during sample cooling.

Microscopic observations have been complemented by the calorimetric measurements performed using a differential scanning calorimeter Perkin–Elmer DSC–1B.

Most of the temperatures quoted in this paper have been measured through microscopic observations (precision $\pm 0.5°K$). The temperatures of transition which are difficult to observe or are not seen by microscopy, have been determined from the thermograms and are marked with an asterisk in the text and tables.

RESULTS AND DISCUSSION

Before discussing the results of thermal analysis it seems important to point out that the liquid-liquid chromatograms have shown the existence of a cis-trans isomeric equilibrium for each compound when dissolved in a solvent. The probable existence of an equilibrium of this kind is shown by chromatograms in Figures 1a, b, c, where peak 2 increases with time. The existence of the same equilibrium in the pure liquid may not, at least at present, be excluded and the results of the thermal and microscopic analysis have to be interpreted taking into account this possibility.

In the following paragraphs, the melting behaviour of the first ten homologues of the series is described in some detail because of the complexity of the experimental findings. Each homologue is identified by its methylene chain length and/or by the parent acid.

Table I summarizes transition temperatures.

$n = 0$ (*Ethanoate*). The DSC curves relating to a sample crystallized from ethanol show a diffuse endothermic transition (Figure 2a). The starting temperature is rather difficult to determine, but the existence of a phase transition is confirmed by the microscopic observations which indicate a

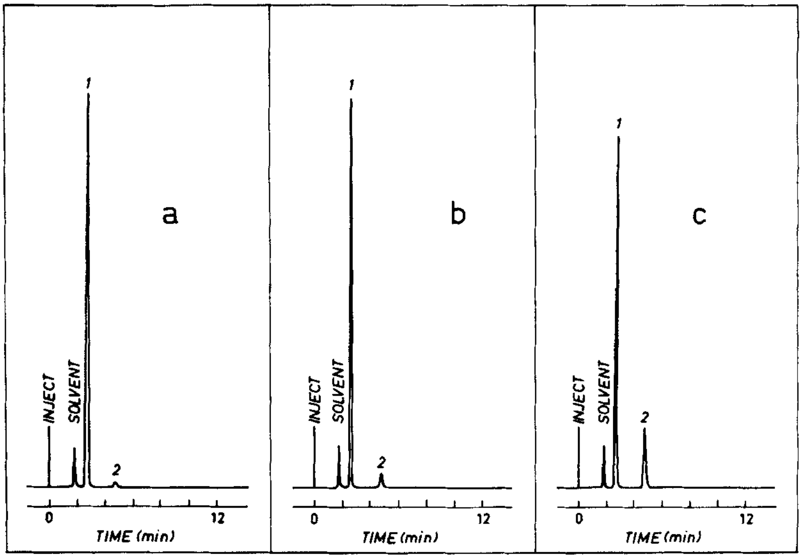
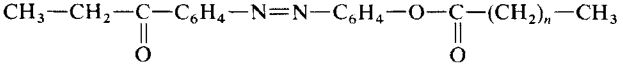


FIGURE 1 Liquid chromatograms for a solution of heptanoate ($n = 5$). Column: lichrosorb Si60 25 cm × 4.6 mm. Flow rate 2 ml/min. Solvent: n-hexane/Ethylacetate (80/20). U.V. detector. a) injection performed immediately after dissolution. b) injection after two hours at room temperature. c) injection after twelve hours at room temperature.

TABLE I

Transition temperatures for



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

n	Transition		Temperature °K
0	K_2	S_B	[a]338.0
	K_1	S_B	~378
	S_B	N	402.0
	N	I	425.5
1	K_2	S_B	[a]349.0
	K_1	S_B	~397
	S_B	S_A	408.0
	S_A	N	409.5
	N	I	431.5
2	K	S_B	366.0
	S_B	S_A	392.5
	S_A	N	409.5
	N	I	428.5
3	K	S_1	357.5
	S_1	S_B	367.0
	S_B	S_C	371.8
	S_C	S_A	372.0
	S_A	N	413.0
	N	I	420.0

TABLE I (*continued*)

n	Transition	Temperature °K
4	K S_A	372.0
	S_A N	411.5
	N I	420.5
	S_A S_C^m	361.0
	S_C^m S_3^m	355.5
5	K S_A	365.0
	S_A N	414.5
	N I	416.5
	S_A S_1^m	[a]363.0
	S_1^m S_2^m	[a]359.5
	S_2^m S_3^m	349.5
6	K S_A	369.5
	S_A N	416.0
	N I	416.5
	S_A S_1^m	[a]363.5
	S_1^m S_3^m	345.5
7	K S_A	367.0
	S_A I	417.0
	S_A S_1^m	[a]360.0
8	K S_A	371.0
	S_A I	417.5
	S_A S_1^m	[a]359.0
9	K S_A	370.5
	S_A I	416.5
10	K S_A	373.5
	S_A I	416.0
11	K S_A	374.0
	S_A I	416.5
12	K S_A	375.5
	S_A I	413.5
13	K S_A	376.5
	S_A I	412.0
14	K S_A	378.5
	S_A I	410.5
15	K S_A	379.5
	S_A I	409.5
16	K S_A	380.5
	S_A I	407.5

[a] Values deduced from DSC curves. m = monotropic phase.

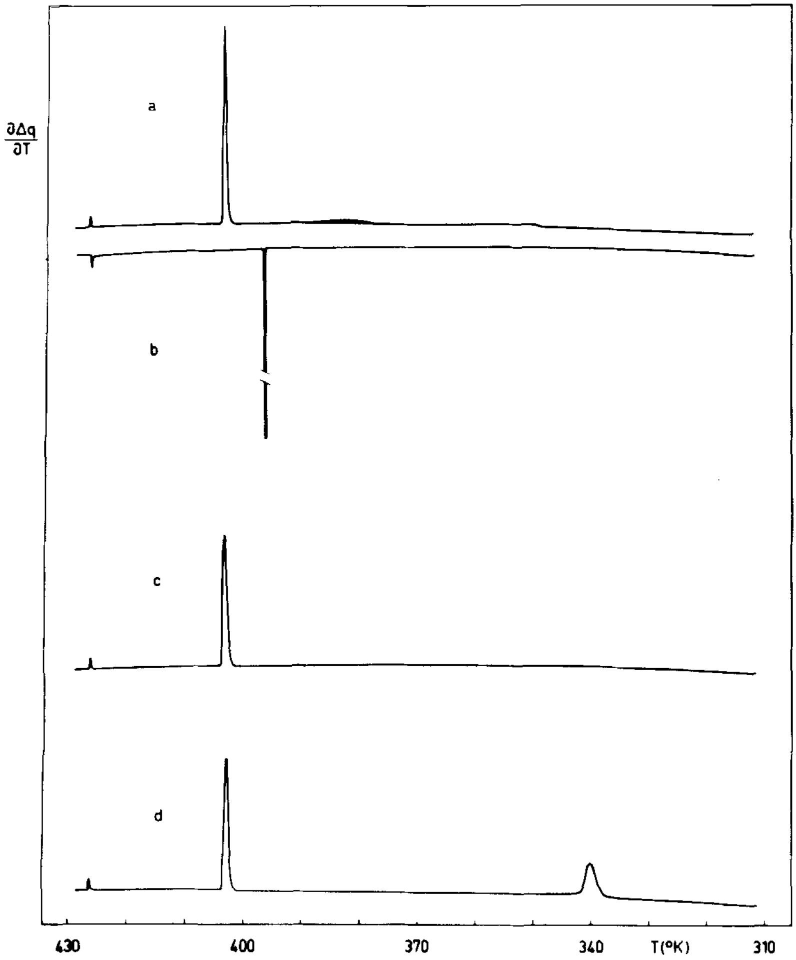


FIGURE 2 DSC thermograms for 4-propionyl-4′-ethanoyloxyazobenzene (*n* = 0). Scan rate 2°K/minute. a) first heating curve; b) cooling thermogram; c) sample heated immediately after cooling; d) sample heated after 9 months.

very slow process. The first transformation is followed by two sharp transitions corresponding to the disappearance of the mosaic texture (Figure 3) at 402°K and to the formation of a nematic phase resulting in the isotropic liquid at 425.5°K.

A striking feature of the nematic phase, which is common to the other homologues, is that it is almost always homeotropic. Under polarized light it appears yellow-black throughout its thermal stability range and the typical schlieren-homogeneous textures are seen just before the N–I tran-

FIGURE 3 S_B-N transition for 4-propionyl-4′-ethanoyloxyazobenzene ($n = 0$) observed at 402°K during heating of the sample. Film between glass slides, crossed polarizers, magnification 80x.

sitions. Cooling the sample, even at the slowest rate (0.5°K/minute), does not lead to a solid (Figure 2b, c). Solidification occurs only after a long time (months) at room temperature and the solid formed is different from the one obtained by crystallization. Heating of previously solidified samples leads to a sharp melting at a lower temperature (Figure 2d).

The properties of the compound may be represented by the scheme:

$$\begin{tikzcd}
K_1 \arrow[dr, "\sim 378"] & & & \\
& S_B \arrow[r, shift left, "402"] \arrow[dl, shift left, "\text{slow}"] & N \arrow[l, shift left] \arrow[r, shift left, "425.5"] & I \arrow[l, shift left] \\
K_2 \arrow[ur, shift left, "{*338}"] & & &
\end{tikzcd}$$

where K_1 and K_2 are two different solids, as indicated by the two different transition temperatures.

$n = 1$ (*Propanoate*) The thermal behaviour of this compound is largely similar to the previous one. The only difference is the presence of two smectic phases as shown by the following scheme:

$$\begin{tikzcd}
K_1 \arrow[dr, "\sim 397"] & & & & \\
& S_B \arrow[r, shift left, "408"] \arrow[dl, shift left, "\text{slow}"] & S_A \arrow[l, shift left] \arrow[r, shift left, "409.5"] & N \arrow[l, shift left] \arrow[r, shift left, "431.5"] & I \arrow[l, shift left] \\
K_2 \arrow[ur, shift left, "{*349}"] & & & &
\end{tikzcd}$$

FIGURE 4 Smectic *B* phase of 4-propionyl-4′-propanoyloxyazobenzene ($n = 1$). Photomicrograph taken at 405°K during an heating cycle performed on a sample previously kept at 404°K for one hour. Film between glass slides, crossed polarizers, magnification 120x.

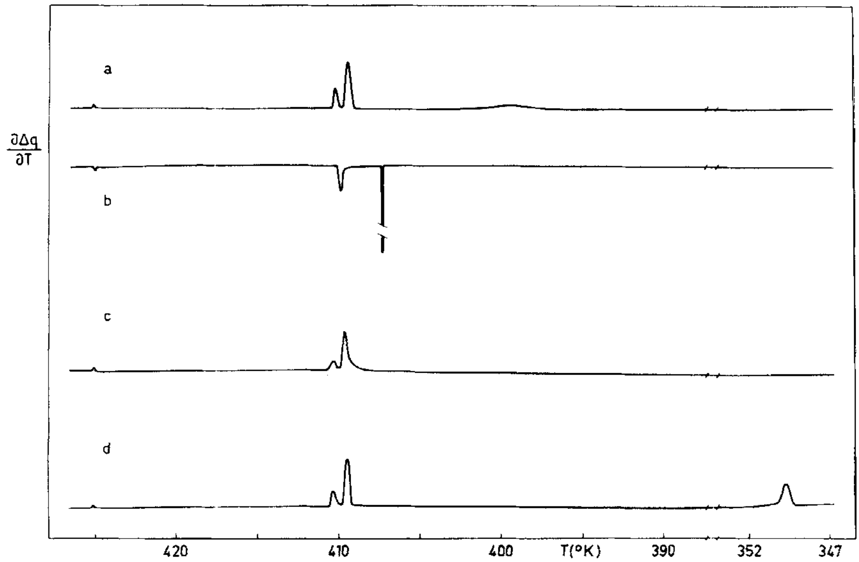


FIGURE 5 DSC thermograms for 4-propionyl-4′-propanoyloxyazobenzene ($n = 1$). Scan rate 2°K/minute. a) first heating curve; b) cooling thermogram; c) sample heated immediately after cooling; (d) sample heated after 6 months.

Figure 4 shows the behaviour of a sample during the first heating cycle and after one hour at 404°K. Figure 5a, d shows the different melting behaviour of samples crystallized from ethanol or from a previously melted solid.

$n = 2$ (*Butanoate*) The transitions of this homologue may be summarized by the sequence

$$K \overset{366}{\rightleftarrows} S_B \overset{392.5}{\rightleftarrows} S_A \overset{409.5}{\rightleftarrows} N \overset{428.5}{\rightleftarrows} I$$

In this case the solid is formed more easily than before and it appears to be the same as that obtained by crystallization from ethanol.

$n = 3$ (*Pentanoate*) Six transitions are observed during the heating of samples crystallized from ethanol as shown in the following scheme:

$$K \underset{\text{slow}}{\overset{357.5}{\rightleftarrows}} S_1 \overset{367}{\rightleftarrows} S_B \overset{371.8}{\rightleftarrows} S_C \overset{372}{\rightleftarrows} S_A \overset{413}{\rightleftarrows} N \overset{420}{\rightleftarrows} I$$

In the temperature range between S_B and S_A phases a very short lived S_C phase is seen, by microscopy, during heating cycles (heating rate 0.2°K/min).

In the DSC curves, during heating cycles, only one peak is observed for the transitions $S_B - S_C - S_A$ even at the slowest heating rate. During cooling cycles, on the contrary, the transition from the *A* phase back to the *B* phase occurs via a more pronounced *C* phase because of the supercooling of the *B* phase and hence it may be observed more easily both at the microscope (Figure 7b) and in the DSC curves (Figure 6b).

The transition from the solid to the unidentified S_1 phase is not seen in samples heated immediately after cooling (Figure 6c) but only in samples kept at room temperature for very long periods of time (months) because recrystallization is a slow process. Figure 7 shows the textures observed when a sample is cooled.

$n = 4$(*Hexanoate*) The main characteristic of this compound is the formation of two monotropic phases, probably observed because of the difficulty of the solidification process. This usually occurs after 6–10 hours at room temperature.

The transition sequence may be summarized by:

$$\begin{tikzcd}
 & K \arrow[r, "372"] & S_A \arrow[r, shift left, "411.5"] \arrow[r, leftarrow, shift right] & N \arrow[r, shift left, "420.5"] \arrow[r, leftarrow, shift right] & I \\
S_3 \arrow[ur, "\text{slow}"] & S_C \arrow[l, "355.5"] \arrow[ur, shift left] \arrow[ur, leftarrow, shift right, "361"'] & & &
\end{tikzcd}$$

where the three transitions K–S_A, S_A–N, N–I are observed during heating. Upon cooling, the smectic *A* phase forms two monotropic phases S_C and

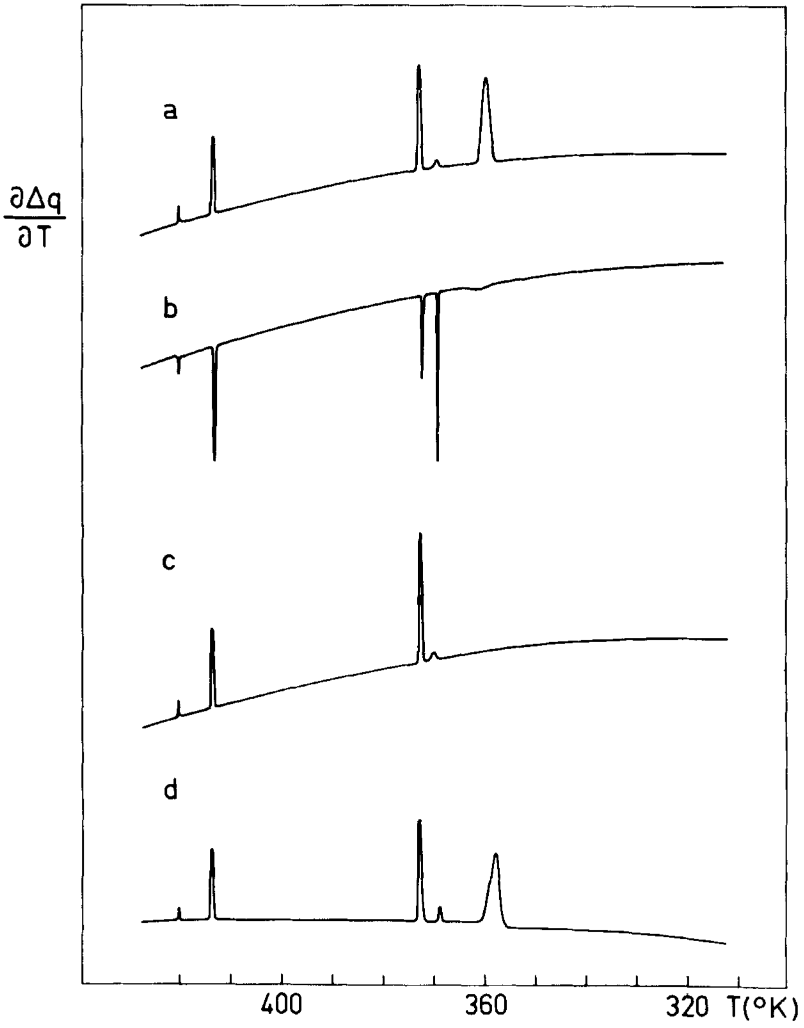


FIGURE 6 DSC thermograms for 4-propionyl-4′-n-pentanoyloxyazobenzene ($n = 3$). Scan rate 2°K/minute. a) first heating curve; b) cooling thermogram; c) sample heated immediately after cooling; d) sample heated after 9 months.

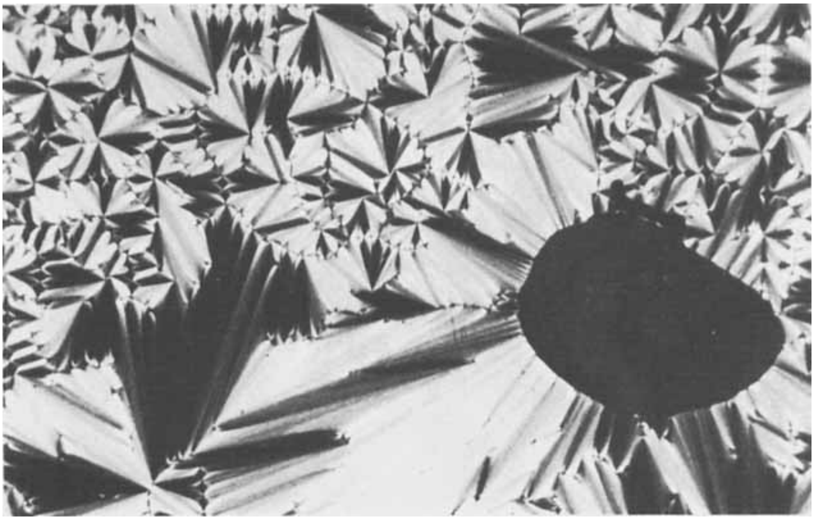


FIGURE 7a Photomicrographs of 4-propionyl-4′-*n*-pentanoyloxyazobenzene ($n = 3$), crossed polarizers, magnification 80 ×, cooling cycle. Focal conic fan texture of S_A phase at 393.5°K.

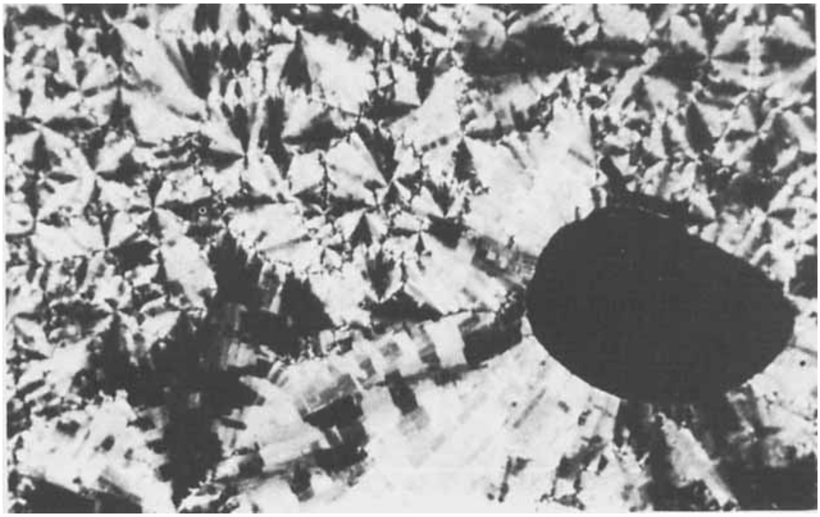


FIGURE 7b Photomicrographs of 4-propionyl-4′-*n*-pentanoyloxyazobenzene ($n = 3$), crossed polarizers, magnification 80 ×, cooling cycle. Broken conic fan texture of the S_C phase at 368.0°K.

FIGURE 7c Photomicrographs of 4-propionyl-4′-*n*-pentanoyloxyazobenzene ($n = 3$), crossed polarizers, magnification 80 ×, cooling cycle. Texture of S_B phase at 365.5°K.

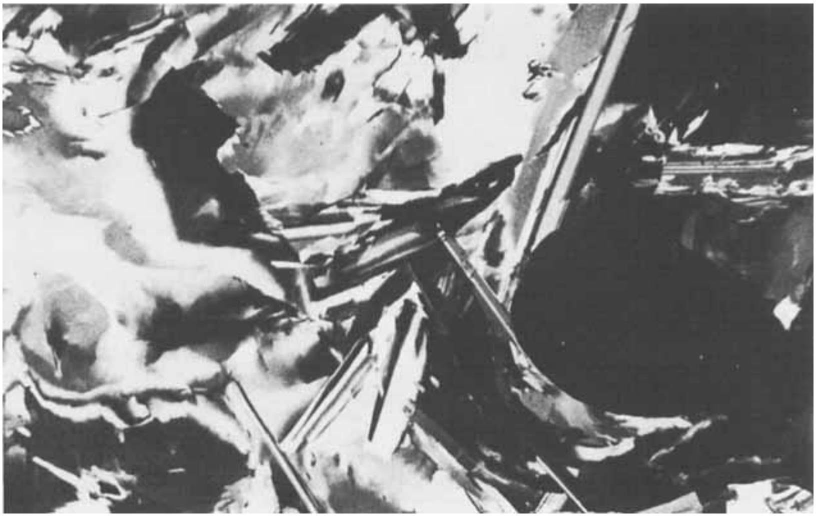


FIGURE 7d Photomicrographs of 4-propionyl-4′-*n*-pentanoyloxyazobenzene ($n = 3$), crossed polarizers, magnification 80 ×, cooling cycle. Texture of unidentified S_1 phase at 359.0°K.

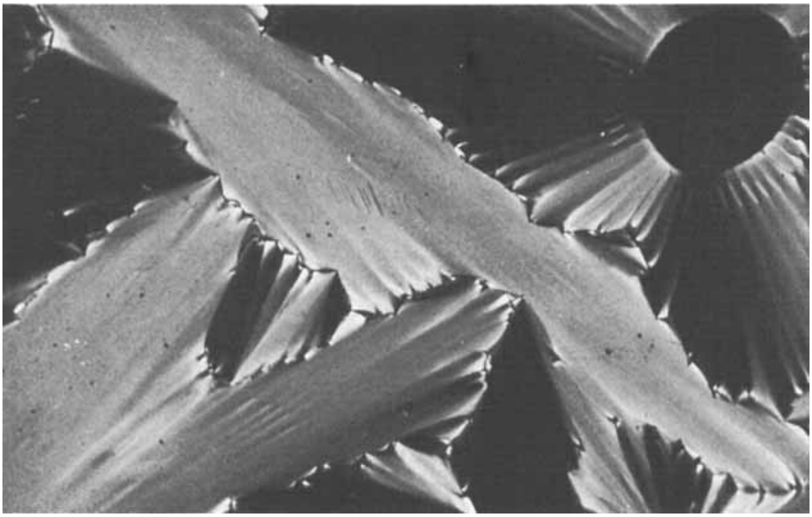


FIGURE 8a Photomicrographs of 4-propionyl-4'-*n*-hexanoyloxyazobenzene ($n = 4$) taken during a cooling cycle, crossed polarizers, magnification 80 × . Focal conic fan texture of S_A.

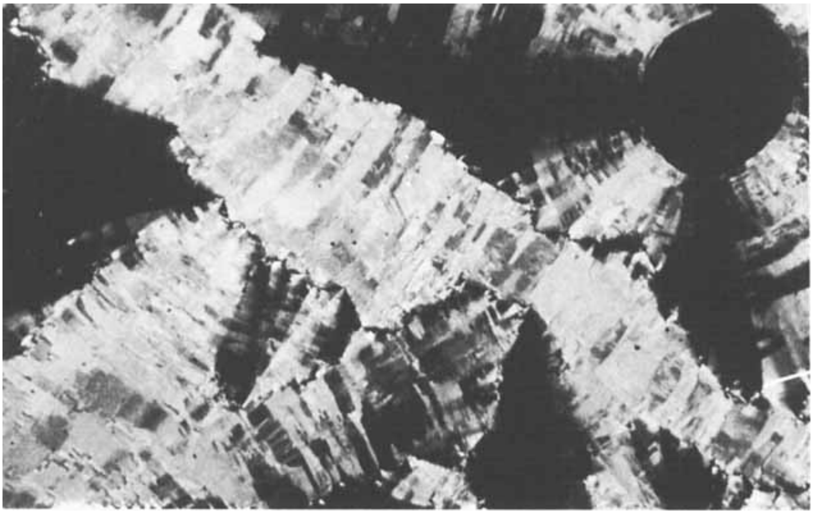


FIGURE 8b Photomicrographs of 4-propionyl-4'-*n*-hexanoyloxyazobenzene ($n = 4$) taken during a cooling cycle, crossed polarizers, magnification 80 × . Broken focal conic fan texture of S_C phase.

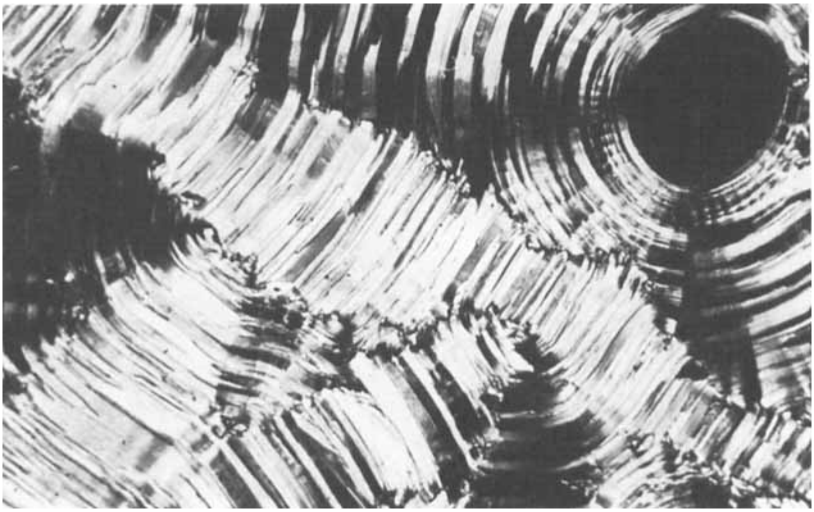


FIGURE 8c Photomicrographs of 4-propionyl-4′-*n*-hexanoyloxyazobenzene ($n = 4$) taken during a cooling cycle, crossed polarizers, magnification 80×. Texture of unidentified S_3 phase.

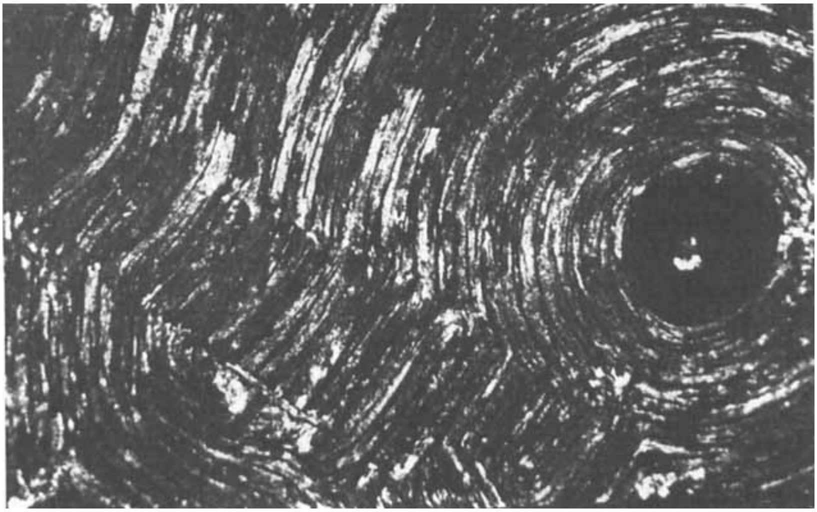


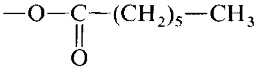
FIGURE 8d Photomicrographs of 4-propionyl-4′-*n*-hexanoyloxyazobenzene ($n = 4$) taken during a cooling cycle, crossed polarizers, magnification 80×. Solid phase after 50 hours at room temperature.

S_3 unless the cooling rate is very slow. In the last case the transition S_C–S_3 may not be observed because the solidification may occur directly from the phase S_C.

Figure 8 shows the characteristic textures of S_A, S_C, S_3 and K as obtained during a cooling cycle.

It may be seen, from Figures 8c and 10b, that the typical textures are very similar. For this reason the corresponding phases have been indicated as S_3 in both cases.

$n = 5$ (*Heptanoate*) As observed in similar compounds,[1,3–5] characterized by the presence of a therminal chain of the type



$$-O-\underset{\substack{\| \\ O}}{C}-(CH_2)_5-CH_3$$

the heptanoate compound shows the most complex behaviour of the homologous series.

On heating three transitions corresponding to K–S_A, S_A–N, N–I, (Figure 9a) are observed; however, during the cooling process (Figure 9b) five transitions are seen by the DSC. They correspond to the formation of nematic and smectic A phases as well as of monotropic phases S_1, S_2, S_3. The initial conditions are, on the contrary, recovered very slowly during a period of the order of months (see Figure 9a, c, d, f).

The transitions seen during the cooling cycle in the DSC curves do not correspond to what is observed with the microscope. The typical textures of the smectic A phase (Figure 10a) remains in fact almost unaltered down to 349.5°K, when a sharp transition takes place (Figure 10b). The texture of the phase formed at this temperature does not change when the sample is cooled down to room temperature whence solidification occurs very slowly. Sometimes the recrystallization process takes place in the temperature range 365–349°K or at the last temperature together with transition in Figure 10b. The phase behaviour may be summarized by the scheme:

$$\begin{tikzcd}
K \arrow[rr, "365"] & & S_A \arrow[r, shift left, "414.5"] \arrow[d, shift left] & N \arrow[l, shift left] \arrow[r, shift left, "416.5"] & I \arrow[l, shift left] \\
S_3 \arrow[u, "\text{slow}"] \arrow[r, shift right] & S_2 \arrow[l, shift right, "349.5"'] \arrow[r, shift right] & S_1 \arrow[l, shift right, "{*359.5}"'] \arrow[u, shift left, "{*363}"'] & &
\end{tikzcd}$$

which may be considered only as indicative because the S_A–S_1 and S_1–S_2 transitions are seen only in the DSC curves and not during optical observations, because the typical fan texture of S_A phase is retained by the sample down to 349.5°K.

From what is known, only a S_B phase may show a texture similar or equal to an S_A phase. This and the low energy corresponding to the S_1–S_2 transi-

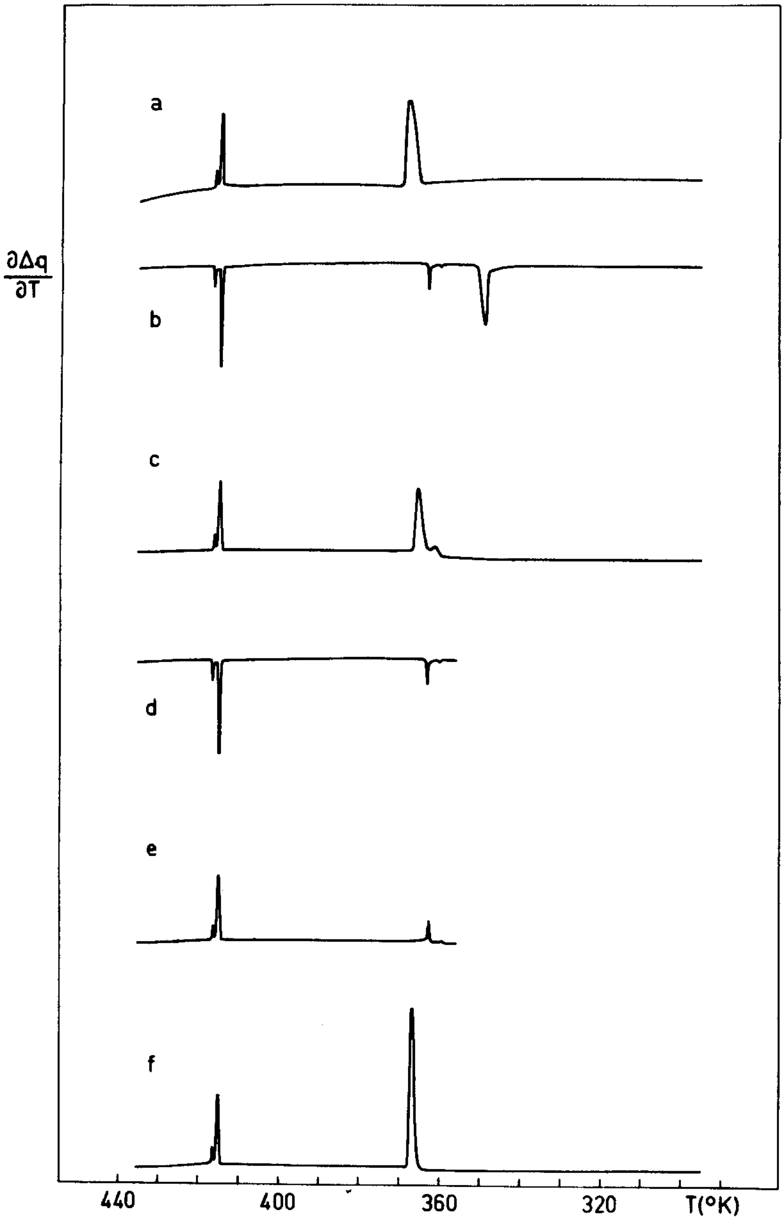


FIGURE 9 DSC thermograms for 4-propionyl-4′-*n*-heptanoyloxyazobenzene ($n = 5$). Scan rate 2°K/minute. a) first heating curve; b) cooling to room temperature; c) sample heated immediately after cooling; d) cooling to 355°K; e) sample heated immediately after cooling; f) sample heated after 9 months.

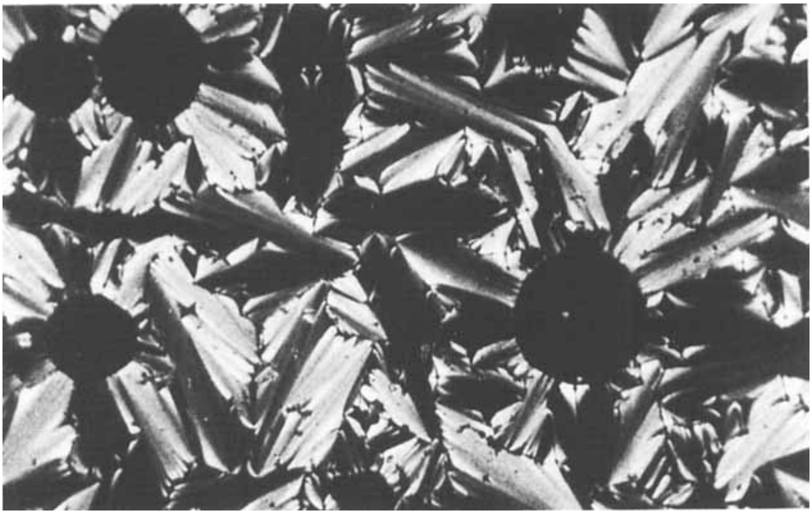


FIGURE 10a Photomicrographs for 4-propionyl-4′-*n*-heptanoyloxyazobenzene ($n = 5$), crossed polarizers, magnification 80 ×. S_A phase.

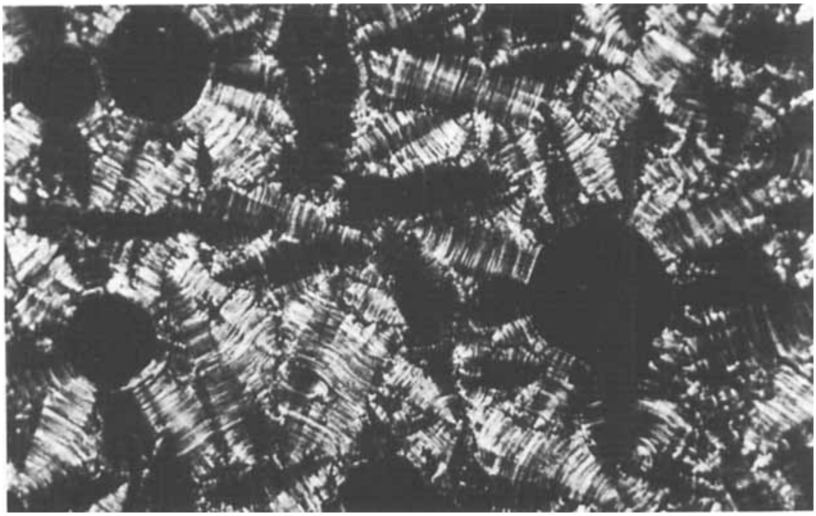


FIGURE 10b Photomicrographs for 4-propionyl-4′-*n*-heptanoyloxyazobenzene ($n = 5$), crossed polarizers, magnification 80 ×. Texture of unidentified S_3 phase.

tion might mean that the DSC peak is spurious. This, however, contrasts with the fact that the compound does not seem to contain impurities, as shown by the liquid–liquid chromatograms. For this reason both in the preceding scheme and in Table I, the two transitions (S_A–S_1 and S_1–S_2) have been reported at the measured temperatures.

$n = 6$ (*Octanoate*) The behaviour of this homologue is similar to the preceding one, with the difference that only two monotropic phases are observed during the cooling process. The thermal behaviour is summarized below:

$$\begin{tikzcd}
K \arrow[rr, "369.5"] & & S_A \arrow[r, shift left, "416"] \arrow[d, shift left] & N \arrow[l, shift left] \arrow[r, shift left, "416.5"] & I \arrow[l, shift left] \\
& S_3 \arrow[ul, "\text{slow}"] \arrow[r, shift right] & S_1 \arrow[l, shift right, "345.5"'] \arrow[u, shift left, "*363.5"']
\end{tikzcd}$$

The temperature range of the nematic phase is limited to only half degree. For this reason the transition N–I is seen more easily during cooling process. The formation of the two monotropic phases is seen clearly in the DSC curve (Figure 11b).

Investigation by optical microscopy shows only the transition occurring at lower temperature. On the basis of the corresponding textures, the phase occurring at lower temperature has been indicated at S_3 (Figure 12b) and

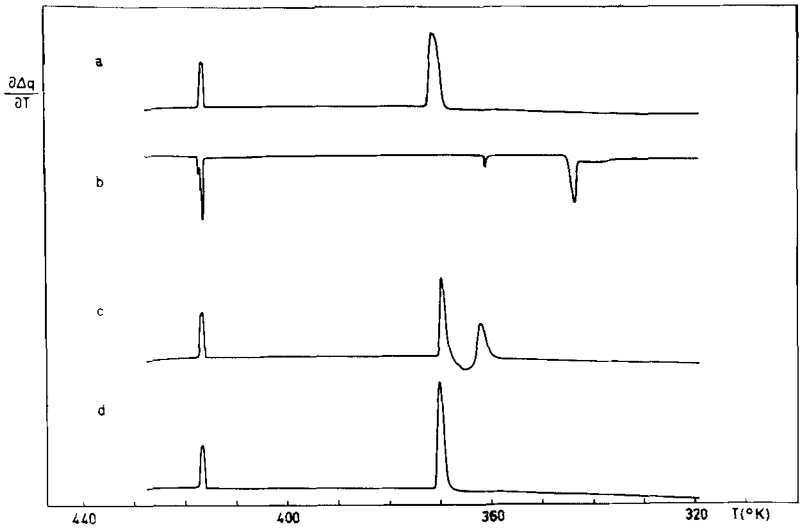


FIGURE 11 DSC thermograms for 4-propionyl-4′-n-octanoyloxyazobenzene ($n = 6$). Scan rate 2°K/minute. a) first heating curve; b) cooling thermogram; c) sample heated immediately after cooling; d) sample heated after 14 months.

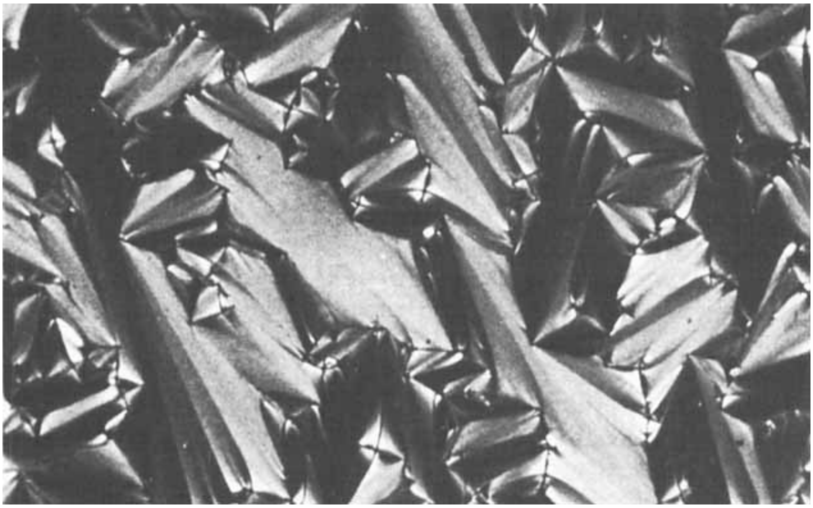


FIGURE 12a Photomicrographs for 4-propionyl-4′-*n*-octanoyloxyazobenzene ($n = 6$), crossed polarizers, magnification 80 ×. S_A phase.

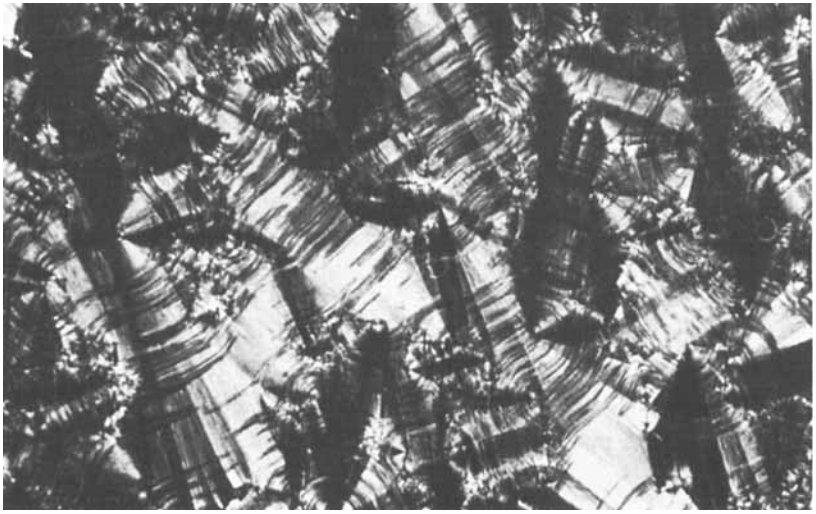


FIGURE 12b Photomicrographs for 4-propionyl-4′-*n*-octanoyloxyazobenzene ($n = 6$), crossed polarizers, magnification 80 ×. S_3 phase formation recorded during the cooling process.

the other one as S_1. During formation of S_3, partial solidification is also observed, as proved by the exothermic-endothermic peaks in the DSC curves relating to samples reheated immediately after the cooling process (Figure 11b, c).

This behaviour may be ascribed to the transition S_3–S_1 coupled with partial crystallization induced by the presence of some solid. Qualitatively it has been observed that the endothermic-exothermic behaviour is markedly influenced by the heating and cooling rates and by the amount of time spent at room temperature. It may be seen, from Figure 11d, that the initial behaviour is restored only if the sample is remelted after a long time at room temperature.

$n = 7$ (*Nonanoate*) This compound does not show a nematic phase; this is to be expected because of decreasing thermal stability range of this phase with the increasing value of n. During the cooling process, the formation of a monotropic phase, which has been indicated as S_1 by analogy with the previous homologue, is seen before solidification. The last process, occurring with some supercooling, is not as slow as in the preceding cases. In addition, the heating curves show the same morphology in samples reheated immediately after solidification and after days at room temperature.

The transitions may be summarized as follows:

$$\begin{tikzcd}
K \arrow[rr, "367"] & & S_A \arrow[r, shift left, "417"] \arrow[dl, shift left] & I \arrow[l, shift left] \\
& S_1 \arrow[ul] \arrow[ur, shift left, "*360"'] & &
\end{tikzcd}$$

$n = 8$ (*Decanoate*) Its behaviour is similar to the homologue $n = 7$ and follows the scheme:

$$\begin{tikzcd}
K \arrow[rr, "371"] & & S_A \arrow[r, shift left, "417{\cdot}5"] \arrow[dl, shift left] & I \arrow[l, shift left] \\
& S_1 \arrow[ul] \arrow[ur, shift left, "*359"'] & &
\end{tikzcd}$$

$n = 9$–16 No monotropic phases are observed for these homologues. The heating and cooling paths for all the compounds may be represented by the simple scheme:

$$K \rightleftarrows S_A \rightleftarrows I$$

The corresponding transition temperatures are summarized in Table I.

CONCLUSIONS

Figure 13 shows in a diagrammatic form the transition temperatures plotted as a function of n. The points representing temperatures for phase formation

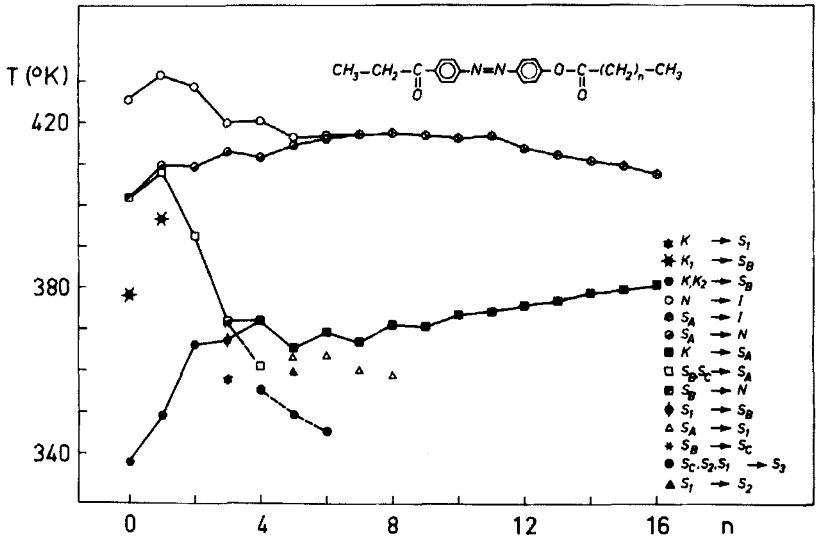
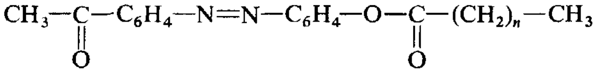


FIGURE 13 Plot of transition temperatures vs. *n* for 4-propionyl-4′-*n*-alkanoyloxyazobenzenes.

of the same type have been connected in the attempt to correlate the various phases.

Figure 13 may be compared with Figure 6 in Ref. [1] which reports the same parameters for the series of general formula



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

with *n* ranging from zero to 16.

From the comparison it may be observed that the addition of a $-CH_2-$ group to the terminal chains causes some changes in the thermal behaviour, although the general characteristics are almost the same.

The behaviour of the transition temperatures N–I, S_A–N, S_A–I and K–S_A is almost the same for both series with a characteristic even-odd trend which becomes less pronounced with increasing *n*. In both series the phase preceding the isotropic liquid on heating is a nematic for $n \leq 6$ and a smectic *A* phase for all the other compounds.

In correspondence to $n = 3$, however, there is an inversion in the trend of the even-odd behaviour of N–I transitions as observed in the case of *p*-alkoxy-*p*′-acyloxyazobenzenes and *p*-alkoxy-*p*′-acyloxyazoxybenzenes series studied by McCaffrey and Castellano.[7]

Also for the transition S_A–N for $n = 11$ there is an anomaly with respect to the other homologues. That does not seem to be attributable to the presence of impurities in the samples. No evidence, however, may be presented regarding the possible existence of a cis-trans equilibrium in the liquid crystals which might be the cause of the observed anomalies.

Beginning with heptanoate, the introduction of an additional —CH_2— becomes less critical and the thermal behaviour of the homologues is almost independent of terminal alkyl chain length. A similar behaviour has been reported for *n*-alkyl-4′-alkoxybiphenyl-4-carboxylates.[5]

The N–I or S_A–I transition temperatures for the homologous series are on average increased by about 25°K (for $m = 1$) with respect to the corresponding compounds with $m = 0$. This and some preliminary results on compounds with $m = 2$, for which the transition temperatures to the isotropic liquid falls to approximately the same level found for the compound with $m = 0$, leads us to the conclusion that an even-odd effect probably exists with regard to m.

Further studies in this direction are at present in progress and will be subject of a later communication.

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