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INVESTIGATION OF THE HOMOLOGOUS SERIES OF 4-PROPIONYL- -4'-n-ALKANOYLOXYAZOBENZENES BY X-RAY DIFFRACTION (*)

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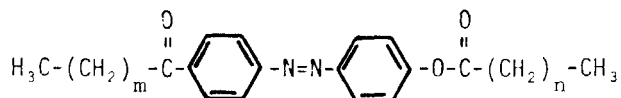
Abstract A study of the homologous series of liquid
crystalline 4-propionyl-4'-n-alkanoyloxyazobenzenes was
performed by x-ray diffraction. Two independent parameters
were used, namely the temperature and the paraffinic chain
length, in order to obtain some structural information. In
particular the molecular layer thickness was obtained as a
function of the temperature for the different phases and
different homologues. A linear dependence of the molecular
layer thickness as a function of chain length was found for
the crystalline phase as it was previously observed for the
smectic A phase. By comparison of the present data with
those of the series 4-acetyl-4'-n-alkanoyloxyazobenzenes,
a bilayer molecular organization similar to that of the
smectic A phase appears as very probable also for the
crystalline phase.

INTRODUCTION

An extensive research program recently started in order

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to better understand the relation between the molecular structure and the mesomorphic properties of liquid crystals. The attention was focussed on several homologous series having the following general formula



The structural properties of the smectic A phases were investigated for the two series with $m=0$ and $m=1$, respectively^{1,2}, leading to a model for the intermolecular organization. According to this model a bilayer arrangement exists with a strong segregation between paraffinic and polar parts of the molecules. Moreover some structural parameters were obtained³ for the different low temperatures phases occurring in the series $m=0$.

This paper presents the results of an x-ray investigation of the series with $m=1$, namely the 4-propionyl-4'-n-alkanyloxyazobenzenes, for n ranging from 1 to 16.

The transition temperatures and the nature of the different phases observed for the different compounds were reported in ref.4.

RESULTS AND DISCUSSION

Experimental details

Experiments were carried out by using a conventional x-ray powder diffractometer. Ni-filtered Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) was used. The divergence of the primary beam impinging on the sample was $\approx 8'$. The generator-sample distance was $\approx 18 \text{ cm}$ and the sample-counter distance $\approx 20 \text{ cm}$.

The sample had a thickness of $\approx 1.5 \text{ mm}$ and was held by two very thin Al sheets fixed to a circular hole in an Al matrix with a diameter of $\approx 1 \text{ cm}$. Heating was achieved by a hot stage (containing electrical resistors) whose temperature was controlled to $\pm 0.1^\circ\text{C}$ by an electronic device developed at G.E.N.G., Grenoble.

Moreover some diffraction patterns were recorded by using an Elliot toroidal camera.

Characterization of the solid phases

As recently a smectic K phase was discovered, the symbol K used in ref.3 will be replaced here by the symbol Cr to indicate crystalline and well ordered smectic phases.

The compounds with $n \geq 5$ show a common solid phase at room temperature, characterized by the diffraction pattern reported in fig. 1a. This phase was called K in ref.4 and will be called Cr_a in the following. By heating all these compounds a transition to the smectic A phase was observed by x-ray diffraction, in agreement with calorimetric and o

optical microscopy techniques, whereas for the compounds with $n \geq 7$ of the $m=0$ series a transition to another well-ordered phase was observed.

The diffraction pattern reported in fig.1a is quite similar to that reported in fig.1a of ref.3: the main difference is the absence in the present case of the peak corresponding to twice the repeat distance d .

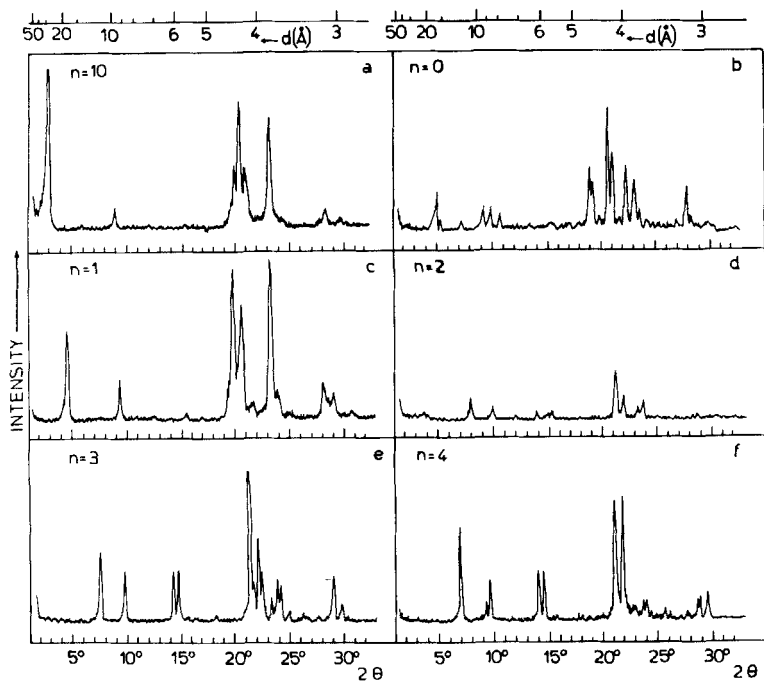


FIGURE 1 X-ray diffraction patterns at room temperature for different 4-propionyl - 4'- n -alkanoyloxyazobenzene homologues.

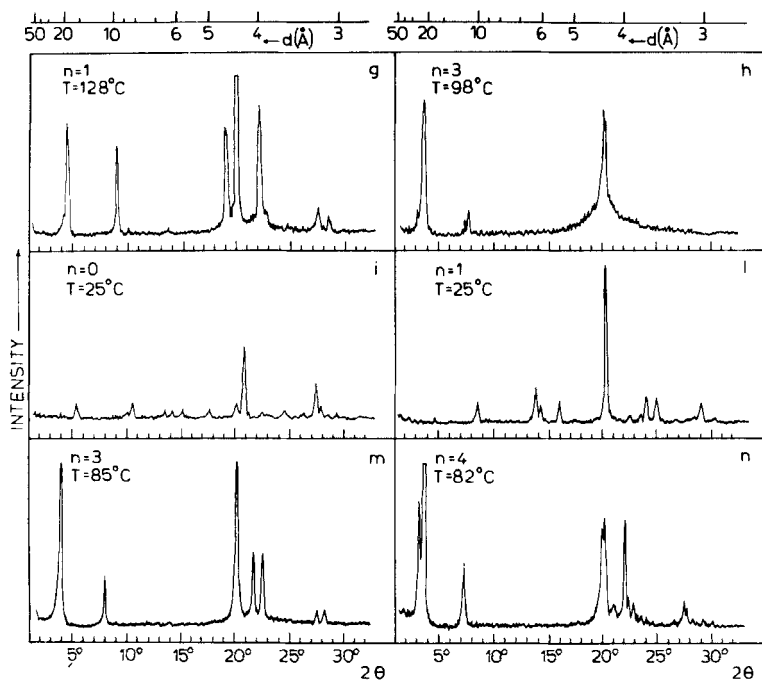


FIGURE 2 X-ray diffraction patterns of different peculiar phases mentioned in the text.

The compounds with $0 \leq n \leq 4$ show at room temperature crystalline phases, each one different from the other ones and different from Cr_a . The corresponding diffraction patterns are reported in fig.1.

The compounds with $0 \leq n \leq 3$ according to ref.4 show a smectic B phase. All these compounds show a similar x-ray diffraction pattern in correspondence to this phase, namely the

one reported in fig.2g. It is evident that this phase is not a smectic B one, which is normally characterized for powder samples by a single high angle peak⁵⁻⁸, but a phase with lower symmetry, namely an ordered smectic phase or a crystalline phase.

Moreover the phases indicated as a smectic C in ref.4, for the compounds with $n=3$ and $n=4$, show the x-ray diffraction pattern reported in fig.2h, which is characteristic of the smectic B phase.

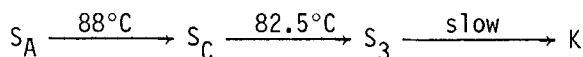
Fig.2i reports the diffraction pattern of $n=0$ crystalline phase indicated as K_2 in ref.4. This pattern was obtained after a month following the cooling down of the sample to room temperature.

For the compound with $n=1$ a transition crystal-smectic B is reported to occur by heating the sample according to the ref.4. Actually the x-ray diffraction patterns are similar in the two phases, but the Debye-Sherrer rings are continuous in the lower temperature phase and discontinuous in the higher temperature one. Fig.2l reports the diffraction pattern of the crystalline phase indicated as K_2 in ref.4, which appears at room temperature after about one month.

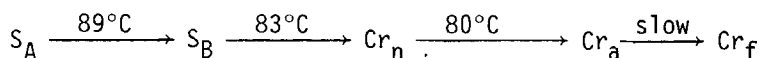
Fig.2m reports the diffraction pattern of the phase obtained by heating the compound with $n=3$, and indicated as S_1 in ref.4. This diffraction pattern is very similar to that of fig.1c; as a consequence also this phase could be either an ordered smectic phase or a crystalline one.

For the compound with $n=4$ a substantially different pha

se diagram by cooling was obtained by x-ray diffraction as compared to the one reported in ref.4. In fact instead of the sequence:



the following phase diagram, including an additional crystal line phase (Cr_n) shown in fig.2n, was obtained:



It should be remembered that the compounds with $5 \leq n \leq 8$ show the interesting hexatic phases ⁹⁻¹².

The layer spacing

As it was the case for the $m=0$ series, it was not possible to derive from the diffraction patterns of the different types of crystalline phases the elementary cell parameters of the corresponding crystallographic structures. Therefore only the positions of the low angle peaks were used, in order to derive the spacing of the molecular layers (reminiscent of the smectic organization) which exists generally in the crystalline phases of mesogenic compounds¹³⁻¹⁴.

Fig.3 reports the temperature dependence of the layer spacings for the homologues with $2 \leq n \leq 8$. It appears that the layer spacing associated to the crystalline phase of the virgin sample corresponding to $n=2$ is higher than that of the phases obtained at high temperature. No layer spacing comparable with that of smectic A is detectable for the virgin sample with $n=4$ on heating.

For the compounds with $n=6$ and $n=8$ layer spacing in the mono

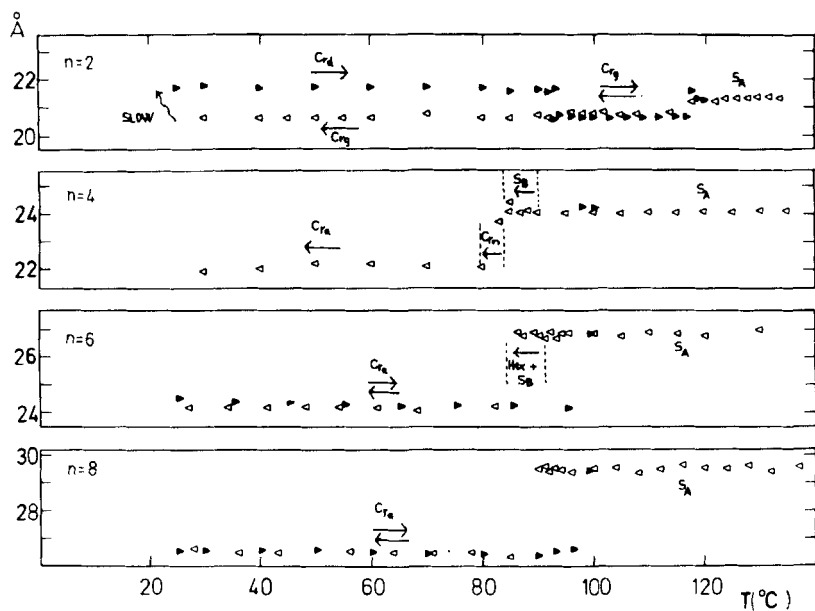


FIGURE 3 Layer spacing d as a function of temperature for the homologues with $n=2$, $n=4$, $n=6$ and $n=8$.

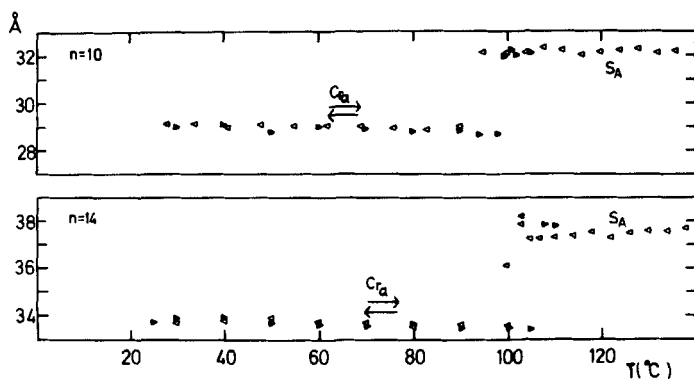


FIGURE 4 Layer spacing d as a function of temperature for the homologues with $n=10$ and $n=14$ in the solid Cr_a and smectic A phases.

tropic phases appear to be similar to those of the smectic A phase, showing that in these mesophases the molecules are in average non tilted.

Fig.4 reports the temperature dependence of the layer spacings for the homologues with $n=10$ and $n=14$. Both these compounds and the homologues with $n=12$ and $n=16$ (which were omitted due to similarity) show an hysteresis effect involving smectic A phase. The data concerning the crystalline phase obtained after cooling were omitted because coincident with data of the crystalline phase of the virgin sample.

Also for the $m=1$ series the layer thickness d varies linearly nearly as a function of temperature, both in the crystalline and smectic A phases for all the compounds of the series. This quantity can take the form³

$$d_{n,i}(T) = d_{n,i}(0) + (\partial d_{n,i} / \partial T) \cdot T$$

where n is the number of the carbon atoms of the aliphatic chain and i is the type of phase. Values obtained for $d_{n,i}(0)$ and $\partial d_{n,i} / \partial T$ are reported in Table I for Cr_a solid phase, whereas the corresponding values for the smectic A phase are reported in ref.2. The temperature coefficients in the solid phase are quite low in relation to the experimental uncertainty, and sometimes negative values are obtained, as it was the case for the $m=0$ series.

Fig.5 reports the variation of the layer thickness as a function of the chain length (at $T=100^\circ C$) for the Cr_a crystalline phase and, for comparison, the data referring to crystalline phase K_a of the $m=0$ series.

TABLE I Values of $d_n(0)$ and $\partial d_n / \partial T$ for Cr_a phase

n	$d_n(0^\circ C) (\text{\AA})$	$\partial d / \partial T \cdot 10^3 (\text{\AA}/^\circ C)$
4	22.0 ± 0.3	1.8 ± 5.3
5	23.4 ± 0.3	-0.5 ± 3.9
6	24.6 ± 0.2	-4.7 ± 3.8
7	26.0 ± 0.2	-4.5 ± 4.0
8	26.7 ± 0.2	-1.9 ± 3.4
9	28.5 ± 0.2	-7.4 ± 3.5
10	29.3 ± 0.2	-4.4 ± 3.1
11	31.0 ± 0.4	-3.3 ± 5.3
12	31.6 ± 0.3	-4.4 ± 3.1
13	33.7 ± 0.3	-15.1 ± 4.2
14	34.0 ± 0.3	-4.5 ± 3.9
15	35.1 ± 0.4	-3.9 ± 4.8
16	36.4 ± 0.4	-3.2 ± 6.8

It appears that inside the experimental accuracy the data for the characteristic crystalline phases of the two series coincide, whereas an appreciable difference was observed² for the layer thicknesses of the smectic A phases in the two series. The difference was attributed to a larger disorder or tilt angle for the series $m=1$. The similarity between the layer thicknesses for the solid phases of the two series supports the hypothesis of a bilayer structure with head-to-tail intermolecular organization, because in the case of the monolayer structure one should observe an increase in the layer

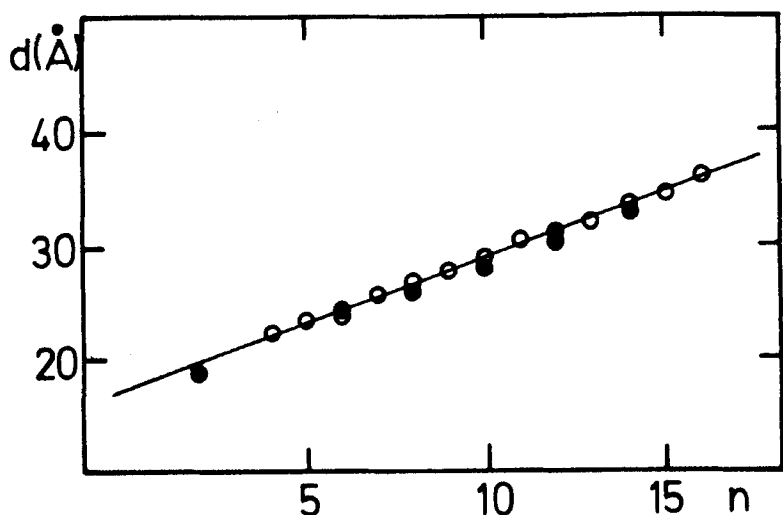


FIGURE 5 Values of the layer spacing d at $T=100^{\circ}\text{C}$ as a function of the number n of methylenic groups in the aliphatic chain. \circ Cr_a ($m=1$). \bullet K_a ($m=0$).

thickness for the series $m=1$, if the same tilt angle is assumed for the two series.

By assuming a bilayer structure a tilt angle of the paraffinic chains $\theta_p = 63^{\circ}$, already calculated for the $m=0$ series, should be adopted also for the Cr_a crystalline phase of the $m=1$ series.

Figure 6 reports the layer thickness difference Δd between Cr_a and S_A phases. For comparison the corresponding data for the $m=0$ series are reported. It appears that the observed Δd are quite similar for both series. However by evaluating the ratio $\Delta d/d_A$, where d_A is the molecular layer thick

ness of the smectic A phase of a given compound, as a function of chain length one obtains a difference between the two series. This quantity is practically independent from the chain length for the series $m=1$, indicating a common change of tilt angle at the considered phase transition, for all the compounds, whereas a slight increase is observed for the series $m=0$, indicating a more complex structural change.

CONCLUSION

Some structural data were obtained for the homologous

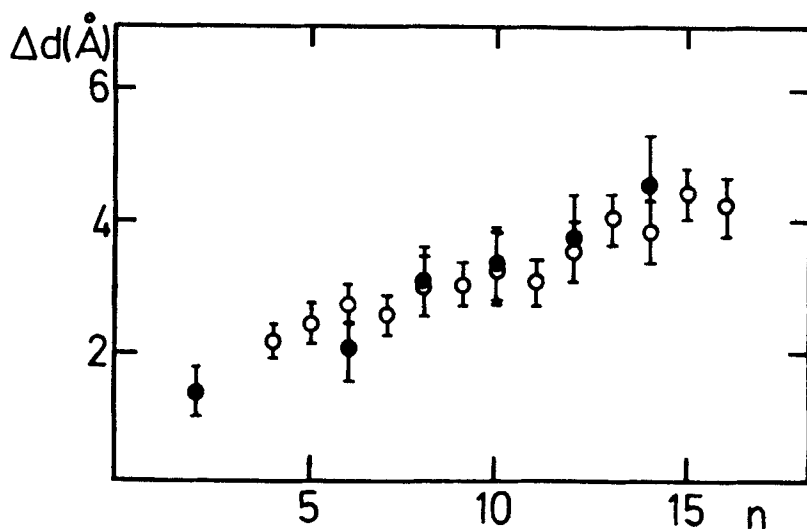


FIGURE 6 Variation of the layer spacing Δd as a function of aliphatic chain length at $T=100^\circ\text{C}$.

○ $\text{Cr}_a\text{-S}_A$ ($m=1$). ● $\text{K}_a\text{-S}_A$ ($m=0$).

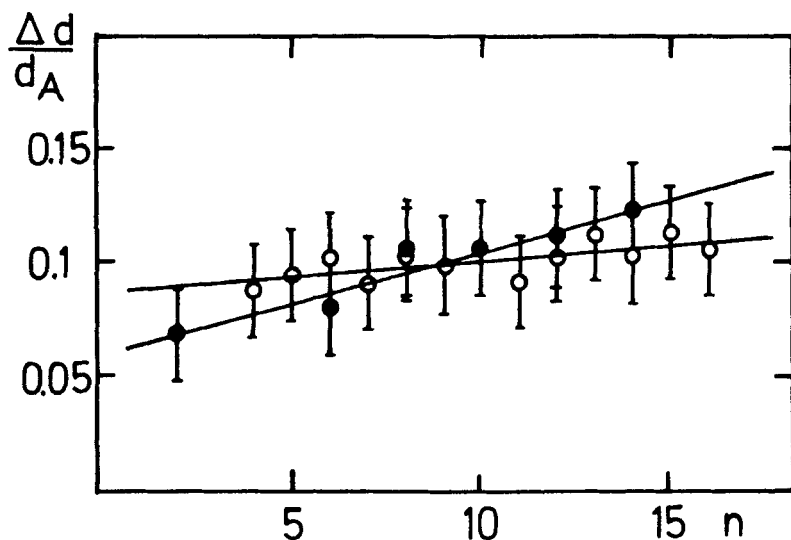


FIGURE 7 Ratio between layer thickness variation Δd and the smectic A layer thickness d_A as a function of the number n of methylenic groups in the chain at $T=100^\circ\text{C}$. $\circ \text{Cr}_a - \text{S}_A$ ($m=1$). $\bullet \text{K}_a - \text{S}_A$ ($m=0$).

series 4-propionyl-4'-n-alkanoyloxyazobenzene by x-ray diffraction. In particular the molecular layer thickness as a function of temperature was obtained for the different crystalline phases and mesophases.

The obtained data were compared with similar data previously obtained for the series 4-acetyl-4'-n-alkanoyloxyazobenzenes. From this comparison a bilayer molecular organization similar to the one found in smectic A seems to be more probable for the Cr_a phase than a monolayer organization.

Of course in the crystalline phase the molecule would

have a quite large tilt angle.

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