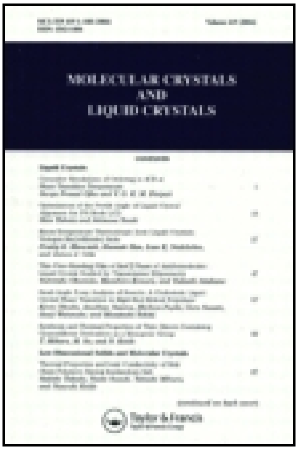

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Investigation of the Homologous Series of 4-Acetyl-4′-*n*-Alkanoyloxyazobenzenes by X-ray Diffraction[†]

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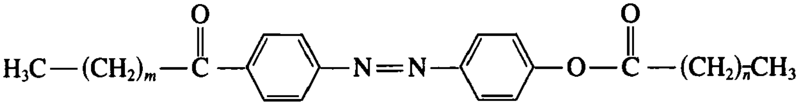
This paper reports an investigation by X-ray diffraction of the homologous series of liquid crystalline 4-acetyl-4′-*n*-alkanoyloxyazobenzenes. By using two independent parameters, namely the temperature and the paraffinic chain length, it was possible to obtain some structural information on two solid phases for comparison with a previously reported model for the S_A phase of the same series. In particular, the molecular layer thickness and, by using previously reported dilatometric data, the aromatic sublayer thickness, the methylene group thickness, the molecular area and the aromatic stem inclination angle were obtained for the different phases.

INTRODUCTION

We have recently started a research program concerning the relation between the molecular structure and the mesomorphic properties of liquid crystal materials. This program foresees the investigation of several homologous series having the following general formula



[†] Presented at the Ninth International Liquid Crystal Conference, Bangalore, India, December 6–10, 1982.

This paper presents the results of an X-ray study concerning the first series, namely the 4-acetyl-4'-*n*-alkanoyloxyazobenzenes, corresponding to $m = 0$ and to 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. 1. According to the different n values, only smectic A and nematic mesophases are observed.

The structure of the smectic A mesophase was presented in Ref. 2. A bilayer organization of the molecules was found to occur with a strong segregation between paraffinic and polar parts of the molecules, together with a pronounced spreading of the aliphatic chains at the interfaces.

RESULTS AND DISCUSSION

Experimental details

Experiments were carried out by using a conventional X-ray powder diffractomer. Ni-filtered Cu K α radiation ($\lambda = 1.54$ Å) was used. The divergence of the primary beam impinging on the sample was $\simeq 8'$. The generator-sample distance was $\simeq 18$ cm and the sample-counter distance $\simeq 20$ cm. The sample had a thickness of $\simeq 1.5$ mm and was held by two very thin Al sheets fixed to a circular hole in an Al matrix with a diameter of $\simeq 1$ cm. Heating was achieved by a hot stage (containing electrical resistors) whose temperature was controlled to ±0.1°C by an electronic device developed at G.E.N.G., Grenoble.

Characterization of the solid phases

The compounds with $1 \leq n \leq 16$ have been investigated. For $n = 5$ and $n \geq 7$ the results obtained are compatible with the phase diagram reported in Ref. 1. In particular, two solid phases were observed in the previous calorimetric investigation[1] during the first heating process, namely K_3 at room temperature and K_1 at higher temperature. Two different diffraction patterns were obtained in the present experiment; these corresponded with the two phases and are shown in Figure 1*a* and in Figure 1*b* respectively. Figure 1*b* corresponds to a higher symmetry (as is reasonable) as a consequence of the disappearance of the very pronounced peak at $2\theta \simeq 24°$ observed in the pattern of Figure 1*a*. Based upon the X-ray data, it cannot be excluded that the K_1 phase is an ordered smectic phase.

For the homologue with $n = 6$, a transition from a K_3 solid into a K_2 solid and then into a K_1 solid was observed—see Ref. 1. In the present experiment, an X-ray diffraction pattern similar to that reported in Figure

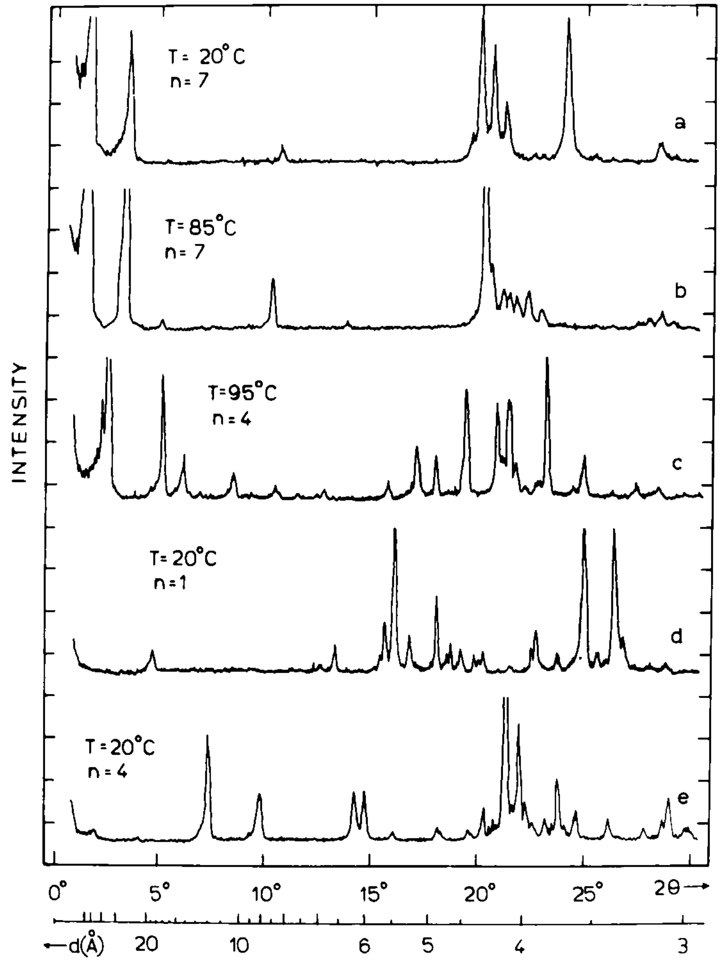


FIGURE 1 Data from the X-ray diffraction patterns of the solid phases of the series of 4-acetyl-4'-*n*-alkanoyloxyazobenzenes.

1*a* was observed in the temperature range of existence of the two phases K_3 and K_2, and the diffraction pattern shown in Figure 1*b* in the temperature range of existence of the K_1 phase. Therefore, concerning the K_3 and K_1 solid phases, X-ray data are in agreement with the data for the previously discussed homologues. Concerning the transition K_3 into K_2, the sensitivity of our apparatus is not sufficient to detect with certainty a distortion of the lattice cell at this transition.

For the homologue with $n = 3$, a transition from a K_3 solid into a K_1 solid was observed—see Ref. 1. In the present experiments, a diffraction pattern similar to that reported in Figure 1*c* was observed in the temperature range of existence of both K_3 and K_1 phases, instead of observing the two other diffraction patterns, as was the case for the homologues with $n = 5$ and $n \geq 7$.

A similar situation was found for the homologue with $n = 1$; a single X-ray diffraction pattern, shown in Figure 1*d*, was observed in the temperature ranges corresponding to the K_3 and K_1 phases of Ref. 1. Therefore the present experiment seems to suggest a more complex solid polymorphism as compared with that indicated by the DSC and optical microscopy data: an eventual X-ray crystallographic investigation of single crystals would more effectively clear up this problem. Moreover the failure to

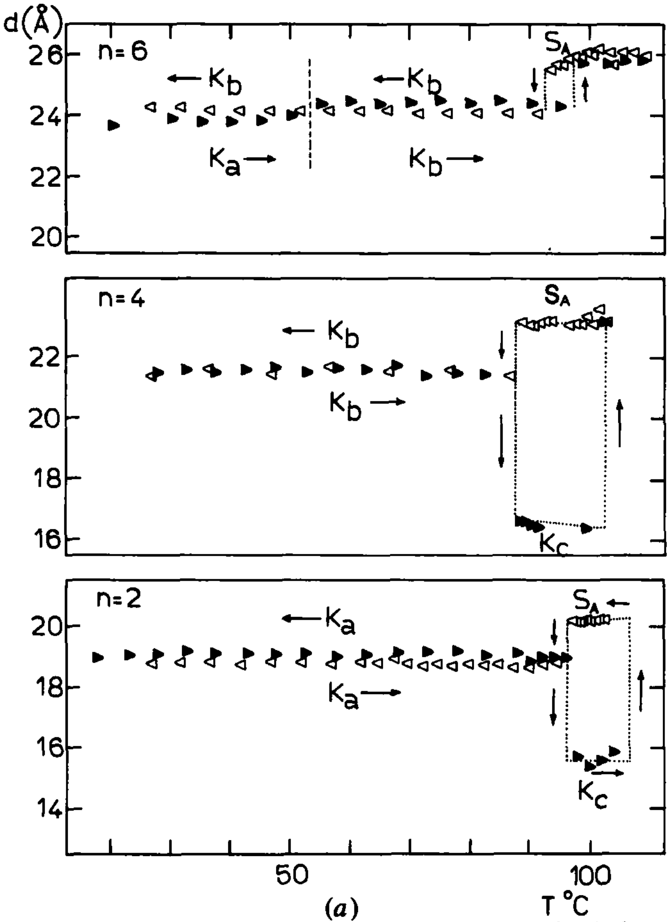
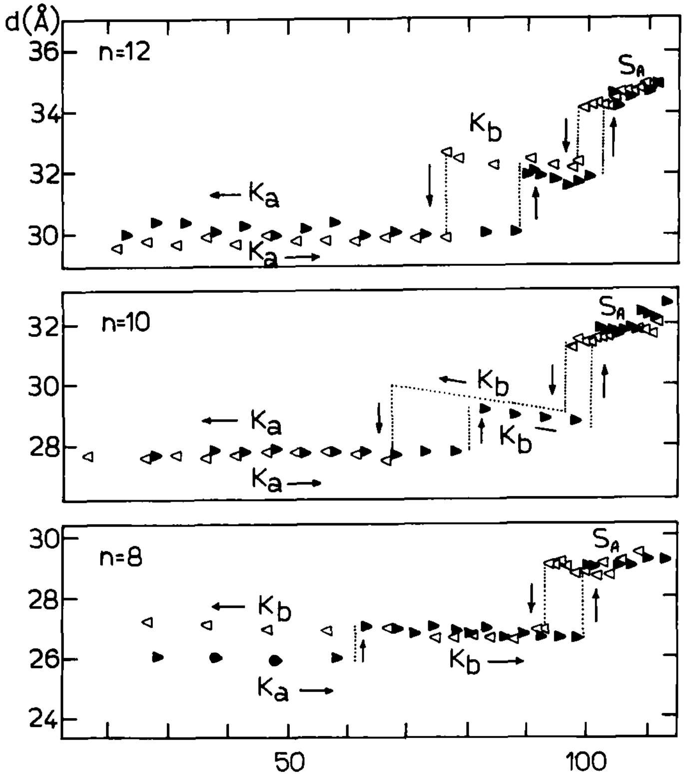


FIGURE 2 Spacing *d* as a function of temperature for the different *n* values in the crystalline and smectic phases. Figure 2*a*: $n = 2,4,6$; Figure 2*b*: $n = 8,10,12$.

observe by X-ray diffraction the transition between the two phases K_3 and K_1 could be attributed to a strong similarity between the two lattice cells. For the homologue with $n = 1$, Ref. 1 reports a smectic B phase; according to the present X-ray diffraction study, this phase appears to be similar to the K_3 phase of the compounds with $n \geq 7$ and therefore is not a smectic B.

For the homologue with $n = 4$, a transition from a K_3 solid into a K_1 solid was reported in Ref. 1. The transition was also observed by X-ray diffraction; however, for the K_3 solid, the diffraction pattern reported in Figure 1*e* was obtained, and not that of Figure 1*a* obtained for the K_3 solid in homologues with $n \geq 7$. For the K_1 solid, the diffraction pattern of Figure 1*c* was obtained instead of that shown in Figure 1*b*. For the same homologue, a transition from the smectic A phase into the K_2 phase was reported by cooling in Ref. 1; in the present experiments, this transition was also observed and the diffraction pattern shown in Figure 1*b* was obtained for the crystalline phase.



(*b*)

FIGURE 2 (*Continued*)

Finally for the homologue with $n = 2$, the transition from K_3 into K_1 reported in Ref. 1 was also observed by X-ray diffraction: for the K_3 solid, a diffraction pattern was obtained similar to that for the homologues with $n \geq 7$ shown in Figure 1*a*. The diffraction pattern of Figure 1*c* was obtained for the K_1 solid and not that of Figure 1*b*. For the same homologue, a monotropic smectic A and a K_2 solid phase were reported in Ref. 1 by cooling the nematic phase. The same transitions were observed here by X-ray diffraction, and a diffraction pattern similar to that of Figure 1*a* was obtained for the K_2 phase.

The layer spacings

It was not possible to derive from the diffraction patterns of the five types of crystalline phase reported in Figure 1 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 spacings of the molecular layers or bilayers (reminiscent of the smectic organization) which exist generally in the crystalline phases of mesogenic compounds.[3,4]

In the two types of solid characterized by the diffraction patterns of Figures 1*a* and 1*b*, it was possible to observe for most of the homologues a peak in the low angle region providing a repeat distance d similar to that found in the smectic A phase. Sometimes, as appears in Figures 1*a*, 1*b*, 1*c*, and 1*e*, a $2d$ repeat distance was also found. Figure 2 reports the temperature dependence of d for the homologues with $2 \leqslant n \leqslant 12$. In the following, each one of the five solid phases will be indicated by K_i, where i is the letter associated with the corresponding diffraction pattern in Figure

TABLE I

n	Phase	$d(T = 0°\text{C})$Å	$\partial d/\partial T$(Å/°C)	n	Phase	$d(T = 0°\text{C})$Å	$\partial d/\partial T$(Å/°C)
2	K_a	18.6	$(2.1 \pm 1.7) \times 10^{-3}$	10	K_a	27.5	$(3.0 \pm 4.0) \times 10^{-3}$
	K_c	11.7	$(3.7 \pm 4.5) \times 10^{-2}$		K_b	31.4	$(-2.6 \pm 2.7) \times 10^{-2}$
	S_A	18.9	$(1.3 \pm 4.0) \times 10^{-2}$		S_A	25.7	$(5.5 \pm 2.1) \times 10^{-2}$
4	K_b	21.5	$(-0.5 \pm 2.0) \times 10^{-3}$	12	K_a	29.9	$(0.6 \pm 4.0) \times 10^{-3}$
	K_c	18.6	$(-2.2 \pm 2.2) \times 10^{-2}$		K_b	33.8	$(-1.4 \pm 1.6) \times 10^{-2}$
	S_A	22.0	$(1.5 \pm 1.5) \times 10^{-2}$		S_A	26.4	$(7.4 \pm 2.5) \times 10^{-2}$
6	K_a	23.9	$(-0.8 \pm 2.1) \times 10^{-2}$	14	K_a	32.4	$(2.0 \pm 4.0) \times 10^{-3}$
	K_b	24.3	-0.00 ± 0.88		K_b	30.5	$(3.4 \pm 8.4) \times 10^{-2}$
	S_A	23.4	$(2.3 \pm 1.7) \times 10^{-2}$		S_A	30.9	$(6.3 \pm 5.2) \times 10^{-2}$
8	K_a	26.15	$(-1.4 \pm 1.2) \times 10^{-2}$				
	K_b	27.4	$(-6.0 \pm 3.0) \times 10^{-3}$				
	S_A	26.9	0.002 ± 0.13				

1. To economize in space, the data for the compound with $n = 14$, which are similar to those for $n = 12$, have not been reported. For the compound with $n = 16$ it was not possible to observe any low angle diffraction peak, probably as a consequence of a partial alignment of the sample.

For the compound with $n = 4$, due to the difficulty of accurately reading the low angle diffraction peaks in the K_e phase, data have been reported for a sample previously heated till the smectic A phase formed. This remained in the K_b phase after cooling to room temperature.

For the compound with $n = 10$, low angle peaks in the K_b phase have not been observed during cooling: an interpretation, by analogy with that

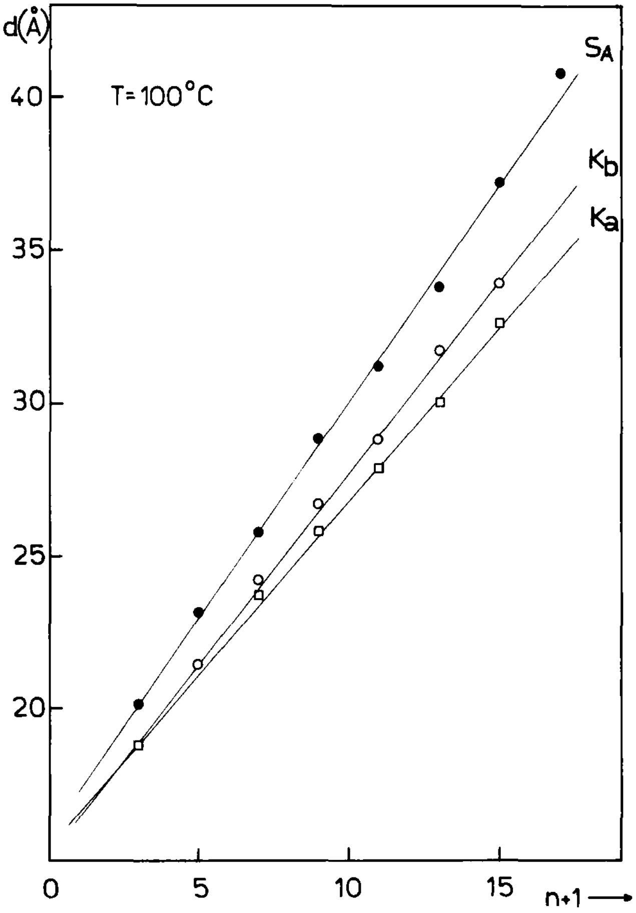


FIGURE 3 Values of the spacing d at $T = 100°C$ as a function of the number $n + 1$ of carbon atoms in the aliphatic chain: □ K_a phase, ○ K_b phase, ● smectic A phase.

for the compounds with $n = 12$ and $n = 8$, is reported in Figure 2*b*. An abrupt increase in the layer spacing d is observed for each compound at the crystal-smectic A phase transition. A similar abrupt change has already been observed in the molecular volume as reported in Ref. 5. The layer thickness d varies linearly as a function of temperature both in the crystalline and the smectic A phases for all the compounds of the series. This quantity, by analogy with the molar volume,[5] can take the form

$$d_{n,i}(T) = d_{n,i}(0) + \frac{\partial d_{n,i}}{\partial T} \cdot T \qquad (1)$$

where n is the number of the carbon atoms of the aliphatic chain and i is the type of phase. The values obtained for $d_{n,i}(0)$ and $\partial d_{n,i}/\partial T$ are reported in Table I.

The temperature coefficients in the solid phases are quite low in relation to the experimental uncertainty, and sometimes negative values are obtained—in particular with the K_b phase. A hysteresis effect involving the smectic A phase is observed for each compound.

Figure 3 reports the variation of the layer thickness as a function of the chain length for the K_a and K_b crystalline phases and for the smectic A phase: the values for all the phases were obtained directly or by extrapolation according to Eq. (1) for $T = 100°C$. It appears that the layer thickness can be considered as a linear function of n, so that the equation[2]

$$d(n,T) = d_a(T) + (n + l)d_p(T)$$

can be applied, where $d_a(T)$ represents the aromatic sublayer thickness and $d_p(T)$ the methylene group thickness for a given temperature. The values obtained at $T = 100°C$ for the different phases are reported in Table II and the physical implications will be discussed below.

Figure 4 reports the layer thickness variations Δd at the K_a-K_b and K_b-S_A transitions. For both transitions an increase of Δd as a function of the chain length is observed, the variation associated with the K_b-S_A transition being always larger than that associated with the K_a-K_b transition.

TABLE II

Aromatic thickness d_a and methylene group thickness d_p at T = 100°C

Phase	d_a	d_p
K_a	15.5	1.13
K_b	15.2	1.26
S_A	15.9	1.42

Molecular surface and structural data

By using dilatometric[5] and X-ray diffraction data, it was possible to derive the molecular area S of the base of the prism which contains two molecules, as was done in Ref. 2 for the S_A phase. The values obtained for the K_a, K_b and S_A phases are reported in Table III. A small decrease in S is observed at the K_a-K_b phase transition, whereas no substantial difference is observed at the K_b-S_A transition. A small decrease in S on increasing the chain length is observed for the S_A phase in agreement with the results of Ref. 2.

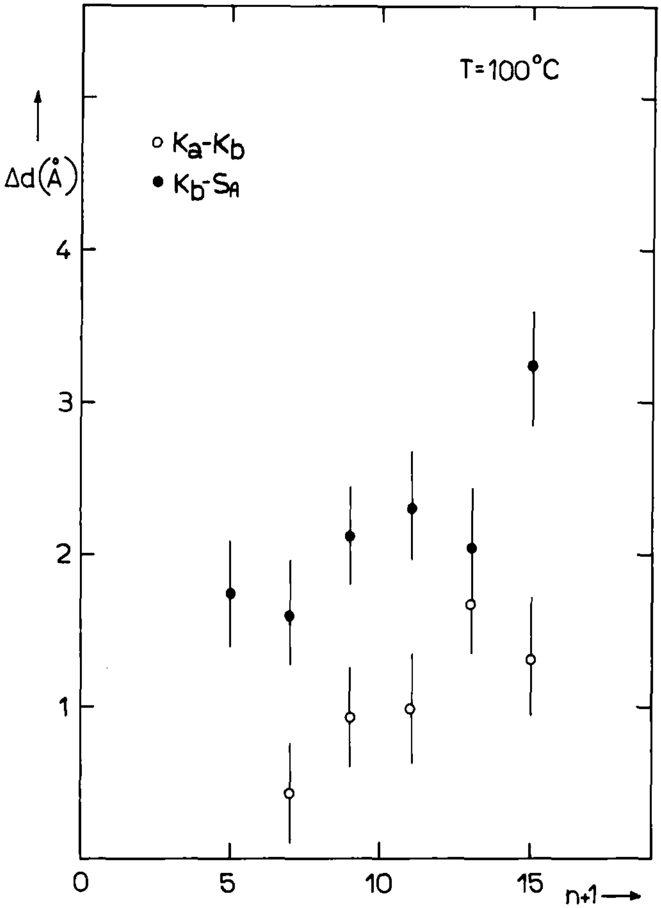


FIGURE 4 Variation of the d spacing at the K_a-K_b transition (○) and at the K_b-S_A transition (●) as a function of the length of the aliphatic chain, calculated at T = 100°C.

TABLE III

Molecular area S (Å^2)

n	K_a	K_b	S_A
2	46.4		45.6
4			45.0
6		44.6	44.9
8	46.0	44.6	44.3
10	46.6	45.3	44.8
12	45.7	44.2	44.6
14	45.7	44.3	43.5
16			42.5

From the experimental values for the molar volume V, the molar volume V_a of the aromatic part, and the layer thickness d, the thickness of the aromatic sublayer d_a was obtained through the relation

$$V/V_a = d/d_a$$

as employed in Ref. 2.

Figure 5 reports the values of d_a for each n value of the series calculated at $T = 100°C$ for the K_a, K_b and S_A phases. There is observed for each phase a slight increase of d_a as a function of the chain length; moreover a slight increase at the K_a-K_b phase transition and a larger one at the K_b-S_A are evident. Δd_a is roughly the same for all homologues at the first transition and slightly increases as a function of n at the second.

By assuming that the aromatic stems are arranged in the solid phases as in S_A on a monomolecular sublayer[2], it is possible to obtain the inclination angle θ_{an} of the aromatic stem of the homologous n in a given phase by the equation

$$d_{an} = d_a \cos \theta_{an} \tag{2}$$

The angle θ_{an} is defined with respect to the normal to the layer. By using for the length d_a of the aromatic stem the value 17.6 Å obtained from a model,[2] the values of θ_{an} are obtained for the K_a and K_b phases and for the S_A—see Figure 6. The inclination of the aromatic stems is about the same in the two solid phases and is almost independent of the length of the paraffinic chain. As a consequence, one can assume that in each of the two solid phases the crystallographic structure is the same for each homologue. In the smectic A phase, the aromatic stems are less tilted as compared with the solid phases. Moreover the tilt angle decreases on increasing the paraffinic chain length, becoming zero for the longest chain examined.

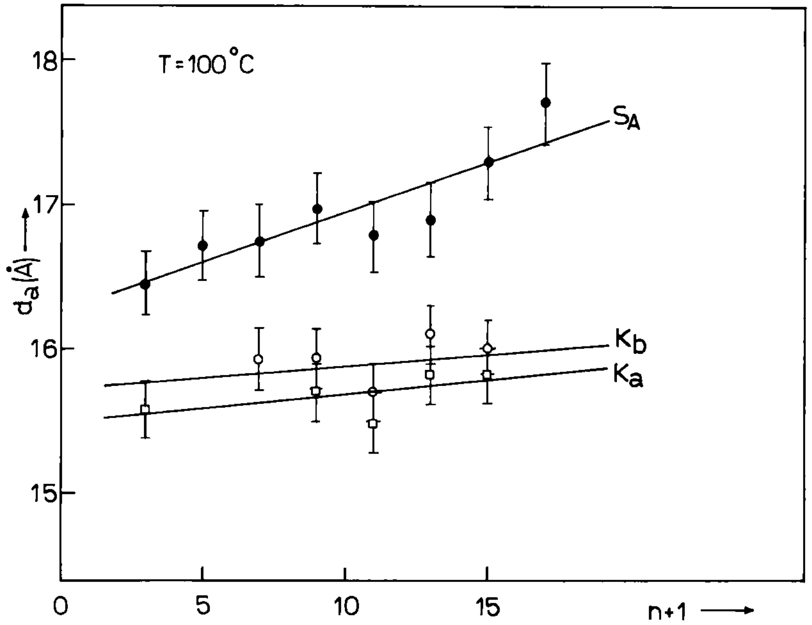


FIGURE 5 Values of the aromatic thickness d_a calculated at T = 100°C as a function of the length of the aliphatic chain: ☐ K_a phase, ○ K_b phase, ● S_A phase.

Table II shows that the methylene group thickness d_p is 1.42 Å for the S_A phase, in agreement with the results of Ref. 2, and 1.26 Å for the K_b phase and 1.13 Å for the K_a phase. In Ref. 2, the strongest argument in favor of a bilayer type arrangement of molecules inside the smectic layers was the d_p value of 1.43 Å, significantly larger than the increment of one methylene group for a crystalline paraffin in its most stretched configuration (1.27 Å). This argument fails for K_a and K_b phases for which a monolayer organization of the molecules could also be assumed. Moreover the other structural data are compatible with both types of organization. If one assumes a bilayer organization similar to that[2] for the S_A, it is likely that the paraffinic chains are tilted, at least in the K_a phase, although a certain disorder cannot be excluded in the K_b phase. In fact the molar entropies associated with the K_a-K_b transitions increase regularly[6] with n up to a value of 5R. The maximum tilt angle of the paraffinic chains with respect to the normal to the layers would correspond, for a given solid phase, to the most stretched configuration and can be calculated by the equation

$$d_p = 2 \cdot 1.27 \cos \theta_p \qquad (3)$$

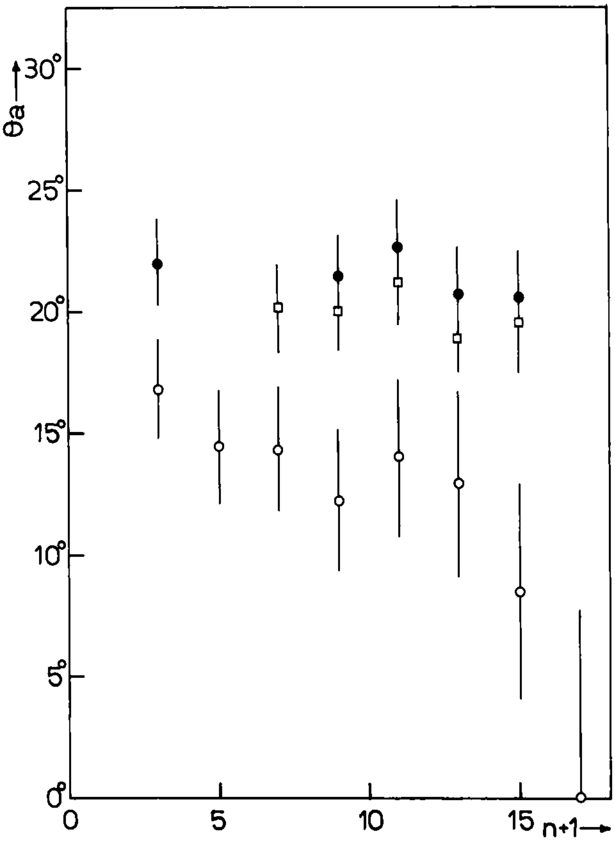


FIGURE 6 Values of the tilt angle of the aromatic stem with respect to the normal to the molecular layers as a function of the chain length: ● K_a phase, □ K_b phase, ○ S_A phase.

where d_p is the methylene group thickness reported in Table II, and 1.27 Å is the thickness of a methylene group for a paraffinic chain normal to the layer. The values $\theta_p = 63°$ and $\theta_p = 60°$ would be obtained in this limiting case for the K_a and K_b phases respectively. In this case, a molecular area $S = 45$ Å^2 would correspond to each chain in the two solid phases, as a consequence of the large tilt angle.

On the other hand, the data are compatible with a monolayer structure, probably with interdigitation of the paraffinic chains, in a similar way to that in model II of Ref. 7. In this case the tilt angle corresponding to the limiting case of the most stretched configuration can be calculated by the equation

$$d_p = 1.27 \cos \theta_p \tag{4}$$

Values $\theta_p = 27°$ and $\theta_p = 7°$ would be obtained in this case for the K_a and K_b phases, respectively. As a consequence, the paraffinic chains would have about the same orientation as the aromatic stems in the K_a phase, and would be about normal to the molecular layers in the K_b phase. A molecular area $S \simeq 22.5$ Å^2 would be associated with each paraffinic chain in the two solid phases; this value is in agreement with the data reported in Ref. 8.

For both monolayer and bilayer structures a head-to-tail intermolecular organization is probably to be assumed.

CONCLUSION

X-ray diffraction has been used to investigate the characteristics of the series 4-acetyl-4'-*n*-alkanoyloxyazobenzenes as a function of temperature. Five types of solid phase have been observed. Some structural information was obtained from the data. In particular the molecular layer thickness as a function of temperature in two solid phases and in the S_A phase was obtained. In addition, the aromatic sublayer thickness, the methylene group thickness, the molecular area and the inclination angle of the aromatic stems were obtained for the same phases. The aromatic stems were assumed to be arranged in a monomolecular sublayer and placed head to tail, whereas the situation for the paraffinic chains on each side of the aromatic sublayer is less clear. The aromatic stems appear to be more inclined in the solid phases as compared with the S_A phase with respect to the normal to the molecular layers.

Both a bilayer molecular organization similar to the one previously found in S_A and a monolayer organization with interdigitation of the paraffinic chains are consistent with the structural data obtained. For both cases the maximum tilt angles of the paraffinic chains were obtained.

References

1. G. Poeti, E. Fanelli and M. Braghetti, *Mol. Cryst. Liq. Cryst.*, **45**, 145 (1978).
2. G. Albertini, E. Fanelli, D. Guillon, S. Melone, G. Poeti, F. Rustichelli and G. Torquati. *J. Chem. Phys.*, **78**, 2013 (1983).
3. P. Sawzik and B. M. Craven in *Liquid Crystals* (ed. S Chandrasekhar), Heyden, London, Philadelphia, Rheine, p. 171 (1979).
4. J. Doucet, J. P. Mornon, R. Chevalier and A. Lifchitz, *Acta Cryst.*, **B33**, 1701 (1977); J. Doucet, A. M. Levelut and M. Lambert., *Acta Cryst.*, **B33**, 1710 (1977).
5. G. Poeti, E. Fanelli, G. Torquati and D. Guillon, submitted to *Il Nuovo Cimento*.
6. E. Fanelli, G. Poeti and M. Braghetti, *Mol. Cryst. Liq. Cryst. Lett.*, **64**, 199 (1981).
7. P. Seurin, D. Guillon and A. Skoulios, *Mol. Cryst. Liq. Cryst.*, **71**, 37 (1981).
8. P. Seurin, D. Guillon and A. Skoulios, *Mol. Cryst. Liq. Cryst.*, **71**, 51 (1981).