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Mesomorphic properties and molecular structure. II. Structure of the smectic A phase in the 4-propionyl-4'-n-alkanoyloxy-azo-benzene series

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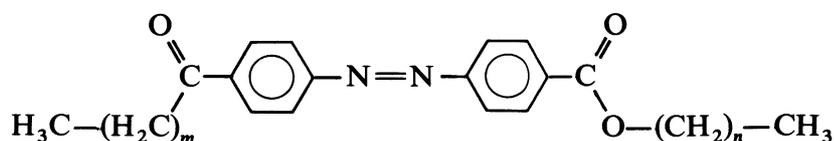
Résumé. — Les paramètres structuraux concernant la phase smectique A des homologues de la série 4-propionyl-4'-n-alkanoyloxy-azo-benzène sont obtenus par dilatométrie et par diffraction des rayons X. La comparaison avec les données de la série 4-acétyl-4'-n-alkanoyloxy-azo-benzène montre que pour les deux séries on peut adopter le même modèle sous réserve de quelques modifications concernant le degré de désorganisation des chaînes aliphatiques et l'angle d'inclinaison des parties polaires des molécules. L'angle d'inclinaison de la partie rigide des molécules smectogéniques dans la phase smectique A est étudié en relation avec la constitution chimique et l'architecture moléculaire.

Abstract. — Structural parameters concerning the smectic A phase in homologues of the 4-propionyl-4'-n-alkanoyloxy-azo-benzene series have been obtained by using dilatometry and X-ray diffraction techniques. The comparison with the data of the previously investigated homologues of the 4-acetyl-4'-n-alkanoyloxy-azo-benzene series suggests that the same model can be adopted for both series with some modifications regarding the spreading of the aliphatic chains and the tilt angle of the aromatic cores. Experimental evidence for the tilt angle of the rigid part of smectogenic molecules in the smectic A phase is discussed in relation to the chemical constitution and molecular architecture.

1. Introduction.

As a part of an extensive program aiming at a better understanding of the relation between the molecular structure and the mesomorphic properties of liquid

crystals, the structure at a molecular level was investigated for the smectic A phase occurring in a homologous series, namely the 4-acetyl-4'-n-alkanoyloxy-azo-benzene [1] having the general chemical formula :



with $m = 0$.

Dilatometry and X-ray diffraction techniques were used to determine several structural parameters concerning the aromatic part and the paraffin chains. From the data obtained, a model was proposed, according to which a strong segregation occurs between paraffin and polar rigid parts of the molecules, with a pronounced spreading of the aliphatic tails at the interface between layers.

This paper reports a similar investigation of the homologous series 4-propionyl-4'-n-alkanoyloxy-azo-

benze which corresponds to $m = 1$ in the chemical formula mentioned above. By comparing the structural parameters of the two series, we also find evidence for a larger molecular motion and for an average tilt angle of the rigid parts in the $m = 1$ series.

2. Experimental results.

All the compounds of the series $m = 1$ have been synthesized recently, and their polymorphism has been described in detail elsewhere [2]. In this work, we have

only considered the even terms of the series, from $n = 2$ up to $n = 16$, which all exhibit smectic A phases in a large range of temperature.

2.1 DILATOMETRIC DATA. — The experimental procedure is the same as used previously for other liquid crystal series [3]. Let us recall that, with the dilatometry technique, we measure the molar volume of the sample as a function of temperature. Among all the information we are able to obtain from such experiments (thermal expansion coefficients, order of a transition, ...) we will only consider here the data necessary for the interpretation and discussion of the smectic A organization at the molecular level.

Figure 1 presents the variation of the molar volume as a function of the length of the aliphatic chain for the two series $m = 0$ and $m = 1$, at the same temperature of 127 °C in the smectic A phase. At this temperature the smectic A phase exists for all the compounds of the series $m = 1$. The molar volumes of the series $m = 0$ were extracted from the overall experimental data published recently [4].

As is often observed for homologous series [5], the volume is a linear function of n :

$$V(n, T) = V_a(T) + (n + 1) \cdot V_p(T)$$

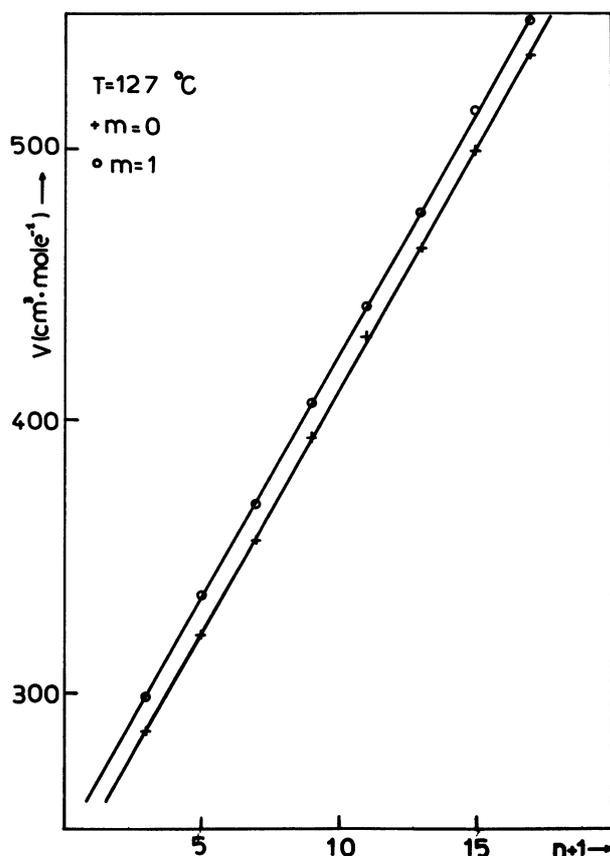


Fig. 1. — Molar volume in the smectic A phase at 127 °C as a function of the length of the aliphatic chain for the two series $m = 0$ and $m = 1$. The lines are obtained by a linear least squares regression fit of the experimental data.

where $V(n, T)$ stands for the molar volume of the n th term of the series, $V_a(T)$ and $V_p(T)$ stand for the molar volume of the aromatic part and of one methylene group of the molecules respectively. As mentioned in a previous paper [1], $(n + 1)$ was used in order to take into account the contribution of the CH_2 group belonging to the terminal CH_3 group.

The values of V_a and V_p which can be obtained from figure 1 are gathered in table I.

The same value of V_p , which represents the volume of one methylene group is found in the two series. In the isotropic phase of alkylbiphenyls [6], the volume of one methylene group is approximately $17.1 \text{ cm}^3 \cdot \text{mole}^{-1}$; the value of $17.8 \text{ cm}^3 \cdot \text{mole}^{-1}$ found for V_p shows that the aliphatic chains are quite disorganized in the two series, with the same volume.

On the other hand, the difference between the volumes of the rigid parts of the molecules for the series $m = 0$ and $m = 1$ is found to be around $13 \text{ cm}^3 \cdot \text{mole}^{-1}$. The two rigid parts are constituted by the aromatic stem and one acetyl group for the series $m = 0$, and by the aromatic stem and one propionyl group for the series $m = 1$. The difference lies only in the addition of one methylene group in the series $m = 1$. The small value of $13 \text{ cm}^3 \cdot \text{mole}^{-1}$ (of the order of one crystalline CH_2 group) indicates a pronounced ordering of the propionyl group in the series $m = 1$, in comparison with the disorganized aliphatic chain linked at the other extremity of the aromatic stem.

2.2 X-RAY DIFFRACTION DATA. — Experiments were carried out by using a conventional X-ray powder diffractometer. Ni filtered CuK_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 $\pm 0.1 \text{ °C}$ by an electronic device developed at C.E.N.G., Grenoble.

Figure 2 presents the variation of the interlayer distance for all the terms of the series as a function of temperature within the stability domain of the smectic A phase. A linear variation of the distance between

Table I. — Values of V_a and V_p at 127 °C as obtained from a linear least squares regression fit of the experimental data presented in figure 1.

m	V_a ($\text{cm}^3 \cdot \text{mole}^{-1}$)	V_p ($\text{cm}^3 \cdot \text{mole}^{-1}$)
0	232.4	17.8
1	245.3	17.8

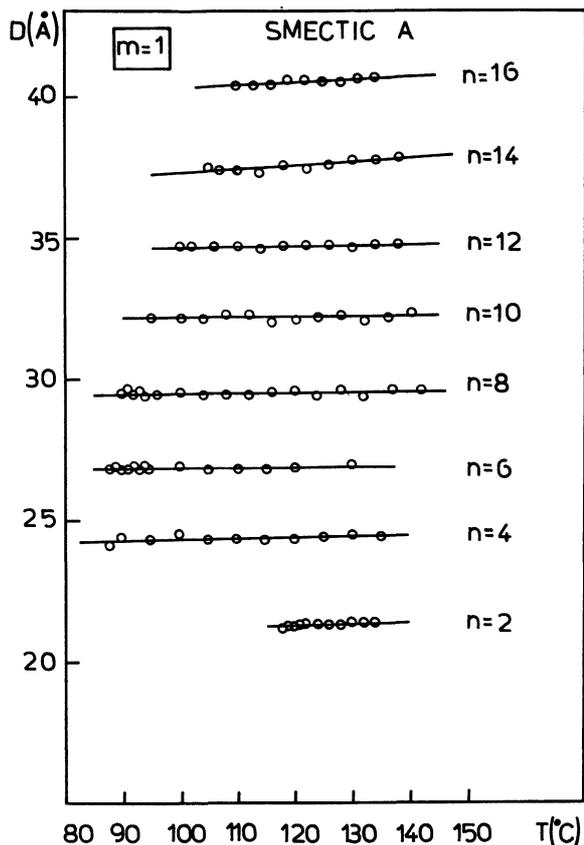


Fig. 2. — Variation of the layer spacing as a function of temperature in the smectic A phase of all the even terms of the series $m = 1$.

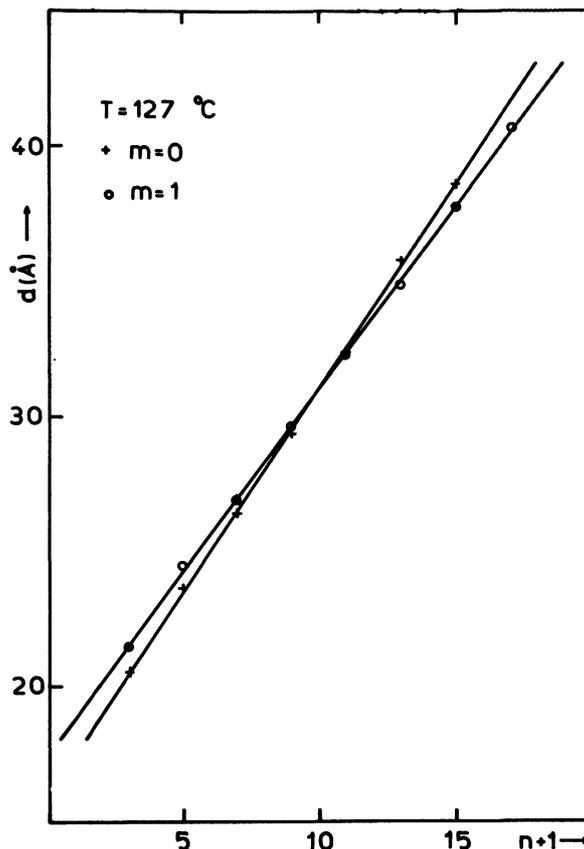


Fig. 3. — Layer spacing in the smectic A phase at 127 °C as a function of the length of the aliphatic chain for the two series $m = 0$ and $m = 1$. The lines are obtained by a linear least squares regression fit of the experimental data.

Table II. — Coefficients of the lines $D(T) = D_0 + \frac{\Delta D}{\Delta T} T$ obtained by a least squares linear regression analysis of the experimental data of figure 2.

n	D_0 (Å)	$\Delta D/\Delta T$ (Å/°C)
2	20.575	0.006 18
4	24.026	0.003 28
6	26.779	0.000 99
8	29.317	0.001 91
10	31.929	0.002 47
12	34.326	0.003 85
14	35.843	0.014 80
16	39.261	0.010 70

smectic planes is observed, whatever the value of n . We have gathered in table II the coefficients of the lines obtained by a least squares linear regression analysis of the experimental data of figure 2.

Figure 3 presents the variation of the interlayer distance as a function of the length of the aliphatic chain for the series $m = 0$ and $m = 1$, at the same temperature of 127 °C. It appears that the interlayer distance is a linear function of n ; but the main feature

is the value of the increment of thickness per CH_2 group, Δ_p , which is quite different in the two cases. For the series $m = 0$, $\Delta_p = 1.51 \text{ \AA}$, whereas for the series $m = 1$ $\Delta_p = 1.35 \text{ \AA}$. Anyway in the two cases, Δ_p is larger than the increment of one methylene group for a crystalline paraffin in its most stretched configuration (1.27 Å). As for the structural model described previously for the series $m = 0$, a bilayer type arrangement of the molecules inside the smectic layers also needs to be involved in the case of the $m = 1$ series.

The difference between the two values of Δ_p seems to indicate that the chains are more disorganized, or more largely spread at the interface in the series $m = 1$ than in the series $m = 0$.

2.3 STRUCTURAL DATA. — An important physical quantity which can be obtained from both the dilatometric and X-ray diffraction data is the molecular area S , that is to say the surface occupied by one molecule in the plane of the layers. More precisely, in the case of a lamellar system which involves a bilayer type of molecular arrangement (see previous section), we need to know the area S of the prism containing two molecules [7]: $S = 2V/Nd$ where V is the molar volume, d is the interlayer spacing and N is Avogadro's number.

Figure 4 presents the variation of S as a function of the length of the aliphatic chain for the series $m = 0$ and $m = 1$ at $T = 127^\circ\text{C}$. Whereas there is a more or less regular decrease in the variation of S with n in the series $m = 0$, S remains stable in the series $m = 1$, especially for n varying from 4 up to 14, where the value of S stays around 45.5 \AA^2 .

To describe the bilayer configuration, we need also to know two other parameters which are the aromatic sublayer, d_a , and the aliphatic sublayer, d_p . d_a and d_p can easily be deduced from the experimental values V , V_a and d through the relations :

$$\begin{cases} d_a = d \frac{V_a}{V} \\ d_p = d - d_a \end{cases}$$

All the values of d_a and d_p have been deduced from the experimental data and are reported in table III for the $m = 0$ and $m = 1$ series, always at the same temperature of 127°C .

We note first the relative stability of the thickness of the aromatic sublayer d_a , in the $m = 1$ series as a function of n (in agreement with the stability of S as a function of n), whereas for $m = 0$ d_a increases slightly, but significantly, with n . In the case of $m = 0$ series, we have concluded that there must be a tilt angle of the aromatic cores (15° to 20°) when n is small; when n increases the tilt angle decreases [1]. In the case of the $m = 1$ series, the variation of the tilt angle of the aromatic cores is much more smaller, since d_a is practically constant. Another interesting

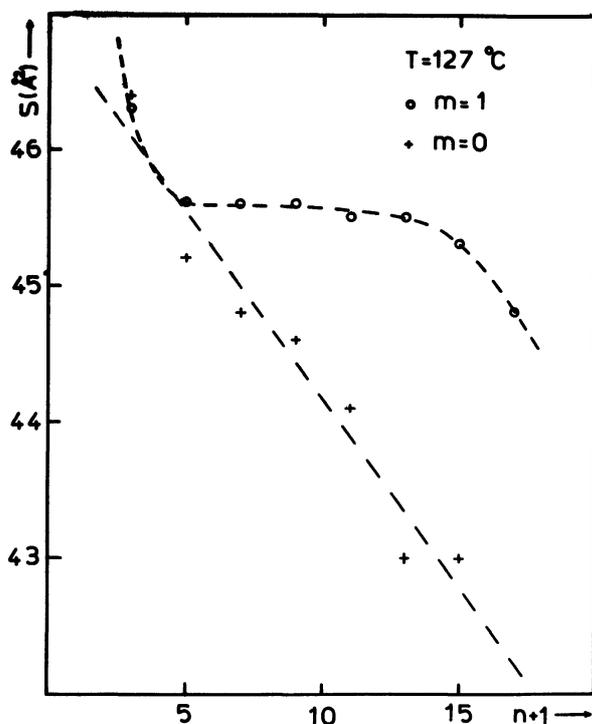


Fig. 4. — Molecular area S in the smectic A phase at 127°C as function of the length of the aliphatic chain for the two series $m = 0$ and $m = 1$. Lines are guides for the eye.

Table III. — Aromatic sublayer spacing, d_a , and aliphatic sublayer spacing, d_p , in the smectic A phase at 127°C as a function of the length of the aliphatic chain for the series $m = 0$ and $m = 1$.

n	$m = 0$		$m = 1$	
	d_a	d_p	d_a	d_p
2	16.7	3.8	17.6	3.8
4	17.1	6.5	17.9	6.5
6	17.2	9.1	17.9	9.0
8	17.3	12.0	17.9	11.7
10	17.5	14.9	17.9	14.3
12	18.0	17.8	17.9	16.9
14	18.0	20.5	18.0	19.7
16			18.2	22.4

feature is the comparison of the specific values of d_a between the two series. When n is small, d_a is larger for the $m = 1$ series than for the $m = 0$ series; this experimental observation can be related to the fact that the aromatic core in the $m = 1$ series is the same as the $m = 0$ series with a supplementary CH_2 group. When n increases, the values of d_a tend to be the same, about 18 \AA in the two cases. As we know that the orientation of the aromatic cores is almost normal to the plane of the layers, this result shows there still remains an average tilt angle of the aromatic cores in the $m = 1$ series, even when the aliphatic chain is long.

Let us now consider the specific values of d_p . When n is small, d_p has the same value in the two cases; but when n increases, it is quite interesting to note that d_p is larger for the $m = 0$ series than for the $m = 1$ series, indicating a more pronounced spreading of the aliphatic chains in the $m = 1$ series.

Moreover, we find that the increment of the paraffin sublayer d_p is 1.40 \AA per CH_2 group for the $m = 0$ series, and 1.32 \AA per CH_2 group for the $m = 1$ series (see Fig. 5). When compared with the increment of d per CH_2 group (1.51 \AA for the $m = 0$ series, and 1.35 \AA for the $m = 1$ series) it is clear that, in the case of the $m = 0$ series, the average tilt angle of the aromatic cores decreases as a function of n , whereas, in the case of the $m = 1$ series, the tilt angle practically does not vary as a function of n .

3. Discussion.

The data obtained suggest that the model proposed for the homologous series with $m = 0$ can be adopted with some modifications for the series with $m = 1$. The aromatic stems are arranged in a monomolecular sublayer and placed head to tail; the paraffin chains are on each side of the aromatic sublayer. As d_p is larger for the series $m = 0$ than for the series $m = 1$, a larger disorder or tilt angle must be assumed for this last series. This fact is reflected by the larger values

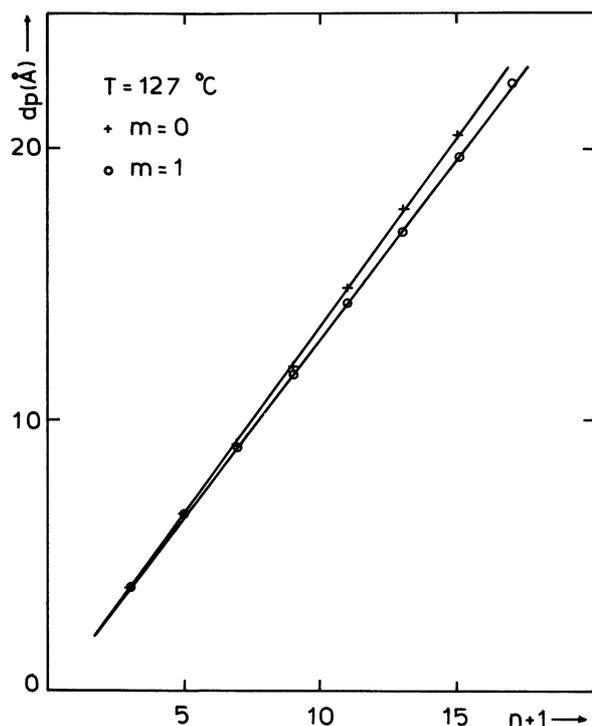


Fig. 5. — Increment of the thickness of the aliphatic sublayer, d_p , in the smectic A phase at 127 °C for the series $m = 0$ and $m = 1$. The lines are obtained by a linear least squares regression fit of the experimental data.

of molecular area reported in figure 4. The increased disorder must be attributed to the addition of one methylene group in the aromatic core of the new series, and to the attractive interaction of this group with the long aliphatic chains of adjacent molecules (see Fig. 6).

No change of volume for methylene groups was observed between the two series, in spite of the increased disorder, so that the aliphatic chains appear more widely spread parallel to the layers, and diffusion from one layer to the next is more difficult for the series $m = 1$. In fact the second-order diffraction corresponding to the layer spacing is quite intense in all the smectic A phases of these compounds, indicating a relatively well defined lamellar structure.

The thickness of the aromatic sublayer is relatively stable for the series $m = 1$; and a striking feature is the similar thickness of the aromatic sublayer when n is high, although there is a propionyl group in the series

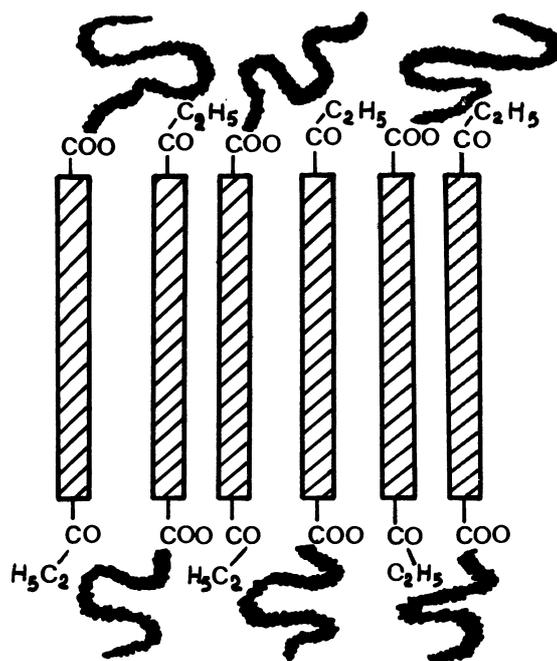


Fig. 6. — Schematic diagram of the structural organization of the molecules inside the smectic A layers for the series $m = 1$.

$m = 1$ and only an acetyl group in the series $m = 0$. The steric hindrance is larger for the propionyl group than for the acetyl group; moreover we have demonstrated that this propionyl group is a well ordered state ($V_{CH_2} = 13 \text{ cm}^3 \cdot \text{mole}^{-1}$); therefore the rotation of the molecule around its molecular axis may not be so easy in the series $m = 1$ as in the series $m = 0$. This would explain the average tilt angle of the aromatic cores resulting in a more pronounced spreading of the aliphatic chains in the interface. This implies a smaller value of the orientational order parameter $s = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle$, where θ is the angle between the long molecular axes and the average direction of these long axes; it also implies a larger average lateral distance in the series $m = 1$, which is confirmed by X-ray diffraction data.

The comparison between the two series has allowed us to find experimental evidence for the tilt angle of the rigid parts of smectogenic molecules in the smectic A phase and to relate this to the molecular structure, and especially to the chemical constitution and architecture of the molecules.

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