X-ray study of the ordered smectic phases in some benzylideneanilines
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1. Introduction. — The phase behavior of the liquid crystal phases of 35 compounds belonging to a doubly homologous series of benzylideneanilines has been investigated by G. W. Smith et al. [1, 2]. These authors have studied N-(p-alkoxybenzylidene)-p-n-alkylaniline compounds with the structural formula:

\[ \text{C}_n\text{H}_{2n+1} \text{O} \overline{\text{O}} \text{CH=N=O} \text{C}_m\text{H}_{2m+1} \]

(we shall use the abbreviation \(n0m\), with \(n\) values ranging from 1 to 7 and \(m\) from 4 to 8, by means of thermal microscopy and differential scanning calorimetry. They found that many of these compounds exhibit several smectic mesophases, up to four for a few compounds: in that case, we designate (S4, S3, S2, S1) these four smectic mesophases obtained on increasing temperature. The same authors have identified S1 and S2 as smectic A and smectic C mesophases, respectively, from texture criteria. However this method doesn’t work with certainty for S4 and S3 which appear with fan or mosaic textures.

By X-ray diffraction, we intended to determine the nature of the S3 and S4 mesophases. Table I gives the list of the studied compounds with their mesophases. In the present paper, we first describe the results obtained by X-ray diffraction performed on single domains; then we deal with powder diagrams and finally we discuss additional features exhibited in the X-ray patterns of some mesophases.

2. Study of single domain X-ray patterns. — Single domains of S4 and S3 phases are obtained by heating single crystals above the melting point. Single crystals
Various phases of the studied compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Phase transitions (from G. W. Smith et al. [1])</th>
</tr>
</thead>
<tbody>
<tr>
<td>40.8</td>
<td>Cr $3^\circ$0 S3 $4^\circ$5 S1 $6^\circ$7 N $7^\circ$0</td>
</tr>
<tr>
<td>50.6</td>
<td>Cr $3^\circ$6 S4 $4^\circ$8 S2 $5^\circ$8 S1 $6^\circ$4 N $7^\circ$0</td>
</tr>
<tr>
<td>50.7</td>
<td>Cr $2^\circ$95 S4 $3^\circ$7 S3 $5^\circ$2 S2 $5^\circ$4 S1 $6^\circ$0 N $7^\circ$0</td>
</tr>
<tr>
<td>70.4</td>
<td>Cr $3^\circ$2 S4 $6^\circ$3 S3 $6^\circ$4 S2 $6^\circ$8 S1 $7^\circ$1 N $7^\circ$2</td>
</tr>
<tr>
<td>70.5</td>
<td>Cr $2^\circ$3 S4 $5^\circ$8 S3 $6^\circ$9 S2 $7^\circ$0 S1 $8^\circ$7 N $8^\circ$0</td>
</tr>
<tr>
<td>70.7</td>
<td>Cr $3^\circ$0 S4 $5^\circ$5 S3 $6^\circ$9 S2 $7^\circ$0 S1 $8^\circ$7 N $8^\circ$0</td>
</tr>
</tbody>
</table>

are collected in a compound-acetone solution after partial evaporation. But only single crystals of 70.7 are big enough to be used as X-ray samples; they are white, transparent and have a plate-like morphology (2 $\times$ 2 $\times$ 0.1 mm$^3$).

X-ray photographs of single domains were taken by using a transmission instrument with a monochromatic convergent incident beam (CuK$\alpha$) perpendicular to a flat film. We shall examine the X-ray patterns of the single domains of the S4 and S3 phases of 70.7.

2.1 THE S4 PHASE. — The two X-ray patterns of the S4 phase of 70.7, as shown in figure 1a, b, are typical of a smectic B phase in which the molecules are tilted, thus forming an angle $\alpha$ with respect to the perpendicular direction of the layers (SBc) [3]; the two main features are: a few Bragg spots and diffuse lines.

a) When the direct beam is parallel to the smectic layers (Fig. 1a), the tilt angle $\alpha$ can be directly measured on the film ($\sim 25^\circ$): it is the angle formed by the line joining the Bragg spots corresponding to the reflections on smectic layers (three orders are visible) and the line perpendicular to the diffuse lines. These lines, which are in fact diffuse sheets in reciprocal space, originate from the strings of molecules moving independently, with a longitudinal motion along the direction of the long molecular axes [3, 4].

b) When the direct beam is parallel to the long molecular axis (Fig. 1b), the film shows the six Bragg spots characteristic of the pseudo-hexagonal molecular packing within the layers of a SBc phase.

2.2 THE S3 PHASE. — The two patterns of the S3 phase (Fig. 2a, b), obtained as previously described, are very similar to those of the S4 phase. Therefore, the S3 phase seems to be a smectic B phase. The main difference with the S4 phase lies in the fact that molecules are perpendicular to the smectic layers (SBA) [4] as is seen from figure 2a.

In conclusion, the S4 and S3 phases of 70.7 appear respectively to be a SBc phase (molecules tilted) and a SBA phase (molecules normal).

3. Study of powder X-ray patterns. — All the smectic phases of the selected compounds have been systematically studied from Debye-Scherrer patterns obtained with a Guinier camera and using a monochromatic focusing beam (CoK$\alpha$); this instrument enables precise determinations of lattice parameters. This study clearly reveals that all the patterns are analogous for a same smectic phase $S_i$ ($i = 1$ to 4) of the various compounds. The main difference lies in the thickness of the smectic layers which depends on the molecular length. An example of the powder patterns of 70.5 is shown in figure 3.
3.1 THE S4 PHASE. — The patterns of the S4 phases (Fig. 3b) are similar to those of TBBA in SBc [3]. Like single domain patterns of 70.7, they imply a three dimensional order which can be explained by a C-face centered monoclinic lattice (c is taken as the direction of the long molecular axis and a and b are the two other base vectors parallel to the smectic layers). In figure 4, we show this lattice orientation with respect to the smectic layers. Table II shows the observed reticular spacings for compound 70.5 and those calculated with lattice parameters deduced by a least-square refinement.

3.2 THE S3 PHASE. — The pattern of the S3 phase of 70.5 (Fig. 3c) reveals two sharp rings at the large diffraction angles which can be indexed, as the single domain study of 70.7 suggests, with a hexagonal lattice: the indexes of the rings are (100) and (101).

3.3 THE S2 AND S1 PHASES. — Powder patterns of the S2 and S1 phases present only one sharp ring due to the Bragg reflection on the smectic layers; the large diffuse ring observed at the large angles, evidence of a liquid-type order within the layers, is in agreement with the nature of these phases assumed by G. W. Smith et al. [1]: S2 and S1 are identified as Sc and Sa respectively.

3.4 COMMENTS ABOUT S4 AND S3 LATTICES. — The lattice parameters for the various smectic phases of all the compounds studied are collected in table III. A few comments can be made:

i) All the S4 lattices are very similar, except obviously the c parameters which are directly related to the molecular length.

ii) All the S3 lattices are also very similar, except the c parameters.

iii) The S3 lattice parameters are almost independent of temperature. On the contrary, the a and b parameters of the S4 phases vary with the temperature. For instance, these variations for compound 70.7 are shown in figure 5. The largest variation is observed for β which decreases when increasing the temperature, whereas c remains constant: this means that molecules straighten up when nearing the S3 phase. Nevertheless,
FIG. 5. — Variation of lattice parameters with temperature in the S4 phase for 70.7 compound.

The S4-S3 transition seems to be accompanied by a discontinuous β variation (about 20°).

iii) We also notice that the variation of the a parameter is correlated with that of β so that the intersections of the long molecular axes (c direction) with a plane perpendicular to them, form a nearly hexagonal lattice: two sides of which are equal to b, the four others to \((a \cos \alpha)/\sqrt{3}\) (where \(\alpha = \beta - \pi/2\) is the tilt angle). These values are given in figure 6 (along with those for compound 70.7 as a function of temperature). We wish to point out that this pseudo-hexagon only differs from a regular one by approximately 1%.

FIG. 6. — Side lengths of the pseudo-hexagon in the S4 phases (for 70.7 compound, their variation with temperature is also given).

3.5 THE S4-S3 PHASE TRANSITION. — The discontinuity of β observed at the S4-S3 transition is indicative of a first order transition. The thermal analyzer thermograms present a peak at the S4-S3 transition, but this peak is too weak to be indicative of the order of the transition (1). Figure 7 shows a thermogram for compound 70.7 obtained with a Mettler apparatus. The S4-S3 transition enthalpy is very low whereas the crystalline-S4 is the highest; moreover, from the lack of peak, the S2-S1 (i.e. \(S_C-S_A\)) transition appears as a second order transition. Figure 8, which represents the layer thickness variation with the temperature for 70.7 again, is in agreement with the order assignments since the only continuity in layer thickness is observed at the S2-S1 transition.

FIG. 7. — Differential thermal analyzer thermogram of compound 70.7.

FIG. 8. — Layer thickness variation with temperature for compound 70.7.

Thus, the S4-S3 transition appear as a first order transition between the \(SB_C\) and \(SB_A\) phases. This is the first time that such a transition has been observed experimentally. R. J. Meyer and W. L. Mc Millan [5] had theoretically predicted this transition, even the phase sequence \(SB_C-SB_A-S_C-S_A\), but they believed it to be a second order one. This disagreement results, perhaps, from their assumption that in the \(SB_C\) phase, all molecular dipoles in smectic layers are parallel to one another, which is inconsistent with our data [6].

Another discrepancy with our results arises from W. Z. Urbach's conoscopic observations on p-ethoxybenzal-p-aminocinnammat-ethyl (\(SB_A\))-TBBA(\(SB_C\))

(1) For 40.7, G. W. Smith et al. [2] have found a big enthalpy transition between S4 and S3 phases (0.96 kcal/mole), which confirms that the S4-S3 transition is a first order transition.
mixtures. This author observed a continuous transition between the two compounds while varying the mixture composition [7].

4. Particularities observed on powder diagrams. The description of the S4 and S3 phases given in the previous paragraph is schematic and thus incomplete since it doesn't take into account the additional features observed on some powder diagrams. We shall examine and discuss these extra features which exist only in a few compounds.

4.1 The double ring. — 4.1.1 The « normal » and « extra » rings (70.7, 70.5, 50.7). — The powder patterns of the S3 phases for compounds 70.7, 70.5 and 50.7 show a double ring, instead of a single one, corresponding to the Bragg reflection from smectic layers. This double ring can be seen in figure 3c after a careful scrutiny. It is worth noting that the double ring is not visible in single domain patterns due to lack of resolution in the device used.

The position of the inner ring is independent of temperature: it corresponds to a constant layer thickness. This thickness is almost equal to the \( c \) parameters of the S4(SB) phases (molecular length); this means that the thickness has the expected value for the S3 phases (SB) in which molecules are perpendicular to the layers. In fact, the layer thickness of the S3 phases is slightly greater (about 0.2 Å) than the value of the \( c \) parameters in the S4 phases. Therefore this ring may be considered as the normal ring.

We shall call the other ring the extra ring. It always corresponds to a layer thickness smaller than that of the normal ring (about 1.5 Å). Moreover, this layer thickness may be constant with temperature (as for 70.5) or may slightly decrease when increasing temperature (as for 70.7: from 29.2 Å at 55 °C down to 28.9 Å at 69 °C).

As regards intensity of the two rings, it is worth noting that the normal ring is most intense just after the S4-S3 transition and its intensity decreases with the temperature whereas the extra ring is most intense near the S3-S2 transition and its intensity increases with the temperature. We also note that just after the S4-S3 transition, two other rings appear, which are broader and less visible, corresponding to smaller layer thicknesses, but disappear quite quickly (about 2 °C) when increasing temperature.

On the whole, the powder patterns of the S3 phases of a few compounds show at least one extra ring. The problem now is to understand the origin of this extra ring.

4.1.2 About the origin of the « extra » ring. — The slight difference between the values of the two layer thicknesses of the normal and extra rings (about 1.5 Å) allows us to eliminate the hypothesis that the two rings correspond to the same lattice because this would imply a lattice with larger parameters than usual smectic ones and thus would produce several other rings, which does not apply in our case.

The extra ring is not due to decomposition, and any other experimental errors can also be eliminated since the double ring is very clear and is only observed in the S3 and not in the S4, S2 and S1 phases. Let us also note that our powder patterns are quite reproducible.

The extra ring might be due to an impurity effect; in fact, it seems that we are dealing with rather pure substances since, for instance, the transition temperatures for 70.7 measured by microscopy and differential thermal analysis are in agreement with the values given by G. W. Smith et al. (see Table I):

\[
\begin{align*}
&\text{Cr} \quad 34.0^\circ \quad \text{S4} \quad 35.0^\circ \quad \text{S3} \quad 68.7^\circ \quad \times \\
&\times \text{S2} \quad 71.7^\circ \quad \text{S1} \quad 83.4^\circ \quad \text{N} \quad 83.7^\circ \quad \text{I}.
\end{align*}
\]

Furthermore, experiments performed with a highly purified sample of 70.7 have given exactly the same results.

Nevertheless, let us assume that the sample is contaminated and that two phases coexist in the S3 range of temperature. This second phase cannot be the S4(SB) phase, which would explain the smaller layer thickness corresponding to the extra ring, because no rings at the large angles proceeding from a SB phase are visible in the powder pattern. The second phase could be the S2 phase (SC), but no diffuse ring at the large angles (a typical feature of X-ray diagrams) can be observed; this eliminates also the possibility of a SA phase. A more conclusive argument which eliminates the SC phase is the following: at the S3-S2 transition, there appears a third inner ring corresponding to the Bragg reflection from the smectic layers in the S2 phase (SC). Thus, a coexistence of S3 and S2 phases can be eliminated.

Therefore, one possible explanation about the origin of the extra ring which remains is that the S3 phases are in fact a mixture of two smectic phases with two different layer thicknesses. One of these phases, that is the SB phase described in paragraph 2, yields the normal ring and the two rings at the large angles corresponding to the molecular hexagonal packing within the layers. The nature of the second phase is more difficult to determine: we have eliminated the SB, SC and SA phases. We assume that this second phase is a SB phase with different layer thickness; on this assumption, the diffraction rings at the large angles would be superimposed. This last hypothesis, which seems the most appropriate, agrees with the conoscopic observations (by Billard on 70.5 [8]): from these observations, the S4 phase is biaxial and the S3 phase uniaxial. It implies the same molecular packing within the layers in the two SB phases, which is likely because the packing depends only on lateral molecular dimensions which are invariant. It also implies a different molecular length in each phase. In this hypothesis, the S3 phase would be a segregation
into domains of the two SB\textsubscript{A} phases. Calculations prove that the domain dimensions need not exceed 7 to 8 layer thicknesses to produce a double-ring effect. This segregation phenomenon looks like the pre-precipitation effect which occurs sometimes in metallic alloys.

Perhaps, other hypotheses explaining the double ring effect are possible, but we don't see another one which can account for all experimental data.

4.1.3 About the molecular length. — We are led to assume that the molecules in the S3 phases of a few compounds can have two different lengths simultaneously, in other words, they can take two conformations. Let us examine for instance the molecule 70.5 (Fig. 9). It seems obvious that the difference between conformation which is itself possibly related to the molecular packing of the benzene rings or to the effects caused by the oxygen atoms.

An interesting point confirms this relationship: the layer thickness 29.6 Å, corresponding to the totally stretched molecule, has been observed in the following conditions: a thin film appears at the surface of an evaporating solution of the S4 phase of 70.5, with the mixture: benzene (15\%) xylene (85\%) (such a mixture is used in the preparation of our powder-pattern samples). The film's powder-pattern shows that the nature of the film is indicative of a SB\textsubscript{A} phase whose layer thickness is equal to 29.6 Å. So, the S4 phase (SB\textsubscript{C}) of 70.5 changes into SB\textsubscript{A} phase in the presence of a solvent, but, after total evaporation (about 2 h), again becomes a SB\textsubscript{C} phase (a powder diagram before total evaporation is shown in figure 3a, the ring corresponding to 29.6 Å is clearly visible). One can assume that in the presence of a solvent, the available volume per molecule increases in such a way that the molecules can take the most stretched conformation and become perpendicular to the layers (4).

This solvent experiment has been performed only on compound 70.5. But for all the selected compounds, the layer thickness and the molecular conformation are correlated in the same way as described for 70.5. All these molecular length considerations allow us to draw the conclusion that in spite of a large thermal motion, the aliphatic chains have a tendency to take a stretched conformation and that minor factors can induce conformation changes which are at the origin of the layer thickness changes.

4.2 Other powder-pattern particularities. —

4.2.1 Compound 70.4. — Compound 70.4 has three smectic phases: a S\textsubscript{A} phase, a S\textsubscript{C} phase, a SB\textsubscript{C} phase, but doesn't possess a SB\textsubscript{A} phase (see Table I). In the SB\textsubscript{C} phase, a double ring phenomena appears a few degrees after the crystal-SB\textsubscript{C} transition, but this time, the double ring corresponding to the Bragg reflection from smectic layers is also accompanied by a splitting into two families of Bragg reflections at the large angles. This implies the existence of two kinds of domains characterized by two different SB\textsubscript{C} lattices. Lattice constant refinement computations, performed from the observed reticular spacings, indicate that the two lattices mainly differ in the c axis length values: 26.6 Å and 28.0 Å. It is significant that the value 28.0 Å is equal to the most stretched molecular length and 26.6 Å to the length with the same alkoxy-chain conformation as 70.5 shown in figure 9b. We note that the domains corresponding to 28.0 Å appear only a few degrees after the crystal-SB\textsubscript{C} transition, and become predominant on increasing the temperature.

(4) The increase of layer spacing may also be due to the presence of solvent molecules between the layers; but this is unlikely because the increase (1.4 Å) is smaller than any dimension of the solvent molecules.
4.2.2 Compound 50.6. — This compound presents five smectic phases. From our X-ray patterns, four of these phases are analogous to the four smectic phases of compounds 70.7 or 70.5: that is S4(SBc)-S3(SBα)-S2(Sγ)-S1(Sα). The fifth phase is an intermediate phase between S4 and S3 (see Table I). Yet, this extra phase behavior is not reproducible when increasing the temperature. New experiments are currently under way.

From our experiments, it can be assumed that when a SBα phase follows a SBc phase, the double ring phenomenon appears; we note that this phenomenon also appears in a SBc phase that is not followed by a SBα phase (70.4), and doesn't appear in a SBα phase that is not preceded by a SBc phase (40.8). Nevertheless, further experiments are required to define rules concerning the occurrence of the domain segregations in no. m compounds.

4.3 DISCUSSION ABOUT THE CLASSIFICATION OF ORDERED SMECTIC PHASES. — In addition to this report, we shall make a short review of the classification problems of S4 and S3.

From miscibility experiments, Demus et al. [9] showed that two smectic phases of the 2-(4-n-pentyl-phenyl)-5-(4-n-pentyloxypentyl)-pyrimidine are not totally miscible with any of the smectic phases yet classified. These two phases have thus been labelled S0 and SF and the phase succession for this compound is as follows:

\[
\text{Cr} \leftrightarrow S_0 \leftrightarrow S_F \leftrightarrow S_C \leftrightarrow S_A \leftrightarrow I
\]

Always through miscibility criteria, Billard [8] has identified the S4 and S3 phases for compound 70.7 and 70.5 as S0 and SF respectively and the S4 phase for 70.4 as SF. But Demus [10] has identified the S4 and S3 phases for 70.7 and 50.6 as S0 and SA respectively, whereas the intermediate phase between S4 and S3 found in 50.6 has not yet been classified. Recently Richter et al. [11], using the same miscibility techniques, made the following investigations:

- the ordered phase of 40.2 is identified as S0;
- the phases V and VI of TBBA are identified respectively as Sb and S0.

The results do not all agree with one another and are not consistent with our X-ray experiments:

i) The S4 phase of 70.4 can't be identified as a Sb phase because usually SF X-ray patterns exhibit only one rather diffuse ring at the large angles (9) where we observe several sharp rings;

ii) The S3 phase of 70.7 has been identified once as a SF phase and another time as a Sb phase although the two authors agree on the identification of S4 as a S0 phase;

iii) The ordered smectic phase of compound 40.2, identified as S0, presents the same X-ray patterns as the S4 phase of 70.7 and the Sb (phase V) of TBBA (SBc phase);

iii) The smectic phase VI of TBBA identified as a S0 phase doesn't present quite the same X-ray patterns as the S4 phase of 70.7: in phase VI, the molecules are not crystallographically equivalent [13], whereas they are equivalent in the SBc phase of 70.7 (S4) and in phase V of TBBA; this is deduced from the presence of an extra Bragg spot not visible on the patterns of 70.7. We see that some discrepancies arise from the comparison between miscibility identifications and X-ray identifications.

In short, from our X-ray patterns, the S4 phase of 70.7 and the smectic ordered phase of 40.2 are two SBc phases, analogous to phase V (SBc) of TBBA; the S4 phase of 70.4 also appears as a mixture of two SBc phases which segregate into domains. The S3 phase of 70.7 appears as a mixture of two SBα phases which also segregate into domains.

Finally, phase VI of TBBA doesn't appear as a Sb phase, but as a phase whose type of order within the layers is indicative of a S0e phase and whose molecules are tilted with respect to the layers [14].

It seems obvious that further investigations on both X-rays and miscibility are necessary to get clearer evidence. Nevertheless, we shall try to give an explanation concerning these disagreements. It has been mentioned above that the SBc phase of TBBA is totally miscible with a SBα phase [7]. On the contrary, the SBc phases presented by no. m compounds do not seem miscible with the SBα phases. Thus it can be assumed that the SBc phases can be either miscible or not with the SBα phases; in the first case, they would be identified as a S0 phase and, in the second case, as a Sb phase. Two SBc compounds of each kind are not necessarily miscible and this would explain the non miscibility of phase V of TBBA with the smectic phase of 40.2. As regards the identification of phase VI of TBBA as S0, we must remember that the structures of phase V (Sb) and VI are very similar, the difference only arising from the extent of the herring-bone type order within the layers, this order being localized in phase V and extending to the whole crystal in phase VI.

On the whole, we feel that the miscibility investigations are insufficient to determine the true nature of these phases and therefore one should be careful in interpreting such miscibility criteria when applied to smectic ordered phases.

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