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Volume and X-ray diffraction study of terephthal-bis-4,n-decylaniline (TBDA)

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Résumé. — On présente une étude systématique du polymorphisme smectique du TBDA par dilatométrie et diffraction des rayons X aux petits angles. En conjuguant les données expérimentales recueillies à l'aide des deux techniques, on a déterminé l'évolution de l'aire moléculaire et l'angle d'inclinaison des molécules en fonction de la température. On a, enfin, discuté les résultats obtenus notamment en relation avec la nature et l'extension de l'ordre dans les mésophases smectiques F, I et C.

Abstract. — This is a systematic study of the smectic polymorphism of TBDA, carried out using dilatometry and small-angle X-ray diffraction. By combining the experimental data collected by the two techniques, the thermal evolution of the molecular area and the tilt angle of the molecules have been determined. The results are discussed particularly in relation to the nature and the spatial extension of order in the smectic F, I and C mesophases.

1. Introduction.

It has become customary to refer to B, E, G and H smectic mesophases (abbreviated to S_B , S_E , S_G , S_H) as three-dimensional crystals. Indeed, the molecules are arranged in an orderly fashion within layers which, in turn, are periodically stacked one above the other and three-dimensionally correlated in space. The molecules are assembled laterally within the layers in either a hexagonal or a rectangular two-dimensional lattice; they are perpendicular with respect to the plane of the layers for S_B and S_E , and tilted for S_G and S_H [1]. Likewise, it is common knowledge that the A and C smectic mesophases (abbreviated to S_A and S_C) are one-dimensional crystals consisting of a periodic stacking of two-dimensional liquid layers; the molecules are oriented perpendicularly for S_A and tilted at a particular angle, often dependent upon temperature, for S_C .

Two additional smectic mesophases, namely S_F and S_I , have recently been identified [2-4]. They are described as a one-dimensional crystalline stacking of positionally uncorrelated layers with long range three-dimensional orientational order [5-7]. For S_F ,

the in-plane positional order is only short range, whereas for S_I it is quasi long range. Molecules are tilted towards the long and the short side of the local rectangular cell for S_F and S_I [7] respectively. A similar mesophase, in which however the molecules are perpendicular with respect to the plane of the layers, has also been identified; this is a hexatic modification of S_B [8].

Over the past few years, much effort has been devoted to the understanding of the smectic polymorphism of the homologous series of terephthalidene-bis (4,n-alkylaniline) (abbreviated to TBAA) [3, 9]. For TBDA, the decyl homologue of TBAA, the following sequence of smectic mesophases : $S_G \rightarrow S_F \rightarrow S_I \rightarrow S_C \rightarrow S_A$ was observed as a function of increasing temperature [10]. In the light of the two-dimensional melting theory of Halperin and Nelson [11], a detailed study of the TBAA homologous series, and especially of TBDA, was undertaken using X-ray diffraction [9]. Among other results, it was shown that, quite surprisingly, the positional order extends significantly further for S_I than for S_F , even though S_I appears at higher temperatures. Intuitively, one might be tempted to associate such behaviour with a

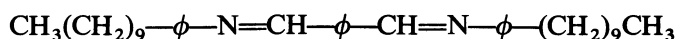
change in the compactness of the molecular arrangement.

To elucidate that last point, and also to profit from the unusually rich smectic polymorphism of the TBAA series, allowing an analysis of the thermal evolution of the packing density of the molecules and of their detailed angle of tilt, it was decided to carry

out a systematic study of TBDA using dilatometry and X-ray diffraction. In this paper, we report the results that were obtained.

2. Experimental

As mentioned above, terephthalidene-bis (4,n-decylaniline) :



exhibits five smectic mesophases. Temperatures and latent heats of transition were determined using differential scanning calorimetry (Perkin Elmer DSC2) and polarizing microscopy (Leitz and Mettler FP52 hot stage) :

T (°C)	71.9	115	148.7	155.7	189.6	191.5	
	K	$\rightarrow S_G$	$\rightarrow S_F$	$\rightarrow S_I$	$\rightarrow S_C$	$\rightarrow S_A$	$\rightarrow I$
ΔH	12.4	$< 10^{-2}$	$< 10^{-2}$	1.54	0.17	1.75	
(kcal/mole)							

In agreement with previous DSC observations [10, 12], the $S_G \rightarrow S_F \rightarrow S_I$ transitions seem to be second order. It is fair to add, however, that NMR measurements suggest that the $S_F \rightarrow S_I$ transition could be very weakly first order [13].

Volume measurements were carried out using the Bekkedahl dilatometric technique [14] already described elsewhere [15]. X-ray diffraction data were collected using a vacuum small-angle camera equipped with a bent gold plated glass mirror (nickel filtered K_α copper radiation from a GX20 Elliott rotating anode X-ray generator) and a CEA-LETI linear position sensitive detector; samples were contained in 1 mm thick Lindemann capillaries, and heated in a Mettler FP52 hot stage.

3. Volume.

Experimental data from dilatometry are all gathered in figure 1, showing the molar volume of TBDA as a function of temperature in the range from 40 to 200 °C. As a whole, the results fully confirm the DSC observations mentioned above. Indeed, $K \rightarrow S_G$, $S_I \rightarrow S_C$, and $S_A \rightarrow I$ transitions are strongly first order : they are characterized by large volume jumps in narrow temperature ranges, namely 9.3, 8.2, and about $8 \text{ cm}^3/\text{mole}$ respectively. It should be noted that the $S_C \rightarrow S_A$ transition could not be determined accurately because of the very narrow temperature range of existence of S_A , of the weakly first order nature of the transition, and of the pretransitional effects of the $S_A \rightarrow I$ transition.

Furthermore, the $S_G \rightarrow S_F$ and $S_F \rightarrow S_I$ transitions seem to be continuous (better seen in Fig. 2). They show no detectable volume jump, but only a slight change of the thermal expansion coefficient. This is all the more interesting since these two transitions correspond to large structural changes [9]. At the former, the three-dimensional correlations between

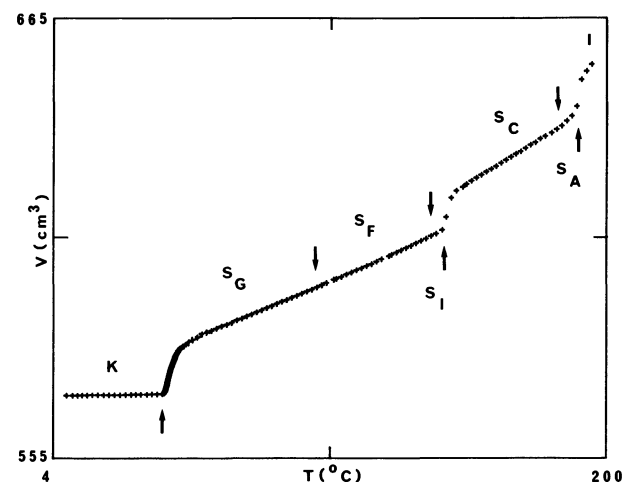


Fig. 1. — Molar volume of TBDA as a function of temperature : arrows indicate the transition temperatures as determined by DSC and optical microscopy.

layers are lost, along with the quasi-crystalline positional order of the molecules within the layers. At the latter, the positional order within the layers suddenly extends to larger distances, and the tilt of the molecules points to different directions with respect to the two-dimensional lattice. Intuitively, one might expect the volume to change significantly from one phase to the next. It is remarkable that, in fact, a change in compactness does not necessarily parallel the spatial extension of positional order itself.

In order to analyse the temperature dependence of the molar volume of TBDA, it is of interest to note that, within the temperature range of each smectic phase, $V(T)$ varies linearly with T :

$$V(T) = V_0 + T(\partial V/\partial T) \quad (1)$$

where V_0 is the molar volume at $T = 0$ °C. Using

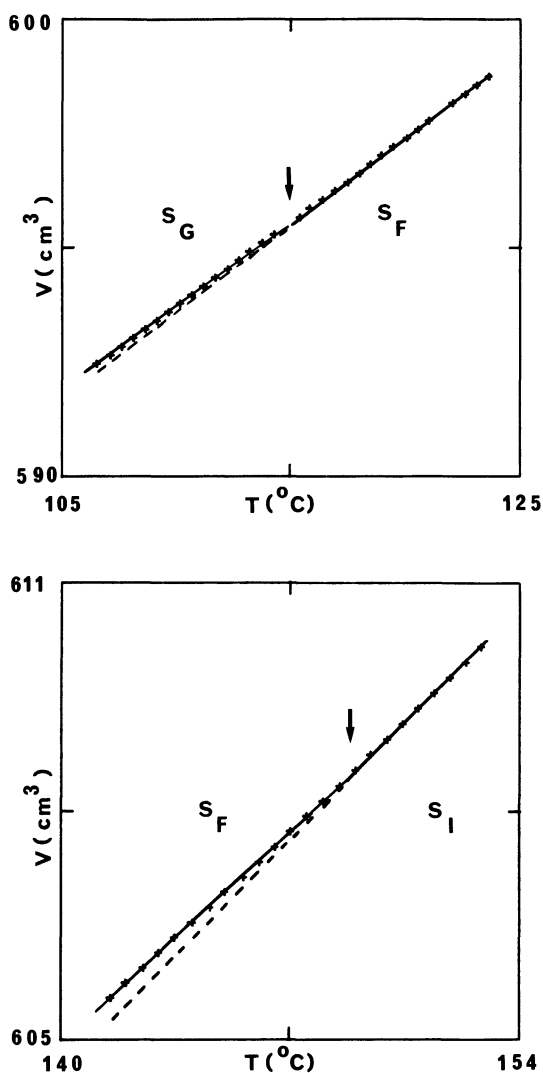


Fig. 2. — Detailed representation of the molar volume of TBDA as a function of temperature at the $S_G \rightarrow S_F$ and $S_F \rightarrow S_I$ transitions.

a linear regression, it is then possible to calculate V_0 and $\partial V/\partial T$ from the experimental data for all the smectic mesophases except for S_A whose temperature range is too narrow; the values obtained are reported in table I along with those of the relative thermal

expansion coefficient :

$$\alpha = (1/V) (\partial V/\partial T).$$

It is useful to compare the volume behaviour of TBDA with that of its butyl analog, TBBA (Table II). The relative volume jumps at the transitions and the volume expansion coefficients are almost the same for the two compounds. The difference in molar volume is, of course, due to the different numbers of methylene groups in the molecules. With the reasonable assumption of additivity of the partial molar volumes of the aromatic and aliphatic moieties, one can easily calculate V_{CH_2} (cm^3/mole) for each mesomorphic structure :

$$V_{CH_2}(T) = 15.61 + 1.25 \times 10^{-2} \times T$$

in good agreement with the values found earlier for other compounds [17]. This shows that, regardless of the actual structure of the mesophase, the average value of V_{CH_2} (17-18 cm^3/mole), which is close to that known for liquid paraffins, depends only on temperature, and that the aliphatic chains are disordered.

4. Layer spacing.

To support previous X-ray data in the field [9], and especially to go into greater detail concerning the transitions between the various smectic phases observed, a systematic X-ray diffraction study of TBDA was carried out in the temperature range from 70 to 200 °C. The layer spacing in the smectic mesophases was deduced from the position of the (001) Bragg reflection in the small angle region, and plotted as a function of temperature (Fig. 3).

Close inspection of the data shows a steady, though very weak, decrease of the spacing throughout the temperature range of the S_G , S_F and S_I mesophases, without any detectable discontinuity at the $S_G \rightarrow S_F \rightarrow S_I$ transitions. On the contrary, a sudden reduction of the spacing accompanies the $S_I \rightarrow S_C$ transition, consistent with the first-order nature of the transition. In addition, at the transition itself, between 154.2 and 156.2 °C, X-ray patterns reveal the coexistence of both S_C and S_I , each being characterized by its

Table I. — Values of the molar volumes at 0 °C (V_0), of the volume expansion coefficients ($\partial V/\partial T$) and $\alpha = (1/V) \times (\partial V/\partial T)$ in the various smectic phases of TBDA. V_0 and $\partial V/\partial T$ have been computed using a linear regression of the volume within the domain of stability of each smectic phase.

Phase	V_0 $\text{cm}^3 \cdot \text{mole}^{-1}$	$\partial V/\partial T$ $\text{cm}^3 \cdot \text{mole}^{-1} \text{K}^{-1}$	$\alpha = (1/V)(\partial V/\partial T)$ 10^4K^{-1}
S_G	554.3	0.358	6.1
S_I	551.7	0.380	6.3
S_I	543.2	0.438	7.2
S_C	537.7	0.526	8.4

Table II. — Comparison of some volumetric measurements of TBBA and TBDA. Values of TBBA are obtained from reference [16].

	TBBA	TBDA
$\Delta V/V$ at $S_G(S_I) \rightarrow S_C$	1.2%	1.3%
αS_G ($K^{-1} \times 10^4$)	6.2	6.1
αS_C ($K^{-1} \times 10^4$)	8.6	8.4
αS_A ($K^{-1} \times 10^4$)	7.6	—
$V(165^\circ C)$ ($cm^3/mole$)	408.1	629.5

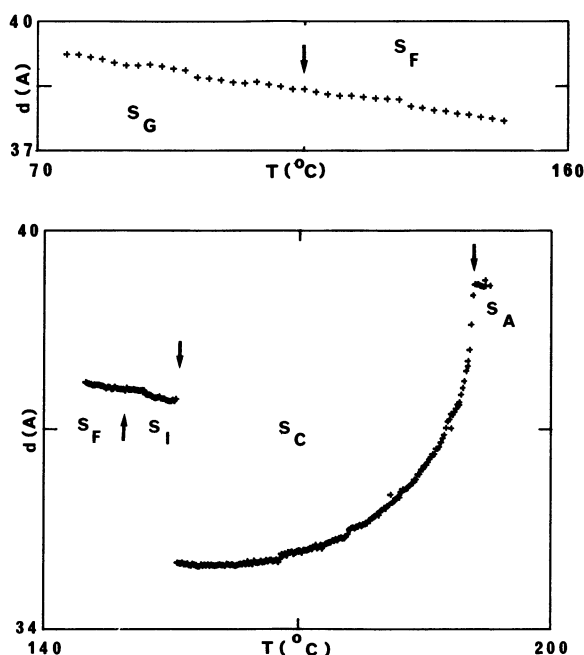


Fig. 3. — Layer spacing of TBDA as a function of temperature : arrows indicate the transition temperatures as determined by DSC and optical microscopy.

own limiting layer spacing. The subsequent increase in the spacing for S_C as a function of increasing temperature, and its levelling out at the transition from S_C to S_A , are well known effects already reported in the literature [18].

5. Molecular area.

In addition to the molar volume, there is another parameter that is useful to know, the molecular area S . For a lamellar system such as a smectic mesophase, particularly when the molecules are symmetrical with identical aliphatic chains at their ends, S has a very simple geometrical sense. It represents the average surface per molecule in the plane of the smectic layers [19]. Clearly the molecular area is directly related to the molar volume V and to the layer spacing d , by :

$$S = V/(Nd) \quad (2)$$

where N is Avogadro's number. It should be emphasized that S must not be confused with σ , which is the average area per molecule in a plane perpendicular to the long axis of the molecules [19]. The latter offers a specific measure of the compactness in the lateral packing of the molecular arrangement. Of course, when the molecules are tilted at an angle θ with respect to the layer normal, σ is given by :

$$\sigma = S \times \cos(\theta). \quad (3)$$

From the experimental values of the molar volume (Fig. 1) and the layer spacing (Fig. 3), the molecular area S of TBDA was calculated as a function of temperature, using equation (2). Inspection of figure 4 reveals the following interesting features. Firstly, S increases slightly with temperature for S_G , S_F and S_I , just as was the case for the molar volume and the layer spacing, without any detectable discontinuity at the transitions $S_G \rightarrow S_F$ and $S_F \rightarrow S_I$. The small thermal dilation observed, about $12 \times 10^{-4} K^{-1}$, is related primarily to the lateral expansion of the molecules within the layers. Secondly, at the transition between S_I and S_C , the molecular area undergoes an important and abrupt increase of about 8.4%, clearly related to the first-order nature of the transition.

Thirdly, and most significantly, the molecular area begins to increase steadily with temperature within the range of the S_C phase, passes through a maximum at about $170^\circ C$, then decreases rapidly to reach a value of 27 \AA^2 at the $S_C \rightarrow S_A$ transition. This behaviour is certainly due to a combination of two con-

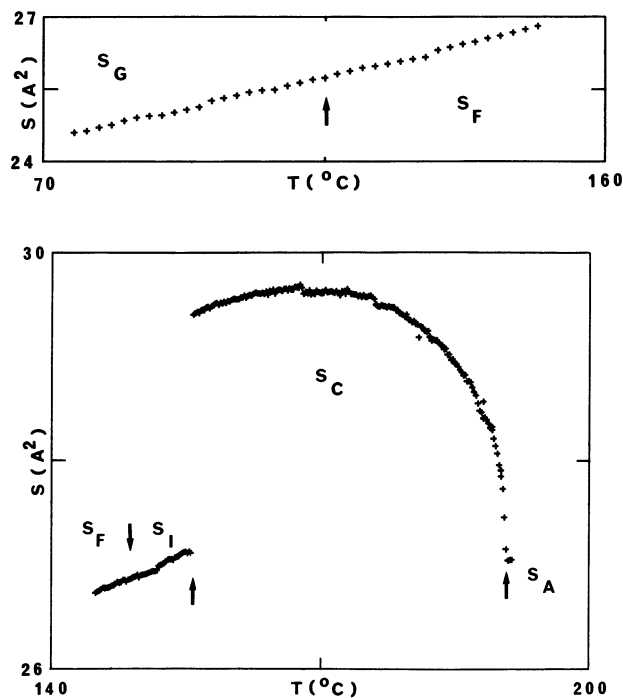


Fig. 4. — Molecular area of TBDA as a function of temperature : arrows indicate the transition temperatures as determined by DSC and optical microscopy.

flicting effects. At low temperatures, the tilt angle of the molecules remains fairly constant (see below), and the growth of S merely reflects the normal thermal lateral expansion of the molecular arrangement. The value of $(1/S) (\partial S/\partial T) = 11 \times 10^{-4} \text{ K}^{-1}$ found at the advent of S_C is indeed very close to that found for S_G , S_F and S_I (where the tilt hardly changes with temperature, as we shall see below). At high temperatures, on the other hand, the decrease of S is clearly related to the decrease of the tilt angle of the molecules.

5. Tilt angle.

With a knowledge of the value of the molar volume and the layer thickness as a function of temperature, one may calculate the temperature dependence of the tilt angle of the molecules, using three different methods.

The first method has already been applied successfully to the case of TBBA [16] and calls upon equation (3) :

$$\theta = \cos^{-1}(\sigma/S).$$

Although S is known experimentally (Fig. 4), σ must be calculated by extrapolation to lower temperatures of the molecular area S in S_A (where $\theta = 0$). As the temperature range of stability of S_A for TBDA is too small to safely permit an extrapolation, it was decided to make use of thermal expansion coefficient of TBBA, $\partial\sigma/\partial T = \partial S/\partial T = 27 \times 10^{-3} \text{ \AA}^2 \text{ K}^{-1}$ which is believed to be a reasonable approximation :

$$\sigma(T) = 27.05 + 0.271 \times (T - 190.7).$$

It should be pointed out that this method for calculating θ uses the assumption that the lateral packing area σ of the molecules does not undergo any discontinuous change at the transitions between smectic mesophases. This is probably true for the $S_A \rightarrow S_C$ transition, which is weakly first-order and which involves layers in the liquid state.

The second method makes use of the fact that the layer thickness of S_A corresponds to the length l of the molecules to a good approximation. As indicated by NMR experiments, the mean molecular configuration (which is disordered at least as far as aliphatic chains are concerned) is indeed very elongated. Using this assumption, the tilt angle is given directly by :

$$\theta(T) = \cos^{-1}[d(T)/l(T)] \quad (4)$$

where $d(T)$ is the layer spacing and $l(T)$ the corresponding molecular length at the same temperature T , extrapolated from S_A using the linear regression :

$$l(T) = 40.04 - T \times 0.0045.$$

The third method involves a comparison of the thickness d_a of the aromatic sublayer (supposed to be perfectly separate from the aliphatic one) with the

length l_a of the aromatic stems of the molecules :

$$\theta = \cos^{-1}(d_a/l_a). \quad (5)$$

The values of d_a and l_a can be deduced from the layer spacing d which is the sum of the thicknesses of one aromatic and one aliphatic sublayer, using the fact that the latter is equal to the volume of two decamethylene chains divided by the molecular area S :

$$d_a = d - 20 \times V_{\text{CH}_2}/S.$$

To obtain l_a , one utilizes the values of d_a calculated for S_A . The value determined is $l_a = 17.1 \text{ \AA}$. Based on NMR observations [13] that show an « all trans configuration » of the three phenyl rings of the aromatic cores, one may assume that l_a is a constant as a function of temperature.

Values of the tilt angle calculated using the three methods presented above are plotted in figure 5.

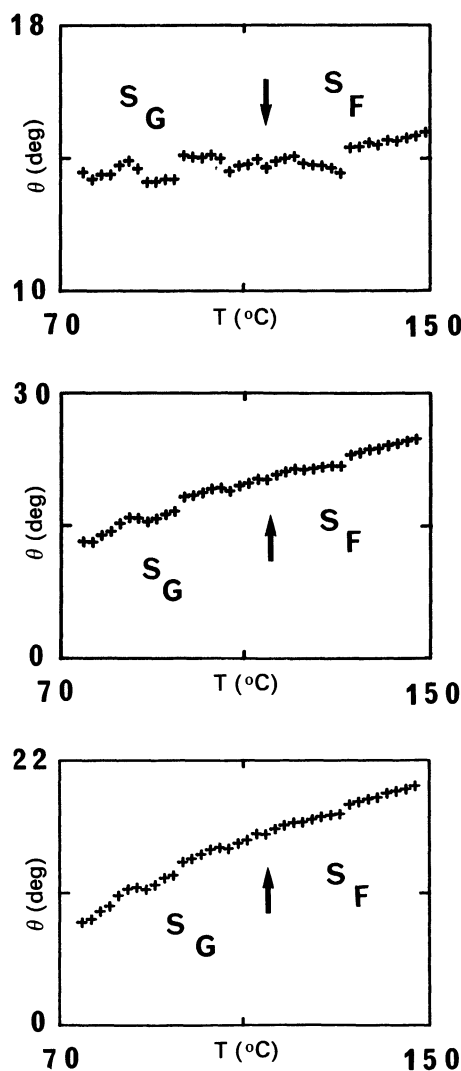


Fig. 5. — Tilt angle of TBDA molecules as a function of temperature : arrows indicate the transition temperatures as determined by DSC and optical microscopy. (a) : Equation (3); (b) : Equation (4); (c) : Equation (5).

They suggest the following remarks. As a whole, the three methods used lead to similar results. Their agreement is perfect for S_C , owing to the liquid state of the layers, which validates the underlying assumptions made. The discrepancies observed for S_G , S_F and S_I are related to the volume jump occurring at $S_I \rightarrow S_C$. This jump is connected with a discontinuous change of σ and l (any change of σ induces a change of l , for l is equal to V/σ).

The second feature worth noting in figure 5 is that, in the temperature range of S_G , S_F and S_I , the tilt angle θ varies continuously upon heating, increasing from about 10° to 20° . In contrast, it is found to decrease for TBBA [16, 20], the butyl homolog of the TBDA considered in this work. This difference in behaviour will be discussed in detail in a forthcoming paper.

Finally, it is of interest to note that, at the transition from S_I to S_C , the tilt angle suddenly increases from about $15\text{-}20^\circ$ to 27° . One is tempted to interpret this

phenomenon as related to the fact that the positional order in S_G , S_F and S_I is efficient enough to lock the molecules in well defined relative positions and to fix the tilt angle with respect to the layers at a given constant value. At the $S_I \rightarrow S_C$ transition, the molecular interactions lose their efficacy, and molecules tilt more drastically in order to relax the elastic constraints imposed upon the paraffinic chains (which are stretched out when the molecular area is small). The question then arises whether or not the first-order nature of the $S_I \rightarrow S_C$ transition is not simply related to the sudden increase in entropy, that is associated with the conformational expansion of the disordered paraffinic chains.

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