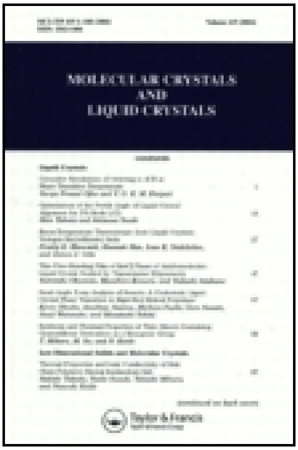

Molecular Crystals and Liquid Crystals

Phase Transition and Structural Studies of 70.8 and TBAA12 Liquid Crystals By Several Experimental Techniques

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Phase Transition and Structural Studies of 70.8 and TBAA12 Liquid Crystals By Several Experimental Techniques†

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The present investigation concerns the phase transitions, the temperature dependence of the layer thickness in all the mesophases, and the determination of some structural parameters of the N(p-n-heptyloxy benzylidene) p'-n-octylaniline (70.8) and of the terephth*a*lylidene-bis-p-n-dodecylaniline (TBAA12) compounds. DSC, optical microscopy and x-ray diffraction techniques were used. In particular x-ray diffraction clearly confirms in 70.8 compound the presence of the S_G and S_C mesophases and shows a phase coexistence at S_B-S_C phase transition. The x-ray diffraction data obtained on the puzzling S_I mesophases are discussed in comparison with the results of previous investigations on similar compounds.

Regarding the TBAA12, which presents an uncommon and quite rich phase sequence (solid, S_G, S_F, S_I, S_C, I), x-ray diffraction shows, in particular, that the layer thickness decreases gradually when the temperature increases until the phase S_C is reached, after which it remains constant until the isotropic liquid phase.

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†Presented at the 11th International Liquid Crystal Conference, Berkeley, 1986.

Whereas its behaviour is similar to that of the compounds with $n=9$ and $n=10$ for the ordered phases, the behaviour in the smectic C phase in TBAA12 is quite different, as compared to the other homologous, perhaps owing to the absence of S_A phase.

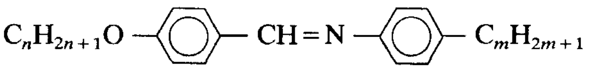
In spite of this different behaviour, the jump observed in the layer thickness at the S_I-S_C phase transition of TBAA12 is coherent with the values previously obtained for homologous with lower n.

Keywords: liquid crystals, x-ray diffraction, phase transitions, DSC, microscopy, smectics

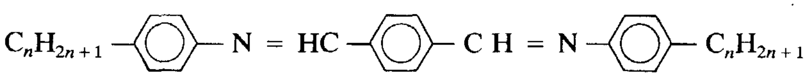
INTRODUCTION

Going on with detailed and compared studies of groups of liquid crystalline compounds which belong to homologous series,[1–4] we present here the phase transition and structural investigations concerning:

a) the compound with $n=7$ and $m=8$ (70.8) of the N-(4-n-alkoxybenzylidene)-4′-n-alkylanilines series with the general structure:



b) the compound with $n=12$ (TBAA12) of the terephthalylidene-bis-(4-n-alkyl-anilines) series with the general structure:



The two series, usually denoted as nO.m and TBAAs, respectively, are very interesting, due to the complex polymorphism shown by a large number of their compounds. Previous results in the nO.m series compounds are reported in Ref. 5; to our knowledge, however, no x-ray investigation have been performed so far on the 70.8 compound.

As regards the term TBAA12, only a high pressure DTA investigation[6] has been carried out until now, to our knowledge.

The results obtained on TBAA12 compound are often compared with the TBAA10 ones due to their similarity. In particular the S_F and S_I mesophases, (a general review is presented in Ref. 7), appear on both compounds. Both S_F and S_I phases can be regarded as quasi-two dimensional systems, the former being the first example[8] of the tilted hexatic phase predicted by Halperin and Nelson,[9] the latter usually[8,10] exhibiting a 2D solid-like order.

So it appears very surprising that the S_F phase occurs at lower temperatures than the S_I phase on both TBAA10 and TBAA12 homologous. Nevertheless, while Benattar[8] and co-workers have suggested an interesting explanation of this fact on the basis of H^2-NMR experiments on the TBAA10 compound, Budai[10] *et al.*, after detailed x-ray studies of free-standing films, would have shown that the S_I phase is truly hexatic in nature: it is not excluded that two types of S_I phases can exist, with different characteristics.

The results of the present study appear to support the conclusions of Benattar[8] for TBAA10 which seem to be valid also for TBAA12 compound.

EXPERIMENTAL

The x-ray diffraction measurements were carried out with a conventional powder diffractometer allowing sufficiently high counting times. Ni filtered CuKα radiation (λ = 1.54 Å), strongly collimated with a system of slits, was used.

The samples had a thickness of 1.5 mm and were held by two thin Al sheets fixed to a circular hole in an Al matrix with a diameter of ~ 1 cm.

Heating was achieved by a hot stage which has an accuracy of ±0.5°C and a stability of ±0.1°C.

Differential scanning calorimetry (DSC) data were recorded by a full-automatized Perkin-Elmer II instrument.

For optical observation a microscope Leitz Ortolux II POL-MK, equipped by a hot stage device FP 5 by Mettler, was used.

RESULTS AND DISCUSSION

1—70.8 compound

The phase diagram obtained by x-ray diffraction is the following:

$$\begin{tikzcd} \mathrm{Sol} \arrow[r, shift left, "48.5^\circ\mathrm{C}"] & S_G \arrow[l, shift left] \arrow[r, leftrightarrow, "53.5^\circ\mathrm{C}"] & S_B \arrow[r, leftrightarrow, "68.5-69.3^\circ\mathrm{C}"] & S_C \arrow[r, leftrightarrow, "70.5^\circ\mathrm{C}"] & S_A \arrow[r, leftrightarrow, "83.5^\circ\mathrm{C}"] & I \end{tikzcd}$$

very slowly at
room temperature

Characteristic diffractograms recorded for different mesophases are shown in Figures 1 and 2. Figure 2a clearly shows the coexistence of

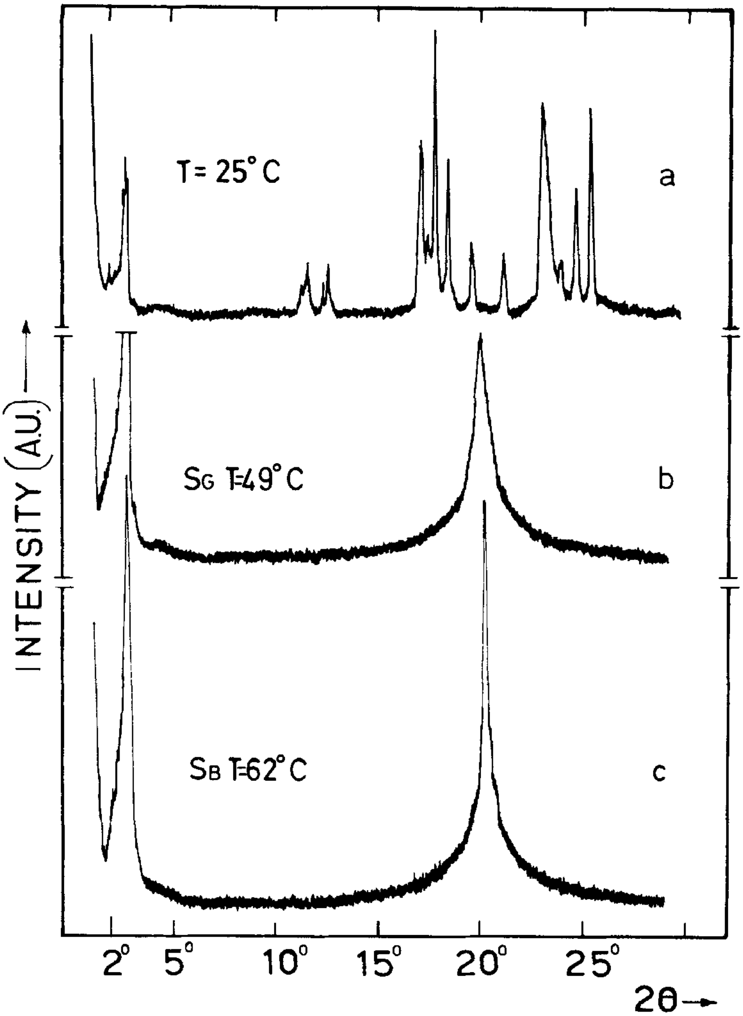


FIGURE 1 X-ray diffraction patterns of the 70.8 compound: a) solid; b) smectic G; c) smectic B.

S_B and S_C mesophases (in a temperature range of about 0.8°C), that is compatible with previous reports.[11-12]

The powder sample x-ray diffraction pattern of the S_G phase (Figure 1b) does not shows any weaker peaks close to the high angle strong one (see Ref. 7, p. 118), so it was not possible to determine the pseudo-hexagonal cell parameters.

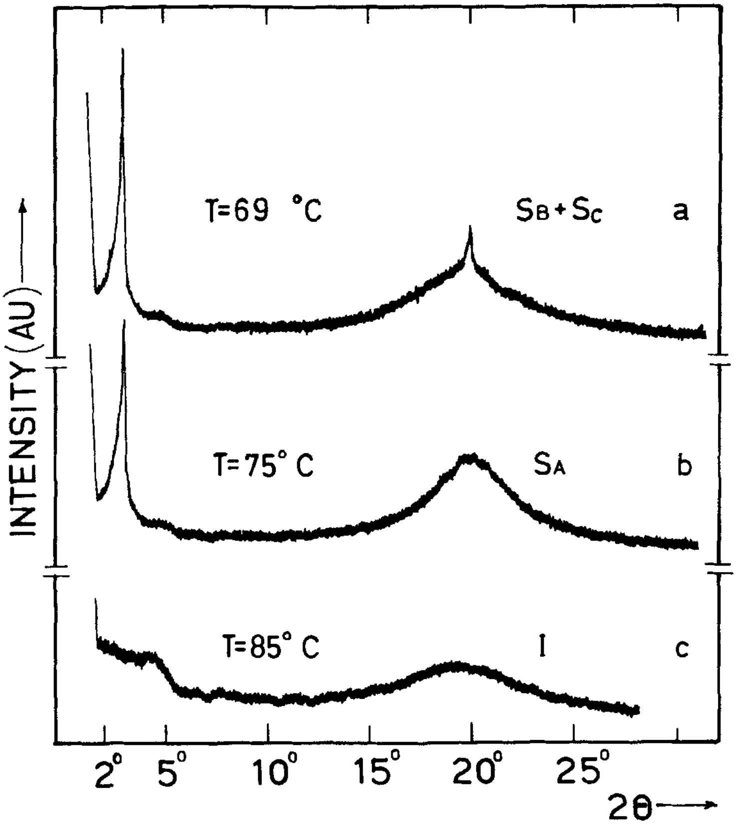


FIGURE 2 X-ray diffraction patterns of the 70.8 compound: a) coexistence of S_B and S_C mesophases; b) smectic A; c) isotropic.

The S_G mesophase is confirmed by DSC thermograms of Figure 3 and by careful optical microscopy and dilatometry[13] investigation.

Therefore the x-ray diffraction results agree with the ones obtained by Richter,[14] while in Ref. 5 the following phase diagram Sol $\xleftrightarrow{48°C} S_B \xleftrightarrow{70°C} S_A \xleftrightarrow{83°C} I$ is shown and it is asserted that no S_G properties are observed in the n o. 8 series compounds.

Figure 4a reports the layer thickness d obtained as a function of temperature. The d increases gradually in the S_B phase until a saturation is reached confirming the practically second order nature of the S_G–S_B phase transition, as deduced from the infinitesimally small enthalpy associated to this transition. During the cooling process the S_G phase remains until room temperature, where the solidification occurs after about a day.

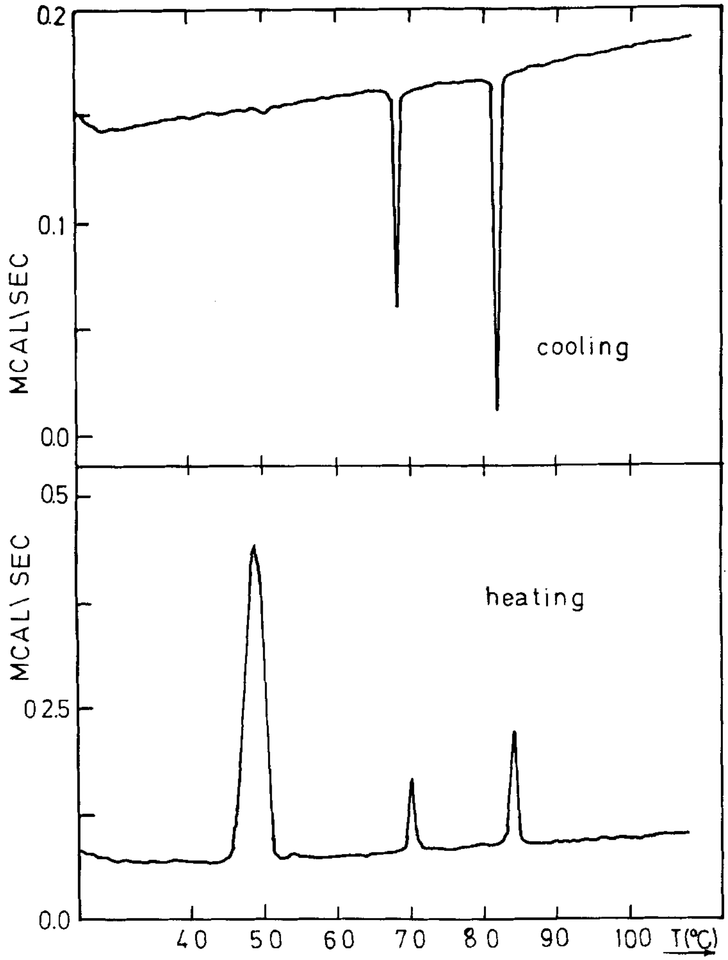


FIGURE 3 DSC thermograms of the 70.8 compound.

The average value of the layer thickness in the saturation region of the S_B is 31.75 ± 0.4 Å, which corresponds quite well to the molecular length as deduced from the model, namely about 31.5 Å.

From the above values and from the average d value in the S_G, i.e. 29.9 ± 0.3 Å, a tilt angle of ~ 19° was found in this mesophase.

Moreover, by using also the large angle Bragg peak, the following hexagonal cell parameters in the S_B phase were found: $a = b = 5.06 \pm 0.07$ Å; $c = 31.75 \pm 0.4$ Å.

The decrease of about 1 Å of the d parameter in the S_A phase, as compared to the S_B phase, can be attributed to the long molecular

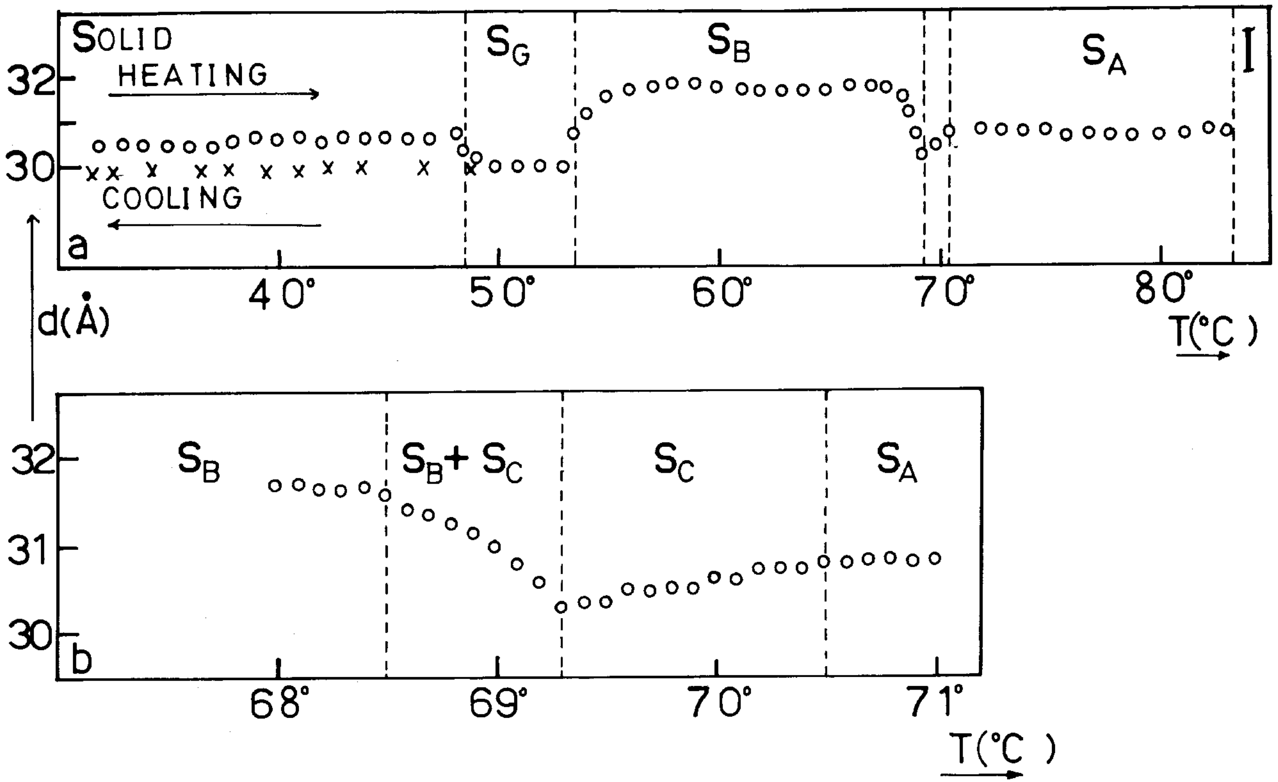


FIGURE 4 a) layer thickness vs. temperature in the 70.8 compound; b) layer thickness from 68° to 71°C in an enlarged scale in the 70.8 compound.

axial fluctuations, in agreement with Ref. 15. From the angular position of the wide-angle diffuse peak in the S_C and S_A phases the lateral intermolecular distance $D = 5.0 \pm 0.07$ Å was obtained by using the modified Bragg equation[16]

$$1.117\ \lambda = 2D\sin\theta \tag{1}$$

To evidence the presence of the S_C mesophase, the layer thickness in the temperature range from 68° to 71°C is presented in an enlarged scale in Figure 4b. In the S_C mesophase the *d* value increases linearly with the temperature so that the tilt angle β, calculated according to $\cos\beta = \frac{d_C}{d_A} = \frac{\text{layer thickness in the } S_C}{\text{layer thickness in the } S_A}$ is $10^\circ \leqslant \beta \leqslant 0^\circ$. Both transitions S_B–S_C and S_C–S_A appear to be of second order, all the more that they are not detected by DSC thermogram.

2—TBAA12 compound

The phase diagram obtained by x-ray diffraction for this compound is the following:

$$\mathrm{Sol}\ \underset{\underset{68^\circ\mathrm{C}}{\longleftarrow}}{\overset{80.5^\circ\mathrm{C}}{\longrightarrow}}\ S_G \overset{113^\circ\mathrm{C}}{\longleftrightarrow} S_F \overset{135^\circ\mathrm{C}}{\longleftrightarrow} S_I \overset{150^\circ\mathrm{C}}{\longleftrightarrow} S_C \overset{181^\circ\mathrm{C}}{\longleftrightarrow} I$$

The typical diffractograms recorded for different mesophases are reported in Figures 5, 6 and 7. The shown phase sequence is confirmed by optical microscopy, dilatometry[13] and DTA investigations.[6] The phase transition temperatures obtained by different experimental techniques coincide within less than 1°C. The DSC thermogram (Figure 8) does not detect the S_G–S_F and S_F–S_I phase transitions, which are obviously of second order. On the other hand the DSC shows, at about 42°C, a little peak probably indicating a solid–solid transition involving structural changes not observable by x-ray diffraction.

Figure 9 reports the layer thickness *d* obtained as a function of temperature. In spite of the fact that x-ray diffraction was already performed for the TBAA10 compound,[17] the measurements were repeated in the present work in order to have a check point with data concerning the homologous previously investigated (see for instance Figures 10 and 11 below), owing also to the controversial nature of the conclusions obtained by different authors on this compound.

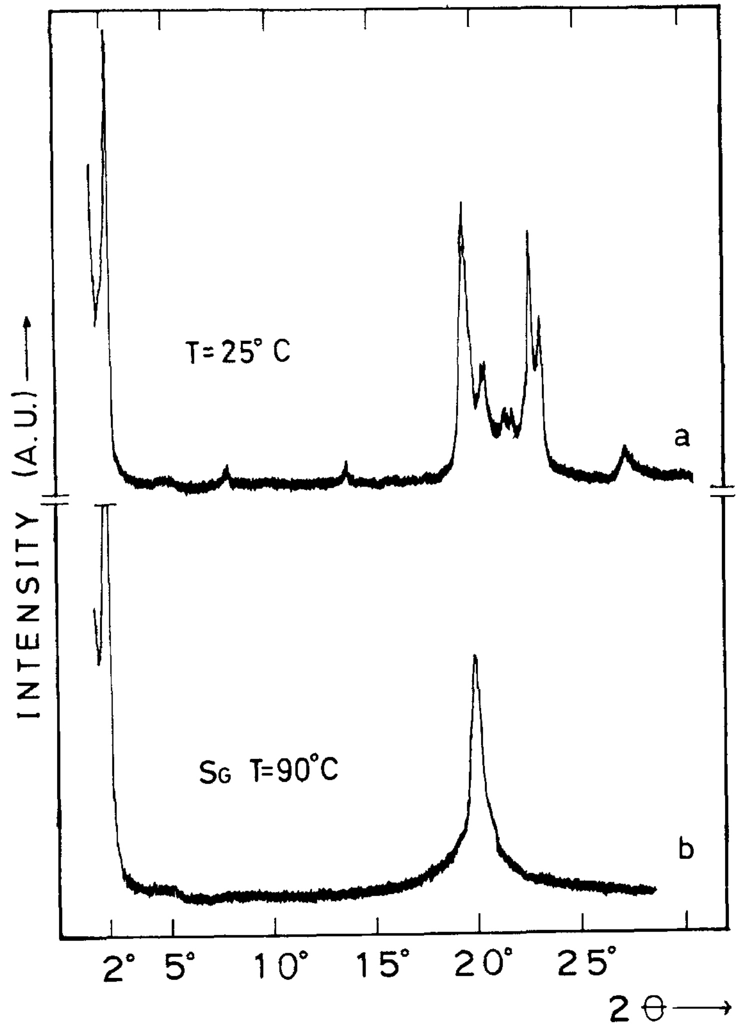


FIGURE 5 X-ray diffraction patterns of the TBAA12 compound: a) solid; b) smectic G.

The results in Figure 9 show that the temperature dependence of *d* for TBAA12 is similar to that of TBAA10 till the transition to S_C (a supercooling effect at the S_G–solid phase transition is observed on TBBAA10 too). Moreover for both compounds the phase transitions are confirmed by a variation of the width of large angle Bragg peaks.

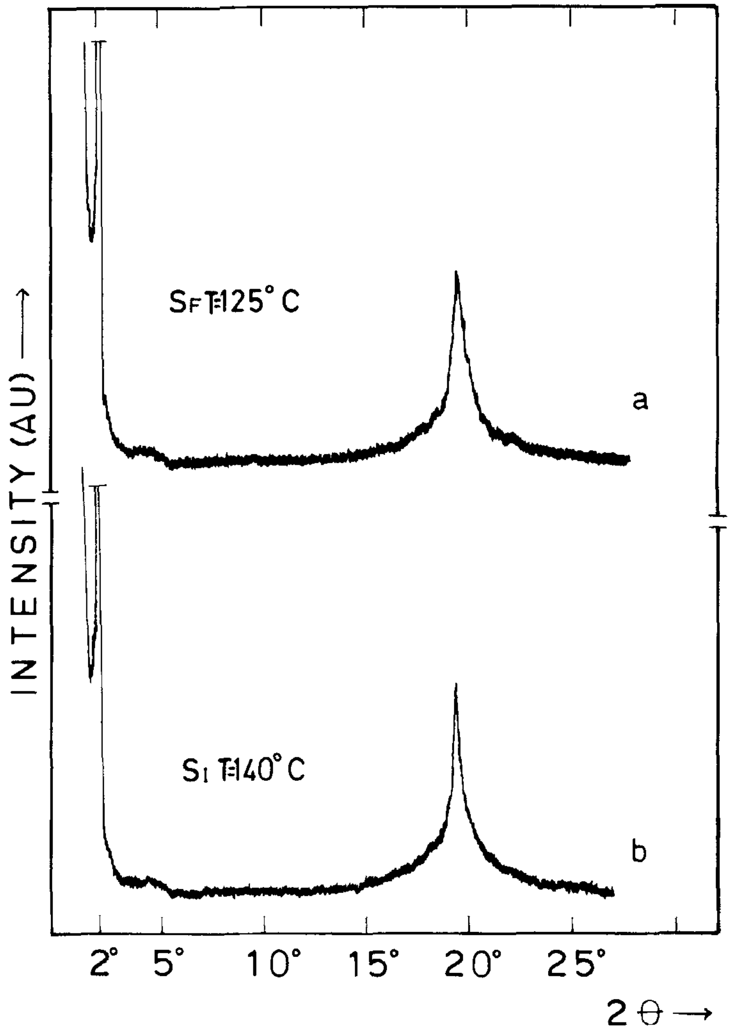


FIGURE 6 X-ray diffraction patterns of the TBAA12 compound: a) smectic F; b) smectic I.

By assuming the lengths of the molecules equal to 41.5 and to 46.5 Å for TBAA10 and TBAA12 respectively, as deduced from the model, and by assuming that each molecule maintains its fully stretched conformation in all the ordered phases, the average tilt angles were calculated for each phase from the average *d* value and are reported in Table I for both compounds. The relatively large width of high angle peak reported in Figure 6a, indicating an in-plane short range

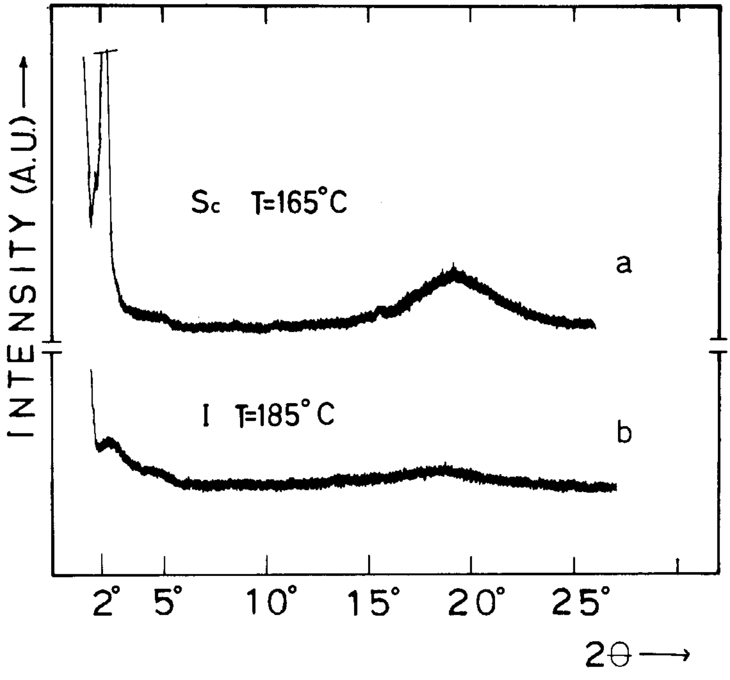


FIGURE 7 X-ray diffraction patterns of the TBAA12 compound: a) smectic C; b) isotropic.

positional order, seems to confirm the hexatic nature of S_F, in addition to TBAA10. On the other hand the narrow peak concerning the S_I phase (Figure 6b) is typical of a long range positional order within the layers. The explanation of the puzzling phase sequence S_F–S_I given in Ref. 8, appears to be supported for both compounds by the fact that the density in S_I phase is lower than in S_F one.[18] Figure 10 reports the values of $d = d_{F,I}-d_C$ i.e. the jump of the layer thickness at the transition into the S_C phase, for several homologous as found in Ref. 17 and in the present experiment. It can be seen that a good agreement exist for $n = 10$ between the two experiments and that the range of linearity is extended until $n = 12$. Figure 11 reports the tilt angle β of the molecules in the S_C phase calculated according to $\cos\beta = d_C/d_A$. The continuous line synthetizes the data of Ref. 17 for $n = 5; 7; 8; 9$.

The different temperature behaviour of β for TBAA10[17] is confirmed by the present data, which are slightly higher than the previous ones. On the other hand a quite different behaviour is observed for

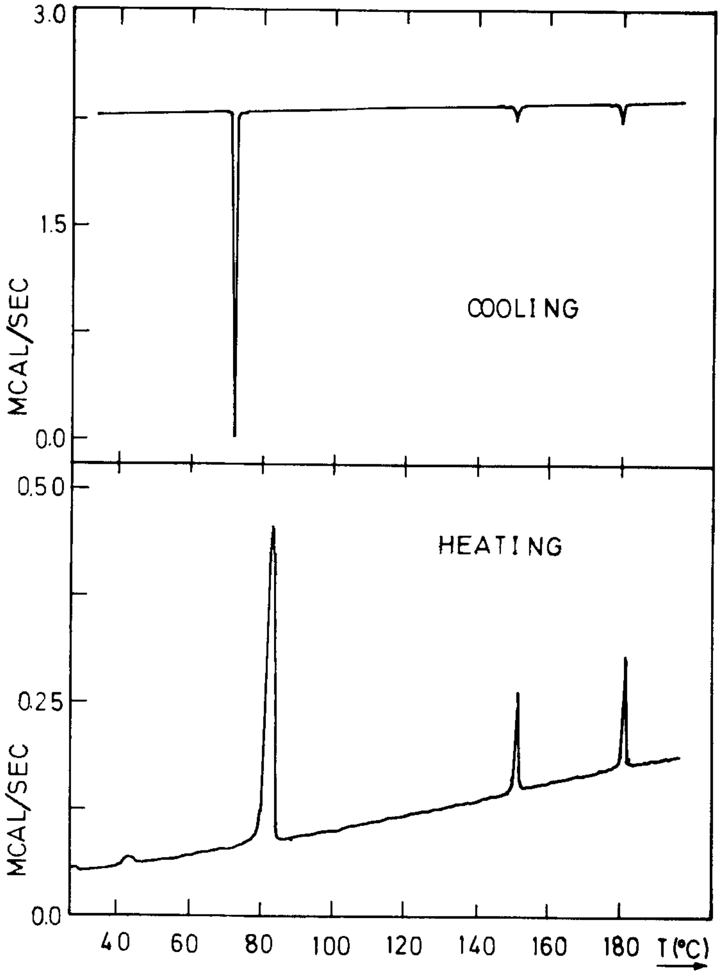


FIGURE 8 DSC thermograms of TBAA12 compound.

TBAA12, which exhibits a constant value of β, likely due to the non-existence of the S_A phase in this compound: actually the extrapolated value according to the curve $d = L - d_A$ of Figure 6 of Ref. 17 was used.

CONCLUSION

The phase diagram of the compound 70.8 was obtained by three different techniques the results of which are in agreement. Moreover

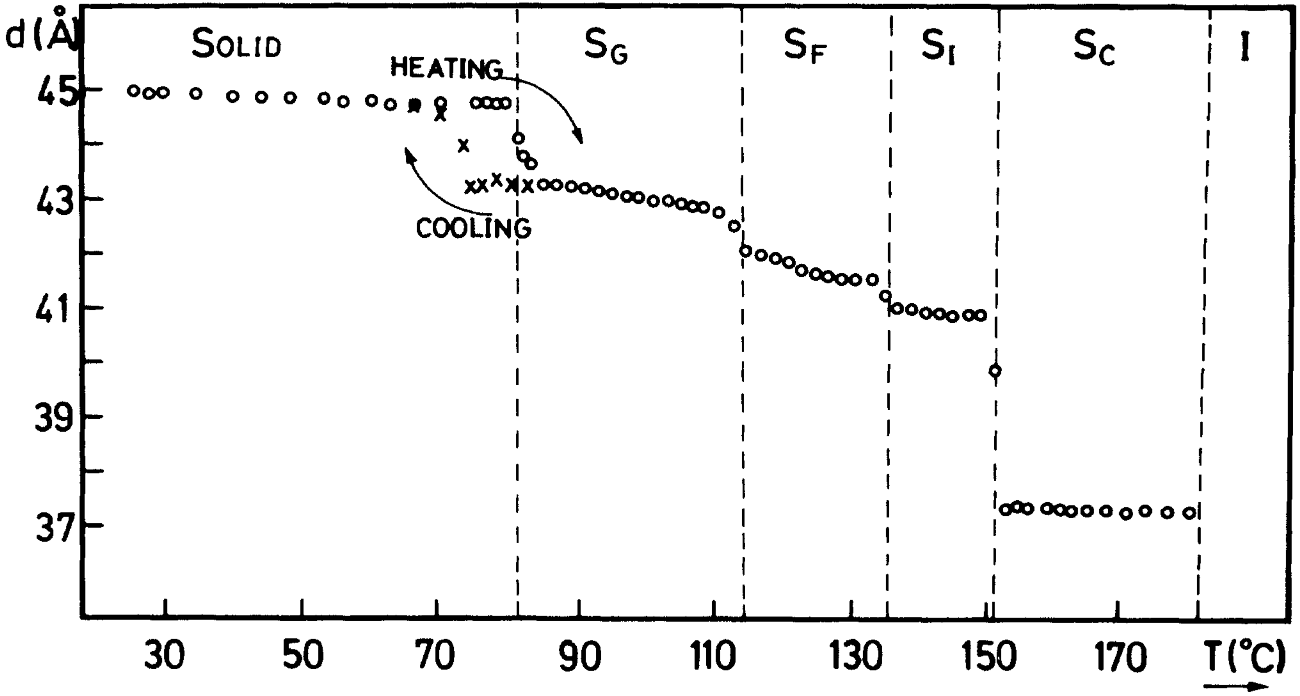


FIGURE 9 Layer thickness vs. temperature in the TBAA12 compound.

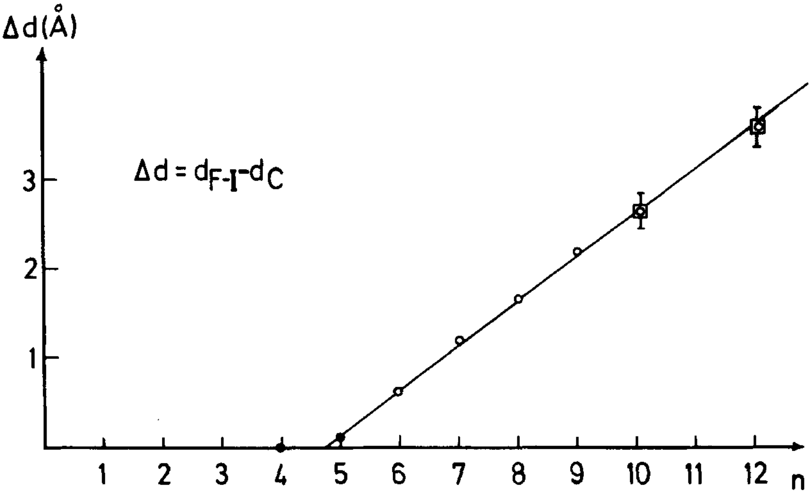


FIGURE 10 Jump of the layer thickness at the transition into the S_C phase as a function of n.

some structural information was obtained for the different phase transitions by using x-ray diffraction. In particular it was shown unequivocally by x-ray diffraction that the compound exhibits the S_G and S_C phases, the existence of which was excluded previously.[5] The transitions S_G–S_B, S_B–S_C and S_C–S_A appear to be of second order or weakly first order. Whereas the S_F phase presents a relatively short range translational order typical of hexatic phases, the S_I is characterized by a far greater in plane correlation length, in agreement with the conclusion of Benattar and coworkers. For the TBAA12 x-ray diffraction shows in particular that the layer thickness decreases gradually as a function of temperature in the ordered phases in a similar way to homologous with n = to 9 and 10. However in the S_C phase the behaviour of TBAA12 is completely different from the other investigated homologous: the tilt angle remains constant as a function of temperature, whereas for homologous with lower n, the tilt angle depends strongly on temperature and tends to zero (with exception of $n = 10$), at the S_C–S_A phase transition. On the other hand, the present experiment shows an extension until $n = 12$ of the linearity region as a function of n of the layer thickness jump $\Delta d = d_{F,I} - d_C$ at the transition either from S_F or from S_I phase to the S_C one.

Acknowledgments

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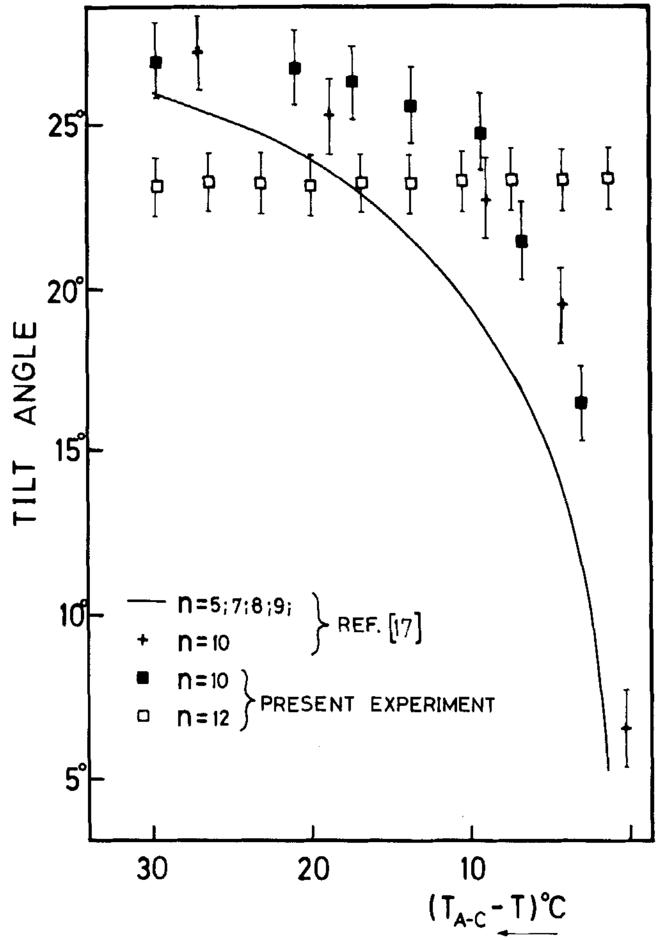

FIGURE 11 Temperature dependence of tilt angle in the S_C phase. $T_{A\text{-}C}$ represents the phase transition temperature from S_C to S_A. For $n = 12$, the abscissa should be replaced by $(T_{I\text{-}C}-T)$, where $T_{I\text{-}C}$ represents the transition temperature from S_C to isotropic liquid phase.

TABLE I

Average tilt angle values concerning the ordered phases of TBAA10 and TBAA12 compounds

Phase	TBAA10	TBAA12
Solid	13.8°	15.5°
S_G	23.8°	22.4°
S_F	26.4°	25.7°
S_I	27.1°	28.15°

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