

X-RAY DIFFRACTION OF THE SMECTIC PHASES OF N-(p-n-HEPTYLOXYBENZYLIDENE)-p'-n-PENTYLANILINE

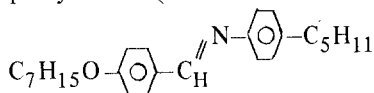
W.H. De JEU and J.A. De POORTER

Philips Research Laboratories Eindhoven, The Netherlands

Received 7 March 1977

Using X-ray diffraction the various smectic phases of N-(p-n-heptyloxybenzylidene)-p'-n-pentylaniline can be classified (with increasing temperature) as S_H , S_B , S_C and S_A , respectively. The long molecular axes are probably tilted with respect to the normal to the layers in the S_A , S_C and S_H phases, and perpendicular to the layers in the S_B phase.

During the last few years alkyl-alkoxy substituted Schiff bases [1, 2] have received considerable attention because they exhibit liquid crystalline behaviour at or slightly above room temperature. Their thermal properties and the various types of mesophases were comprehensively described by Smith and Gardlund [3, 4], but they gave no more than a preliminary classification of the smectic phases based on the textures only. In this letter we give X-ray results for the four smectic phases of N-(p-n-heptyloxybenzylidene)-p'-n-pentylaniline (often abbreviated as 7O.5):



The results lead to a classification of the smectic phases (with increasing temperature) as S_H (tilted B), S_B (normal B), S_C and S_A , respectively.

According to ref. [3, 4] the various transitions occurring in 7O.5 between the crystalline state (K) and the isotropic phase (I) are:

K 23 S_4 58.0 $S_3(S_B)$ 64.4 S_C 68.3 S_A 79.6 N 83.2 I.
(60) (710) (40) (680) (510)

The transition temperatures are in degrees centigrade, while the numbers between parenthesis give the transition enthalpies in cal/mol. The smectic phase labelled S_4 was not classified. Billard [5] performed some miscibility studies [e.g. 6] with 7O.5 and concluded that the S_4 phase should be identified with S_G and the S_3 phase with S_F instead of S_B . The latter result seems somewhat unlikely for the following reasons. The S_F phase has been reported to be a biaxial phase with liquid layers, exhibiting schlieren textures similar to those in the S_C phase [7]. However, the S_3 phase of

7O.5 can occur in homeotropic textures over the whole temperature range. Secondly, the transition enthalpy is relatively large in the case of $S_C S_3$ and small for $S_3 S_4$, indicating that possibly both the S_3 and the S_4 phase have ordered layers.

In order to check the classification of the smectic phases of 7O.5 the X-ray diffraction patterns of unorderd samples were recorded using a Guinier camera and $CoK\alpha$ radiation ($\lambda = 1.78892 \text{ \AA}$). Besides the sharp 001 reflection at small Bragg angle θ reflections were observed around $\theta = 12^\circ$. Isodensitraces of the reflections in this region are given in fig. 1. For the S_C phase approximately the same diffuse reflection is observed as for the S_A phase (fig. 1a), indicating in both cases liquid layers as expected. For the S_3 phase one single sharp reflection is observed around $\theta = 12^\circ$ (fig. 1b), which is characteristic of a normal S_B phase [6, 8]. Hence the original classification of the S_3 phase is correct. For the S_4 phase two strong reflections are observed and several weaker ones (fig. 1c), indicating either an S_H or an S_G phase. We shall compare this result with the X-ray diffraction patterns of the smectic phases of terephthal-bis-butylaniline (TBBA). This compound has been studied in detail by Doucet et al. [10]. Besides an S_A and an S_C phase, an S_H phase is observed and a so-called smectic VI phase. Miscibility studies recently showed the latter phase to be an S_G phase [9]. The S_H phase is characterized by pseudo-hexagonal order within the layers, and the S_G phase by a herringbone type of arrangement (molecular rotation frozen out). In both cases the long molecular axes are tilted with respect to the normal to the layers. The X-ray diffraction patterns are quite similar, the main difference being in the extinction rules [10]. In

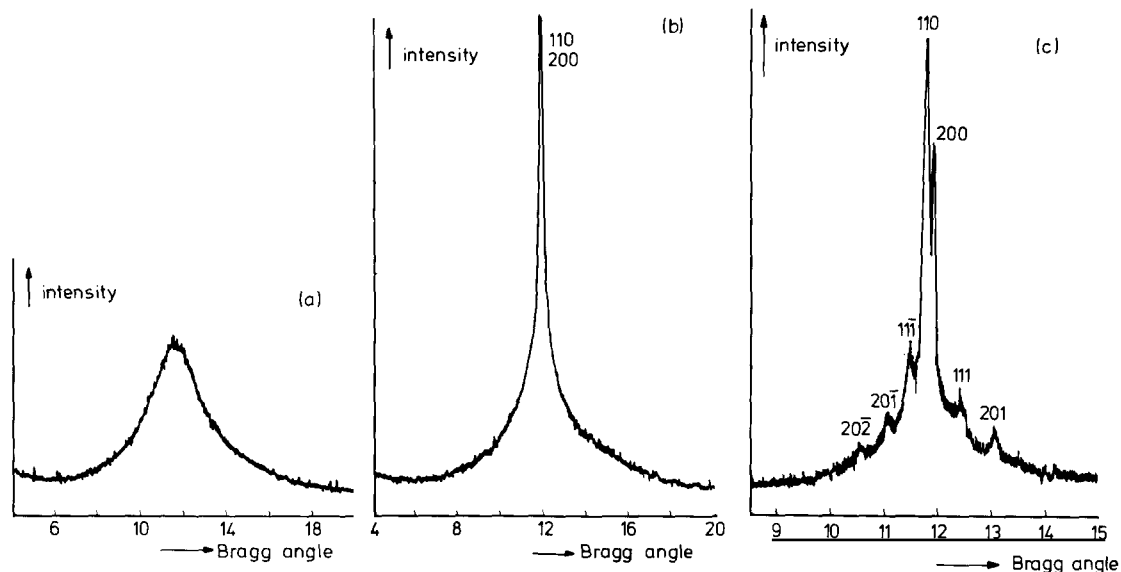


Fig. 1. X-ray diffraction pattern of unordered samples of 7O.5 in the smectic A phase (a), the smectic B phase (b), and the smectic H phase (c, expanded scale).

the S_H phase hkl reflections with $h + k = 2n + 1$ (n integer) are not found, while in the S_G phase this condition is restricted to $k = 0$. For the S_4 phase of 7O.5 we did not observe any of these additional allowed reflections like $h1l$, even h , whereas an excellent agreement between observed and calculated reflection angles was obtained with the reflections assigned by analogy with those in the S_H phase of TBBA. (See table 1 and fig. 1c). The monoclinic lattice parameters for the S_H phase of 7O.5 at room temperature are:

$$\begin{aligned} a &= 9.9 \pm 0.2 \text{ \AA}, \\ b &= 5.11 \pm 0.04 \text{ \AA}, \\ c &= 27.9 \pm 0.7 \text{ \AA}, \\ \beta &= 118^\circ \pm 1^\circ. \end{aligned}$$

The cell volume is approximately 1240 \AA^3 , with two molecules per unit cell.

The strong 001 reflection, which characterizes the layer thickness, shows a rather curious behaviour throughout the various smectic phases of 7O.5. In the S_A and S_C phases the thickness is constant at 27.7 \AA . At the $S_C S_B$ phase transition there is a discontinuous increase to 28.9 \AA , while at the $S_B S_H$ transition there is again a decrease to 25.6 \AA . In the S_H phase the thickness increases slightly with decreasing temperature, reaching a value of 25.9 \AA at room temperature. At the $S_B S_H$ transition both reflections are observed over a trajectory of about 5°C , one probably corresponding to supercooled S_B regions. The length of an all-stretched 7O.5 molecule, as calculated from molecular models, corresponds approximately to the thickness of the smectic layers in the S_B phase. Hence it is reasonable to expect that in this phase the long molecular axes are, on average, perpendicular to the layers. In order to explain the smaller layers thickness in the other smectic phases we assume that the long molecular axes are tilted with respect to the normal to the

Table 1
Observed and calculated Bragg reflections for the S_H phase of 7O.5 at room temperature.

hkl	θ_{obs}	θ_{calc}
001	2.15	2.160
002	4.24	4.247
003	6.33	6.340
004	8.45	8.441
$20\bar{2}$	10.57	10.587
$20\bar{1}$	11.09	11.075
$11\bar{1}$	11.48	11.463
110	11.78	11.787
200	11.93	11.926
111	12.46	12.470
201	<u>13.07</u>	<u>13.073</u>

Table 2
Classification scheme for the various smectic phases.

	Long molecular axes parallel to layer normal	Long molecular axes make angle with layer normal
Liquid layers	A a)	C
Hexagonal packing within layers	B a)	H (tilted B)
Herringbone packing within layers	E b)	G

a) Uniaxial phase;

b) Uniaxial phase if the planes of the phenyl rings of adjacent molecules are perpendicular to each other and/or there is no rotational coupling between the layers; otherwise biaxial.

layers. Then the tilt angle must have a constant value of about 17° in the S_A and the S_C phases, while varying between 27.5° and 26° in the S_H phase. The latter result agrees well with the angle β of the monoclinic lattice. Following De Vries [11] the uniaxiality of the S_A phase can still be understood if the tilt directions of adjacent layers are uncorrelated. The $S_A S_C$ phase transition then is related to the onset of coupling of the tilt directions of the various layers. This possibility seems to have been overlooked in the usual discussion of $S_A S_C$ phase transitions. Using conoscopy we observed that in the present case of 70.5 the angle between the main optical axis and the normal to the layers grows with decreasing temperature from zero at the $S_A S_C$ phase transition.

A combination of the structural information available at present for the various smectic phases of different compounds allows us to set up a simple classification scheme (see table 2). We have tentatively used the symbol H for the tilted B phase. Originally the symbol H was introduced for a smectic phase of N-(p-n-butoxybenzylidene)-p'-ethylaniline (BBEA or 40.2) [12] which is now known to be identical with the S_G phase [9]. Some further remarks about table 2 are:

(i) It is assumed that as soon as the molecules within a layer tilt, the tilt directions of adjacent layers are coupled. As discussed above this is not necessarily always true. In that case the headings of the columns of table 2 should read: tilt directions of the layers uncor-

related, and correlated tilt directions, respectively.

(ii) In general the scheme of table 2 is in agreement with the miscibility rules of Sackmann et al. [6], which require that two phases are given the same symbol if they are miscible. However, it seems that the S_B and the S_H phase have been found to be miscible. As the symmetry of these phases is definitely different, a different symbol still seems appropriate.

(iii) In the case of optically active molecules the S_C and the S_H phase take the form of the chiral phases S_C^* and S_H^* . The symmetry of the S_A and the S_B phase is not compatible with a chiral phase. For the S_E and the S_G phase this point has not been investigated yet.

(iv) The scheme of table 2, based upon experimental investigations, is compatible with the theoretical scheme used by Meyer and McMillan [13].

Note added in proof: The correct classification of the smectic phases of 70.5 was reported independently by J. Doucet et al. at the Sixth International Liquid Crystal Conference, August 1976, Kent, Ohio (USA).

References

- [1] H. Kelker and B. Scheurle, *Angew. Chem.* 81 (1969) 903.
- [2] J.B. Flannery and W. Haas, *J. Phys. Chem.* 74 (1970) 3611.
- [3] G.W. Smith, Z.G. Gardlund and R.J. Curtis, *Mol. Cryst. Liq. Cryst.* 19 (1973) 327.
- [4] G.W. Smith and Z.G. Gardlund, *J. Chem. Phys.* 59 (1973) 3214.
- [5] J. Billard, *Compt. Rend. Ac. Sc. (Paris)* 280B (1975) 573.
- [6] H. Sackmann and D. Demus, *Mol. Cryst. Liq. Cryst.* 21 (1973) 239.
- [7] D. Demus, S. Diele, M. Klapperstück, V. Link and H. Zschke, *Mol. Cryst. Liq. Cryst.* 15 (1971) 161.
- [8] A. de Vries, in: *Liquid crystals, Proc. Bangalore Liq. Cryst. Conf., Pramana, Suppl. no. 1* (1975) p. 93.
- [9] L. Richter, D. Demus and H. Sackmann, *J. Phys.* 37 (1976) C3-41.
- [10] J. Doucet, A.M. Levelut and M. Lambert, *Phys. Rev. Lett.* 32 (1974) 301.
- [11] A. de Vries, *J. Phys. Lett.* 35 (1974)L-139; abstracts Vth Int. Liq. Cryst. Conf., Stockholm (1974) p. 150.
- [12] A. de Vries and D.L. Fishel, *Mol. Cryst. Liq. Cryst.* 16 (1972) 311.
- [13] R.J. Meyer, *Phys. Rev. A* 12 (1975) 1066.