Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

X-Ray Studies in the n-Pentyl 4-[4-n-Dodecyl-Oxybenzylidene-Amino]-Cinnamate in the S_I Phase

S. Diele [a], D. Demus [a] & H. Sackmann [a]
[a] Sektion Chemie, Martin-Luther-Universität, Halle-Wittenberg, GDR, Mühlpforte 1, 402, Halle

Version of record first published: 20 Apr 2011.

To cite this article: S. Diele, D. Demus & H. Sackmann (1980): X-Ray Studies in the n-Pentyl 4-[4-n-Dodecyl-Oxybenzylidene-Amino]-Cinnamate in the S_I Phase, Molecular Crystals and Liquid Crystals, 56:7, 217-224

To link to this article: http://dx.doi.org/10.1080/01406568008070494

Mol. Cryst. Liq. Cryst. Vol. 56 (Letters), pp. 217-224
0140-6566/80/5607-0217$04.50/0

Printed in the United States of America

X-RAY STUDIES IN THE n-PENTYL 4-[4-n-DODECYLOXYBENZYLIDENE-AMINO]-CINNAMATE IN THE S_I PHASE

S. DIELE, D. DEMUS and H. SACKMANN
Sektion Chemie, Martin-Luther-Universität
Halle-Wittenberg, GDR, Mühlpforte 1, 402 Halle

(Submitted for Publication January 22, 1980)

Abstract: Results of X-ray studies in oriented and not oriented samples of n-pentyl 4-[4-n-dodecyloxybenzylidene-amino]-cinnamate in the smectic modifications I, C and A respectively are reported. Special emphasis is led to the S_I phase, the structure of which is determined to be monoclinic with parameters a=5.04Å; b=8.40 Å; c=37.8 Å; ß= 106°. An attempt was made to present a model of the packing of the molecules regarding shifts of the molecules, too.

INTRODUCTION

Recently the new smectic phase type S_I was established in the nonyl and decyl homologues of the terephthylidene-bis-n-alkylanilines [1,2,3,4].
By use of miscibility relations also in other sub-

stances S_I phases could be classified [5,6]. Especially in n-pentyl 4-[4-n-dodecyloxybenzylideneamino]-cinnamate, a substance which formerly was claimed to possess a S_B phase, by new investigations [1,2,5,6] the polymorphism S_I, S_C, S_A was found.

Now we investigated oriented and non-oriented samples of this substance in S_I, S_C and S_A phases. A first description of the X-ray pattern of non-oriented samples was given in [7] [§].

EXPERIMENTAL

Oriented samples were obtained by cooling the substance from the isotropic state into the smectic one within a magnetic field of about 1.5 Tesla. The field was applied during the whole exposure time. The samples were enclosed in glass capillaries with a diameter of 1.5 mm. The samples were irradiated from different directions with Cu K_α radiation. The diffraction was recorded by a flat film. The investigations of non-oriented samples were performed with a Guinier camera (diameter: 114.6 mm).

The Bragg angles Θ of the layer spacings as a function of the temperature were measured with a

---

[§] A. de VRIES: private communication. According to conoscopic observation the low temperature form of the decyl homologue is biaxial. It should belong to the S_I phases.

goniometer [8] which allowed a sufficient accuracy of the angle determination.

RESULTS

S_I phase

The patterns of non-oriented samples are characterized by one outer reflex besides the inner one, which indicates the layer structure. The outer reflex exhibits a sharp profile.

The layer spacings as a function of the temperature were calculated according to Bragg's law and are given in Fig. 1. The layer spacings are smaller than the length of the molecule L = 39.7 Å, measured by a model assuming a full stretched molecular form. From these values a tilt angle can be derived.

By means of patterns of oriented samples, the inclination and the packing of the molecules within the smectic layers could be determined. The hexagonally arranged maxima were observed on the outer reflex (Fig. 2 lower part), when the X-ray beam is nearly parallel to the long axes of the molecules. Therefore, a hexagonal packing of the molecules within a plane perpendicular to their long axes can be supposed.

Two different orientations of the smectic layer with respect to the magnetic field were obtained. In most of the cases, the layer normal is inclined with respect to the magnetic field (Fig. 2 upper part, the field direction is indicated by an arrow).

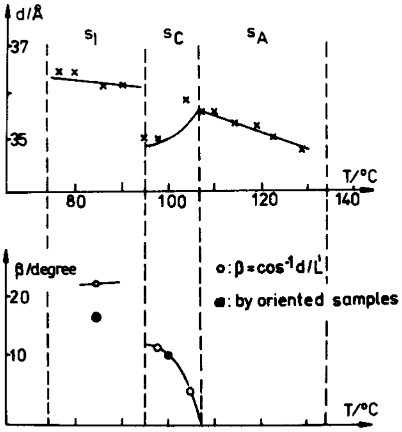

Figure 1

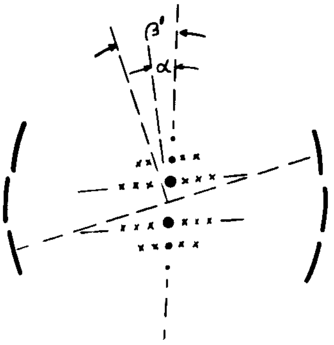

Figure 3

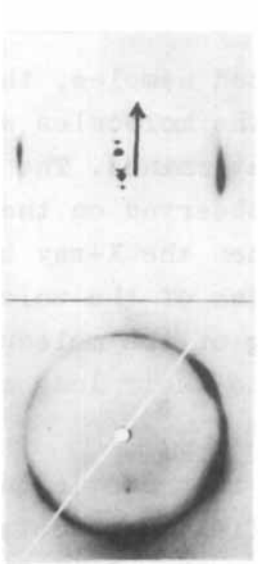

Figure 2

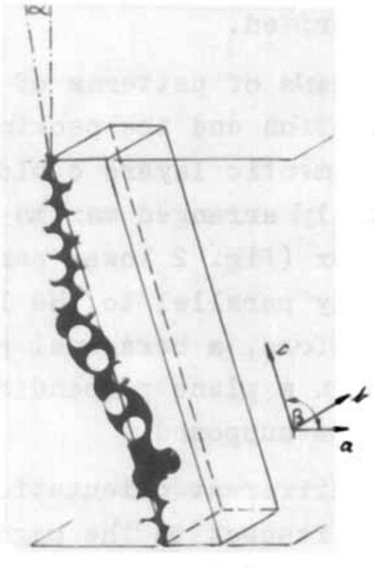

Figure 4

In some other cases an orientation was obtained, which is represented schematically in Fig.3. This pattern can be explained by the rotation of a monoclinic cell around the c -axis. It should be emphasized that the use of the term "monoclinic cell" is very doubtful, because 3-dimensional long range order is implied. But there are no experimental hints to prove the existence of such a 3-dimensional correlation. Interferences with hk1 or hk2 could not be observed. Therefore the c-axis as well as the monoclinic angle ß only represent an averaged direction of the molecules.

The observed interferences in Fig.3 were indexed on the basis of a face centered cell following from the hexagonal packing. A simple relation attributes from the 110 direction (14°) to the 100 direction (16°) and to the monoclinic angle ß = 106°. The calculated parameters are

$a = 5.04$ Å; $b = 8.40$ Å; $c = 37.8$ Å; $\beta = 106°$

Recently, Leadbetter et al.[9] investigated smectic F phases. The pattern, as well as the obtained results are very similar to the results reported here. That means that the S_F and the S_I phases cannot be distinguished up to now from a structural point of view.

The inner spots caused by the smectic layers are located on diffuse lines representing a translational movement of strings of molecules. This was also found in other liquid crystalline phases and is connected with shifts of molecules parallel to the c axis [10,11]. In the pattern described here the direction of the shifts is different from the direction of the c axis. The shift direction is tilted by an angle α of about 9^{o} to the layer normal.

The Figure 4 shows a comparison of the lattice of the S_I phase with a model of the molecule. The long aliphatic chain forms an angle of about 10^{o} with the layer normal if the c axis is assumed to be an averaged molecule axis. Thereby, the shift direction is determined by the direction of the rigid chains in the S_I phase.

S_C and S_A phases

At the I-C transition the layer spacings d are altered by a jump to lower values. Analogous jumps were observed in other substances with long alkyl chains also, and were explained by a loss of rigidity of the alkyl chains [12,13]. The tilt angles (indicated with o in fig.1) according to

$$\cos \beta = \frac{d_C}{d_A} \quad \text{with} \quad d_A = 35.7 \text{ Å} \quad (T = 110\ ^{o}C)$$

are unexpectectedly small, as compared with the tilt angles in other S_C phases. However, this result shows a very good agreement with the values obtained from the pattern of oriented samples (indicated with ■ in Fig.1).

The pattern taken at a temperature $T = 100^{o}C$ yields a tilt angle of 10^{o}.

Further it should be emphasized that the difference of the inclination between the averaged molecular axis and the shifts of the molecules does not occur in the S_C phase. The angle is zero within the limits of error.

That means that the transition into the S_C phase is connected with an intra-molecular reorganization which is based on a higher mobility of the alkyl chains, leading simultaneously to a loss of order within the smectic layers. On the base of the higher flexibility of the chains the molecules are able to form an averaged molecular long axis which is responsible for the tilt direction as well as for the direction of shifts. The layer spacings of the A phase are quite different from the length of the molecules in the most extended form. However, by means of oriented samples it was possible to prove the orthogonal arrangement of the molecules in this phase.

REFERENCES

1 L. Richter, Dissertation Halle/S. 1980

2 H. Sackmann, Proceedings of the III. Liquid Crystal Conference Budapest 1979 in print

3 L. Richter, D. Demus, H. Sackmann, in preparation

4 A. Wiegeleben, L. Richter, J. Deresch, D. Demus, Mol.Cryst.Liq. Cryst. in print

5 N.K. Sharma, L. Richter, B. Walter, S. Diele, W.Weißflog, H. Sackmann, D. Demus, Proceedings

of the III. Liquid Crystal Conference Budapest 1979 in print

6 N.K. Sharma, Dissertation Halle/S. 1979

7 S. Diele, P. Brand, H. Sackmann, Mol. Cryst. Liq. Cryst., 16, 105 (1972)

8 S. Diele, L. Nasta, H. Sackmann, Kristall und Technik 12, 1063 (1977)

9 A.J. Leadbetter, J.P. Gaughan, B. Kelly, G.W. Gray, J.W. Goodby, J. Physique (Paris) Coll. C 3, 40, 178 (1979)

10 A.M. Levelut, M. Lambert, C.R. Acad. Sci., 272, 1018 (1971)

11 A. de Vries, D.L. Fishel, Mol. Cryst. Liq. Cryst., 11, 375 (1970)

12 S. Diele, D. Demus, A. Echtermeyer, U. Preukschas, H. Sackmann, Acta Physica Polonica A 55 125 (1979)

13 S. Diele, H. Hartung, H. Krüger, D. Vetters, P. Ebeling, D. Demus, Proceedings of the III. Liquid Crystal Conference Budapest (1979) in print