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

Investigation of a Smectic Tetramorphous Substance

D. Demus [a], S. Diele [a], M. Klapperstück [a], V. Link [a] & H. Zaschke [a]
[a] Sektion Chemie, Martin-Luther-Universität Halle, 402, Halle, German Democratic Republic

Version of record first published: 21 Mar 2007.

To cite this article: D. Demus, S. Diele, M. Klapperstück, V. Link & H. Zaschke (1971): Investigation of a Smectic Tetramorphous Substance, Molecular Crystals and Liquid Crystals, 15:2, 161-174

To link to this article: http://dx.doi.org/10.1080/15421407108083232

Molecular Crystals and Liquid Crystals. 1971. Vol. 15, pp. 161–174

Printed in Great Britain

Investigation of a Smectic Tetramorphous Substance†

D. DEMUS, S. DIELE, M. KLAPPERSTÜCK, V. LINK and H. ZASCHKE

Sektion Chemie,
Martin-Luther-Universität Halle,
402 Halle, German Democratic Republic

Received October 27, 1970; *in revised form March* 8, 1971

Abstract—2-(4-*n*-pentylphenyl)-5-(4-*n*-pentyloxyphenyl)-pyrimidine has been prepared. By microscopic investigation, differential scanning calorimetry, dilatometric measurements and X-ray investigation, four different smectic modifications have been stated. The microscopic textures and the relations of miscibility suggest that two of these modifications can be assigned to the group smectic A and C. The other two smectic modifications cannot be assigned to any of the five known groups of smectic modifications. Their characteristics require the establishment of two new groups of smectic modifications with the arbitrary symbol smectic F resp. G.

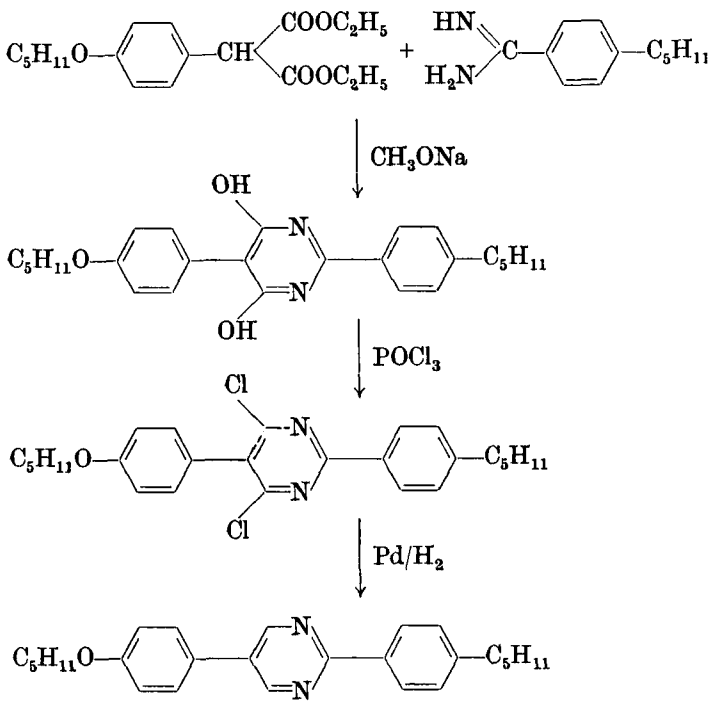
1. Introduction

In recent years Sackmann and coworkers[1,2] have worked systematically on the problem of polymorphism in the smectic state of thermotropic liquid crystals. Investigating their microscopic textures, relations of miscibility and X-ray diffraction patterns, they have found five groups of smectic modifications, which they called A, B, C, D, E. It is to be assumed that there are more than these five groups. In order to find new groups of smectic modifications the best chance is to investigate substances which exhibit polymorphism in the smectic state.

2. Preparation of the Substance

We have synthesized a substance with four smectic modifications in the following way:

† Presented by title at the Third International Liquid Crystal Conference in Berlin, August 24–28, 1970.



2-(4-*n*-Pentylphenyl)-5-(4-*n*-pentyloxyphenyl)-pyrimidine
A detailed description of the preparation is given in reference 3.

3. Scheme of Transitions and Microscopic Textures

This pyrimidine derivative shows the following transitions:

crystalline $\xleftarrow{79}$ smectic IV $\xleftarrow{102,7}$ smectic III $\xleftarrow{113,8}$ smectic II $\xleftarrow{144}$ smectic I $\xleftarrow{210}$ isotropic liquid

All transitions can be observed under the microscope (polarized light, magnification 120 ×). Starting from the crystalline state one obtains by the first heating unspecific textures, namely paramorphoses. In this case it is difficult to see all transitions.

With decreasing temperature one obtains specific textures and the transition phenomena are more visible.

The textures have been observed for two preparations: preparation 1 has been made with not especially treated glasses, preparation 2 has been made with especially cleaned glasses.

The typical texture of smectic I is a focal conic texture, especially a fan-shaped texture, as known from the observation of the smectic A-modifications.[1,2] This texture has been photographed for preparation 1 (Fig. 1). The characteristics of this texture were first described by Friedel[8] and are given in some review articles.[9,10,11] Preparation 2 shows in the same temperature interval a pseudo-isotropic texture.[2]

By cooling of preparation 1 the transition to the modification smectic II takes place. Smectic II usually shows a broken fan-shaped texture (Fig. 2). The focal domains of the texture given in Fig. 1 are preserved in the outer contours, but the inner details are altered. A great number of discontinuities appears. Smectic II also occurs in a smectic schlieren texture, which has been photographed for preparation 2 (Fig. 3). The broken fan-shaped texture as well as the smectic schlieren texture are typical of smectic C-modifications.[1,2]

By further cooling, the transition to smectic II takes place and the picture of Fig. 2 alters to Fig. 4, which has been photographed for preparation 1. This texture has some similarities with the fan-shaped texture, but there are many stripes in the focal domains.

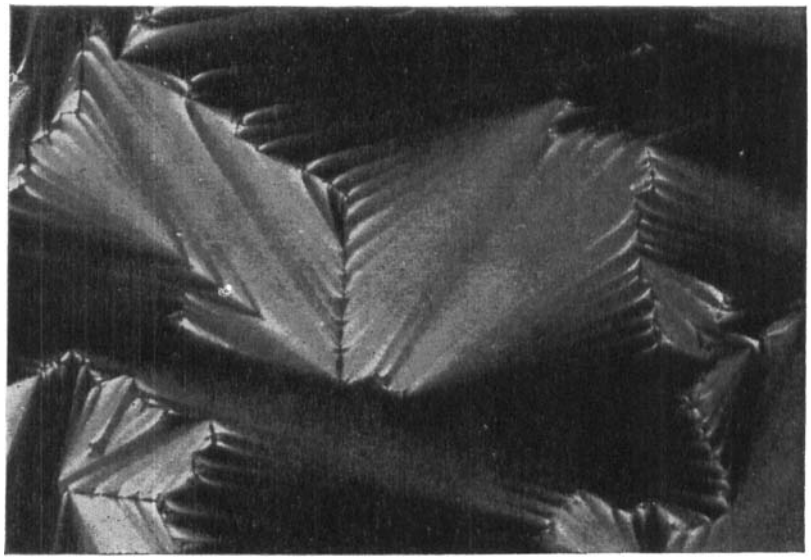


Figure 1. Focal conic (fan-shaped) texture of smectic I.

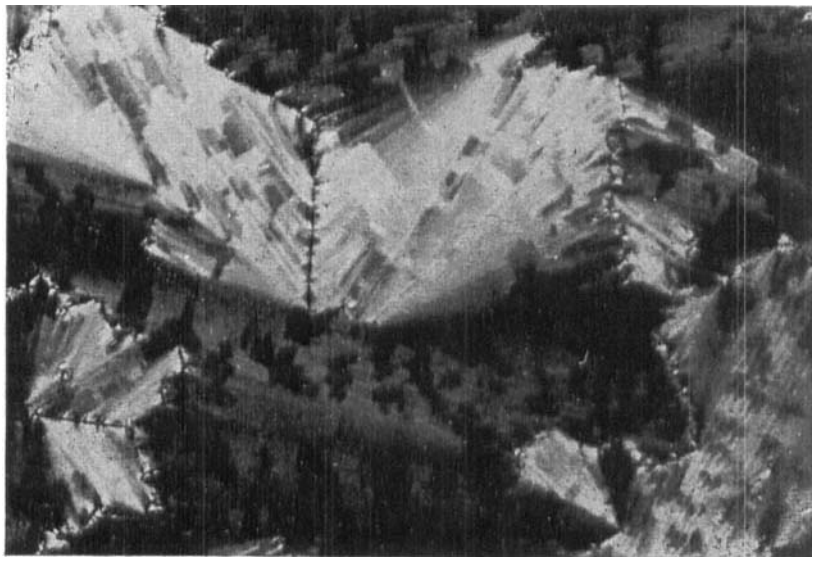


Figure 2. Broken fan-shaped texture of smectic II.

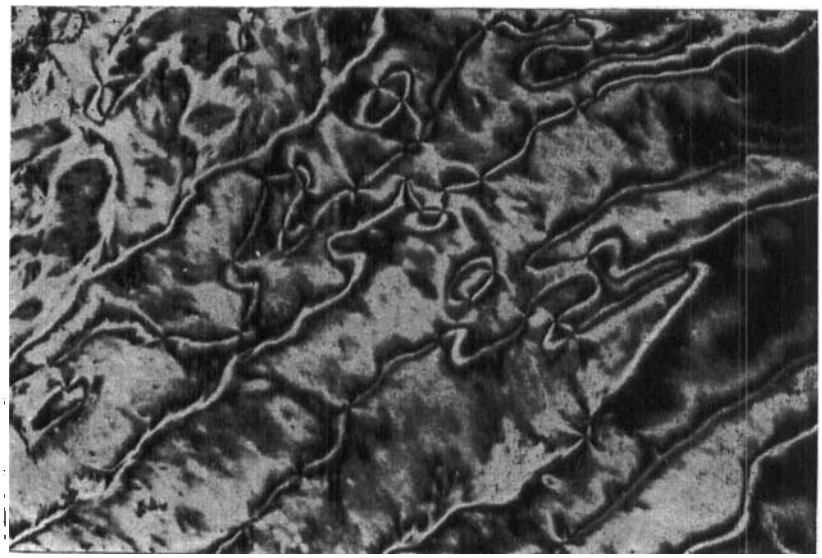


Figure 3. Schlieren texture of smectic II.

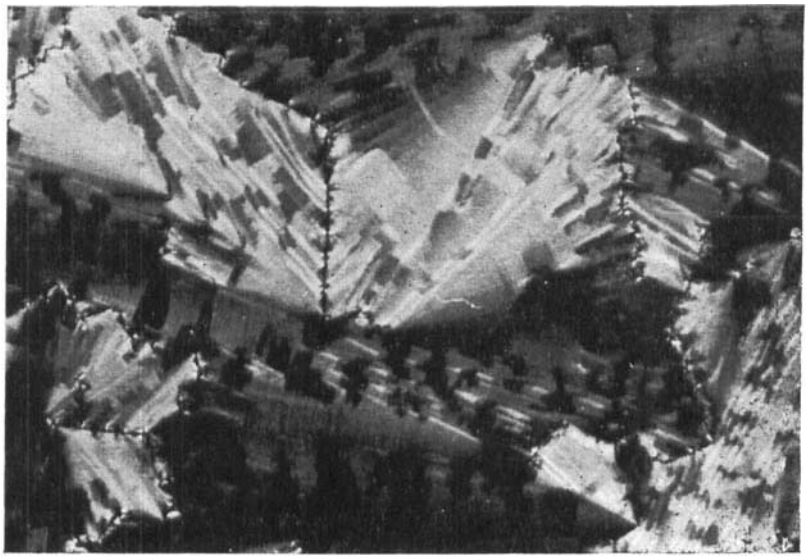


Figure 4. Striped fan-shaped texture of smectic III.

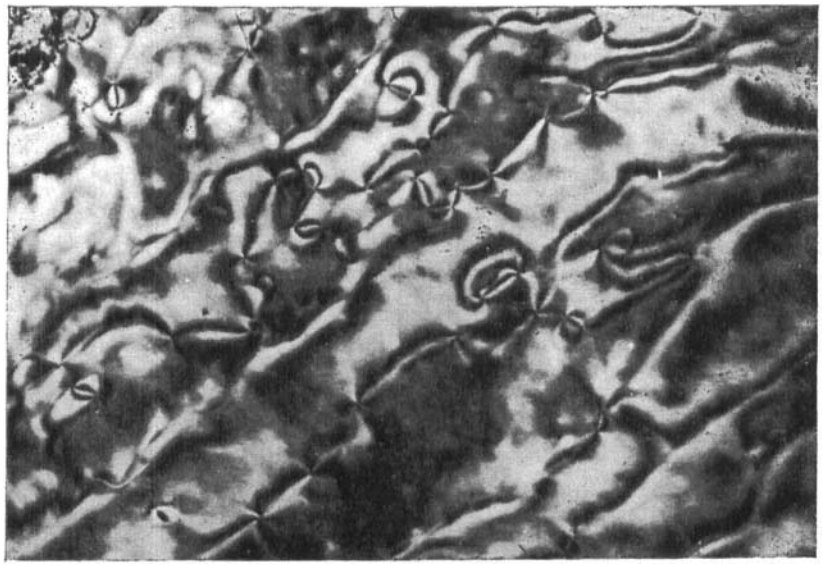


Figure 5. Schlieren texture of smectic III.

In preparation 2 smectic III also occurs in a schlieren texture (Fig. 5) which is very similar to the smectic C-modification.

After the transition to smectic IV the texture of Fig. 4 alters to the texture of Fig. 6, which has been obtained for preparation 1. This texture consists of optically homogeneous domains. Only some contours of the fan-shaped texture are preserved. Under the same circumstances preparation 2 shows a mosaic texture (Fig. 7), which is similar to the mosaic texture of the smectic B-modifications.[1,2]

On the second heating to higher temperatures preparation 1 shows the textures of Figs. 6, 4, 2 and 1 and preparation 2 shows the textures of Figs. 7, 5, 3 with only very little differences. These textures are typical of the four smectic modifications and can be used together with other properties for the identification of the type of the smectic modification.

All four smectic modifications are viscous and can be deformed by slight pressure on the cover glass of the microscopic preparation.

4. Calorimetric Investigation

In order to confirm the transitions seen under the microscope we have investigated the substance by thermal analysis with a Perkin–Elmer differential scanning calorimeter DSC 1B. The curve given in Fig. 8 was obtained. All transitions are indicated by a peak in the curve.

By evaluation of the curve we have calculated the enthalpies and entropies of transition (see Fig. 8). The peak of the transition smectic C/smectic A was too small to allow the quantitative evaluation of the enthalpy of transition. Only the order of magnitude has been estimated.

5. Density Measurements

By a capillary method we have investigated the thermal expansion of the compound up to the smectic A modification. Because of experimental difficulties we were not able to measure the density of the crystalline and isotropic liquid state. The densities range between 1.1 and 1.05 and there are anomalies in the neighbourhood

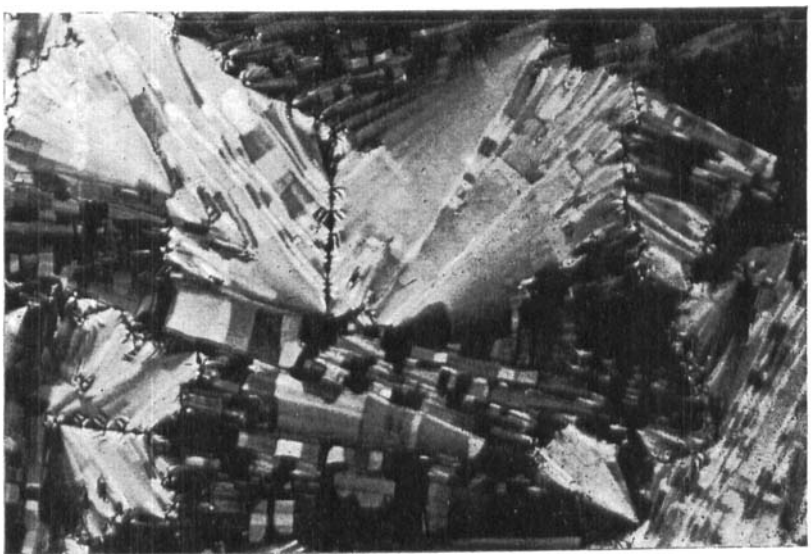


Figure 6. Texture of smectic IV.

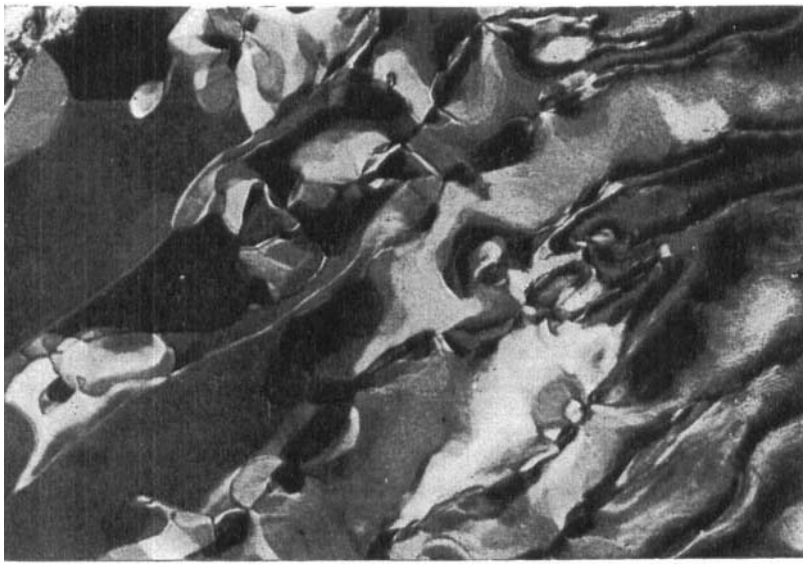


Figure 7. Mosaic texture of smectic IV.

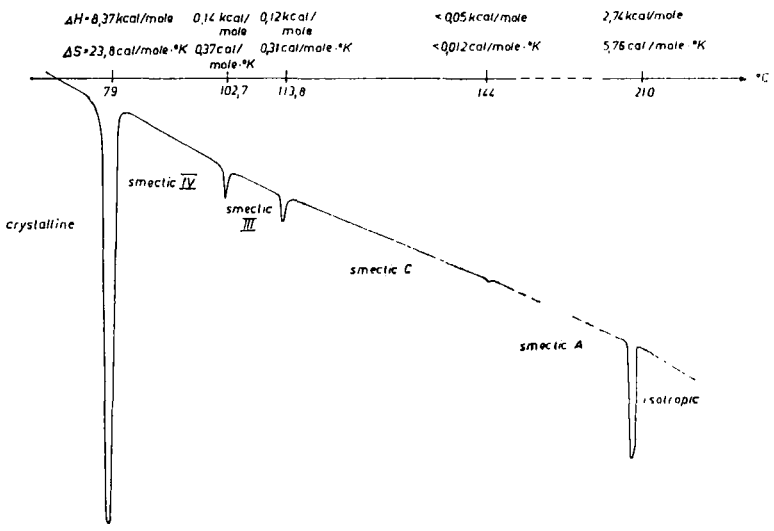


Figure 8. Results of calorimetric investigation.

of the transition temperatures (Fig. 9). These anomalies can be better seen from the curve showing the temperature dependence of the thermal expansion coefficient (Fig. 10).

The curve of the density is nearly linear in the region of smectic I, smectic II, smectic III; in the case of smectic IV the curve is concave to the temperature axis. The density changes of the transitions are relatively small:

0.26% smectic IV/smectic III, 0.52% smectic III/smectic II, 0.20% smectic II/smectic I.

All transitions exhibit pre- and post-transition effects (Fig. 10).

6. X-ray Diffraction Measurements

For a better characterization of the smectic modifications we have made some preliminary X-ray diffraction measurements. (Guinier-method).

The smectic I modification shows one sharp inner ring (with its second order) and one diffuse outer ring (Fig. 11a). This behaviour is the same as in the case of the smectic A modifications: the inner ring indicates the distance of the layers (here $d = 26.8$ Å, calculated molecule length from Stuart–Kalotten *ca.* 30 Å), the

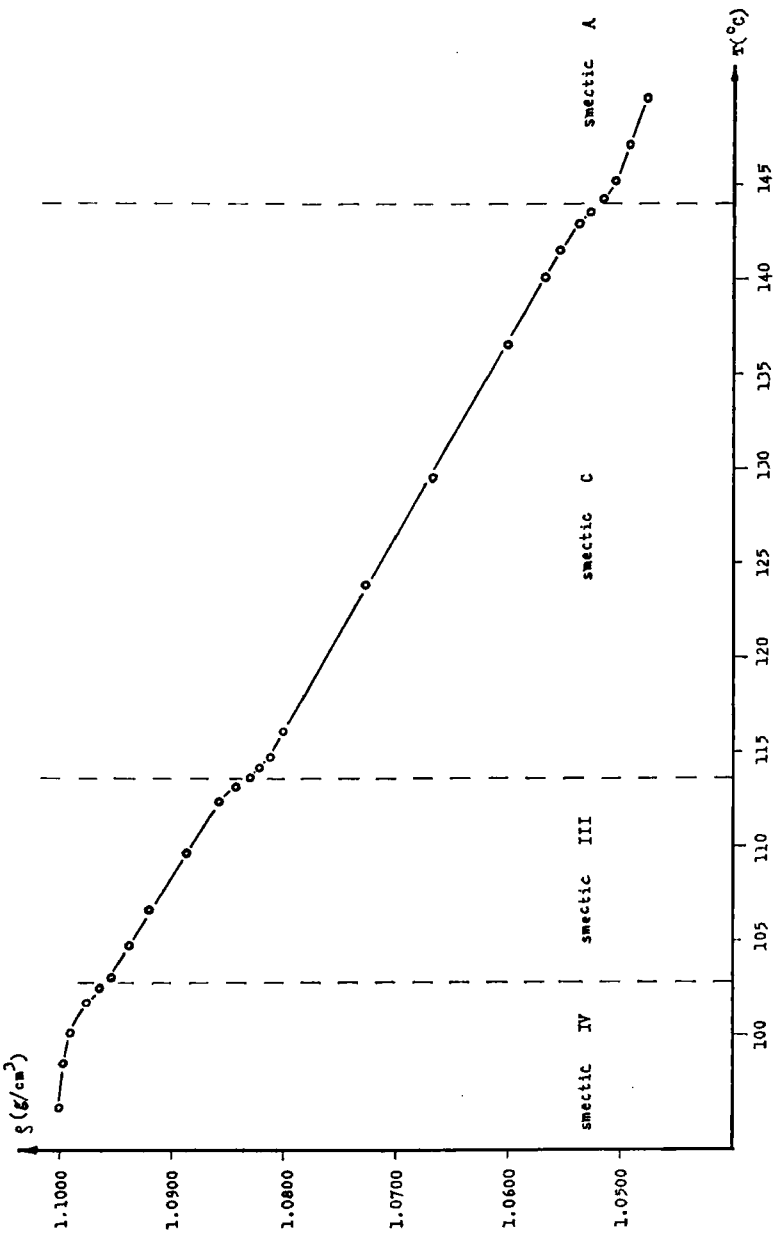


Figure 9. Temperature dependence of density.

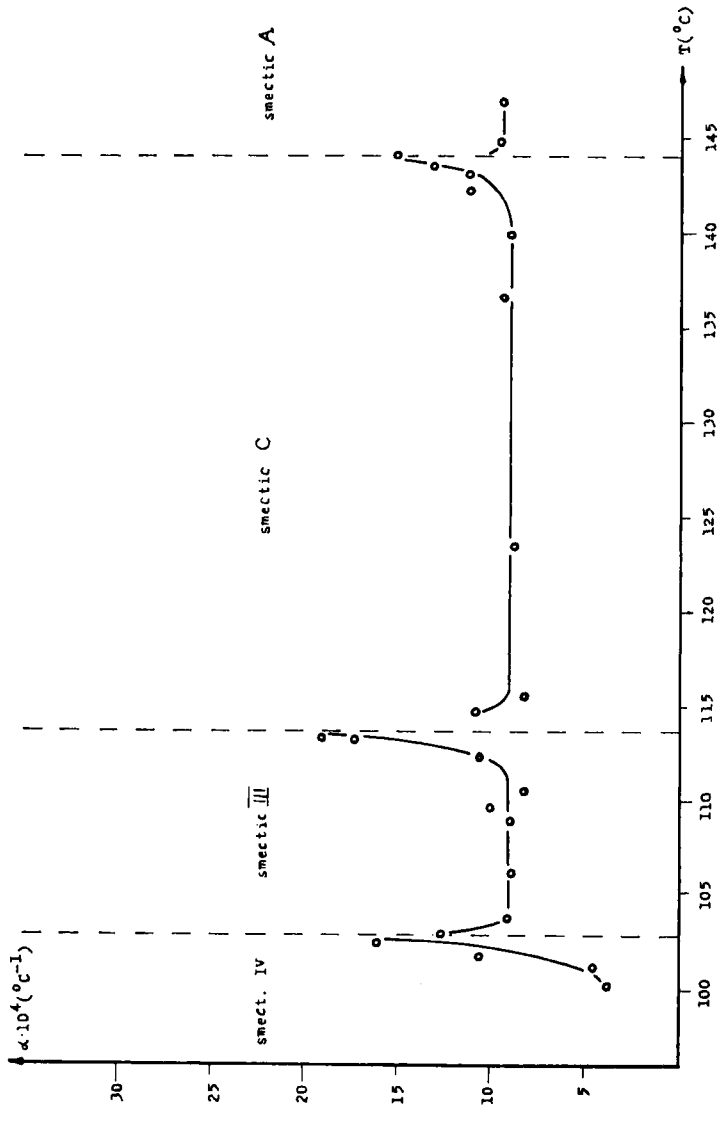


Figure 10. Temperature dependence of the thermal expansion coefficient.

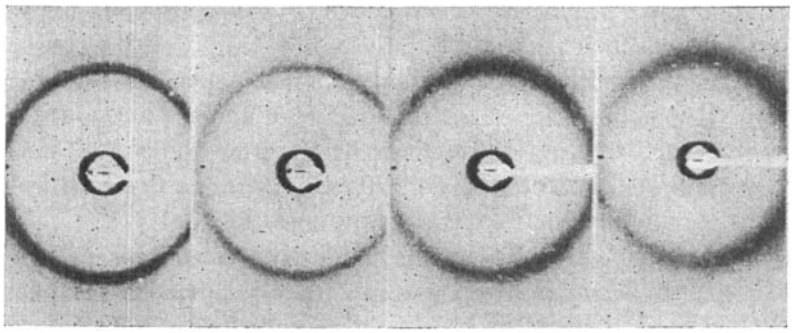
diffuse outer ring is a measure of the distance of the molecules within a layer (*ca.* 4.5 Å). Together with the observation of the microscopic texture it is to be assumed that smectic I is a smectic A modification.

The X-ray diffraction pattern of smectic II (Fig. 11b) shows only slight differences from smectic I: the inner ring is a little larger ($d = 23.4$ Å), the outer ring is somewhat sharper. The microscopic texture of smectic II suggests a smectic C-modification; with this the X-ray diffraction pattern is compatible.

The X-ray diffraction pattern of smectic III is very similar to that of smectic II, only the inner ring is a little larger, ($d = 23.0$ Å) the outer ring is somewhat sharper (Fig. 11c). The smectic IV modification shows a very altered picture (Fig. 11d): there is a sharp and textured inner ring (with its second order ($d = 22.1$ Å)); and several outer rings. This points to a layer structure with a specific not random arrangement of the molecules within the layers.

7. Investigation of the Relations of Miscibility

The results of the texture observation and the X-ray diffraction measurement show that smectic I is a smectic A modification and smectic II a smectic C modification. According to the rule of selected miscibility of Sackmann and coworkers[1,2] regions of an uninterrupted series of mixed liquid crystals are possible between



(a) (b) (c) (d)

Figure 11. X-ray diffraction patterns. (a) smectic I; (b) smectic II; (c) smectic III; (d) smectic IV.

modifications having the same symbol. In order to confirm the designation of the smectic modifications I and II as A and C we have investigated the diagram of state of the substance with 2,5-*di*-(4-*n*-heptylphenyl)-pyrazine,[4,5] a compound which has 2 smectic modifications A and C respectively. Figure 12 shows that there are indeed regions of uninterrupted modifications, while the regions of smectic III and smectic IV are separated by heterogenous regions from the other smectic phases. With some other substances we have tried to find a series of uninterrupted mixed liquid crystals between smectic III or IV and smectic B, but in all cases without success.

8. Discussion

The substance investigated shows four smectic modifications. All transitions are reproducible with increasing and decreasing temperature. We have confirmed the transitions by microscopic observation, thermal analysis and density measurements.

By X-ray diffraction measurements, the texture observation and the relations of miscibility, smectic I was found to belong to the group smectic A, and smectic II to the group smectic C. For this reason there is only a very small transition enthalpy between the two modifications according to the other investigated cases of a transition smectic A/C.[6,7]

The structures of the smectic phases I, II and III seem to be not very different. In all three cases the X-ray diffraction pattern shows a sharp inner ring and a diffuse outer ring, which suggests a layer structure with random distribution of the molecules within the layers. The modification smectic III shows differences in the texture as well as in the X-ray diffraction pattern from the smectic modifications marked B, D and E.[1,2] By this reason it is necessary to assign this modification to a new group marked F.

Smectic IV shows an X-ray diffraction pattern with several rings, but it seems to be not really crystalline: it shows a viscous behaviour, the microscopic texture can be altered completely by slight pressure on the cover-glass of the microscopic preparation; the transition smectic III–smectic IV cannot be noticeably supercooled; from this modification starts a noticeable region of mixed crystals in the

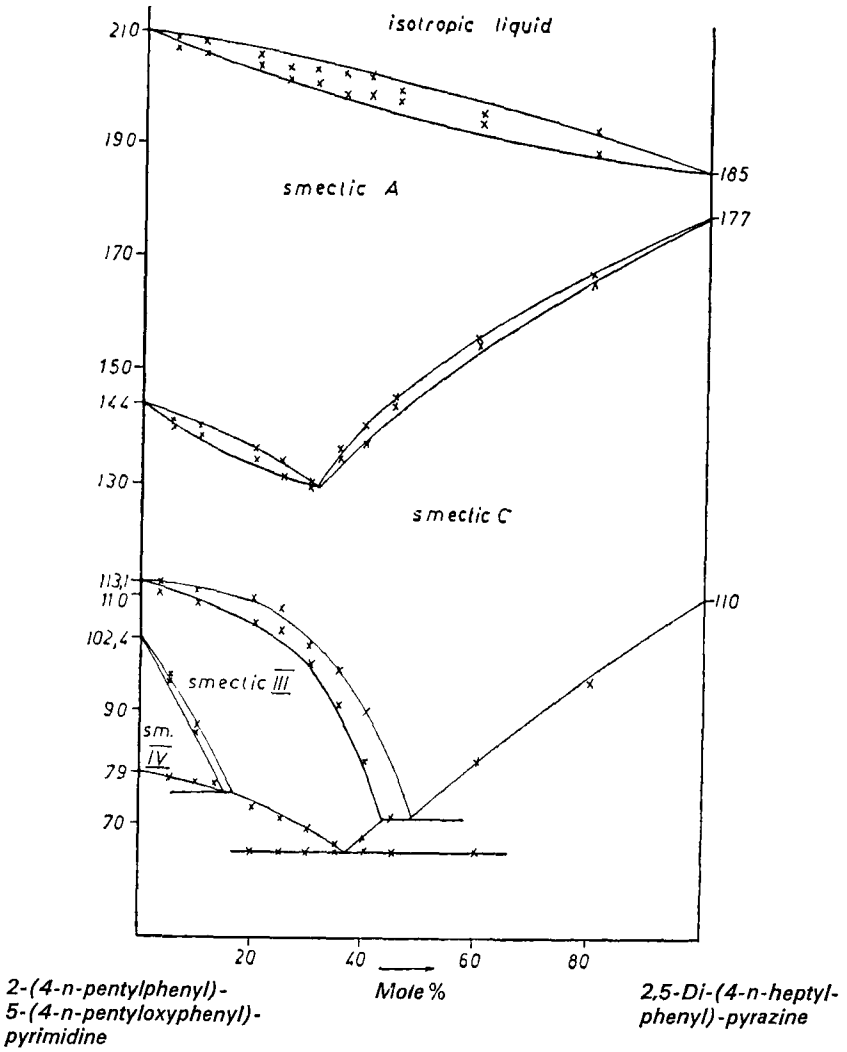


Figure 12. Diagram of state, obtained by microscopic investigation.

binary system (see Fig. 12). By means of this preliminary investigation we cannot exactly describe the structure of this modification, but the X-ray diagram points to a new group of smectic modifications marked G.

Some homologues of the investigated substance have been pre-

pared and also show polymorphism in the smectic state. Further detailed investigation of these substances is in preparation.

Acknowledgements

We are indebted to Prof. Sackmann and Prof. Schubert for helpful discussions and their interest in this work.

REFERENCES

1. Sackmann, H. and Demus, D., *Fortschr. chem. Forschg.* **12**, 349 (1969).
2. Sackmann, H. and Demus, D., *Mol. Cryst.* **2**, 81 (1966).
3. Schubert, H. and Zaschke, H., *J. prakt. Chem.* **312**, 494 (1970).
4. Schubert, H., Hacker, R. and Kindermann, K., *J. prakt. Chem.* 4, **37**, 12 (1968).
5. Weißenborn, H., *Diplomarbeit Halle*, 1967.
6. Arnold, H., *Mol. Cryst.* **2**, 43 (1966).
7. Arnold, H., Demus, D., Koch, H. J., Nelles, A. and Sackmann, H., *Z. phys. Chem.* Leipzig, **240**, 185 (1969).
8. Friedel, G., *Ann. Phys.*, **18**, 273 (1922).
9. Brown, G. H. and Shaw, W. G., *Chem. Rev.* **57**, 1049 (1957).
10. Gray, G. W., *Mol. Structure and the Properties of Liquid Crystals*, London–New York, Academic Press, 1962.
11. Chistyakov, I. G., *Liquid Crystals* (in Russian), Moscow 1966.