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

X-ray Diffraction and Polymorphism of Smectic Liquid Crystals 1. A-, B- and C-modifications

S. Diele [a], P. Brand [a] & H. Sackmann [a]
[a] Martin-Luther-Universitat, 402 Halle-Saale Sektion, Chemie, German Democratic Republic

Version of record first published: 28 Mar 2007.

To cite this article: S. Diele , P. Brand & H. Sackmann (1972): X-ray Diffraction and Polymorphism of Smectic Liquid Crystals 1. A-, B- and C-modifications, Molecular Crystals and Liquid Crystals, 16:1-2, 105-116

To link to this article: http://dx.doi.org/10.1080/15421407208083583

Molecular Crystals and Liquid Crystals. 1972. Vol. 16, pp. 105–116

Printed in Great Britain

X-ray Diffraction and Polymorphism of Smectic Liquid Crystals I. *A*-, *B*- and *C*-modifications†

S. DIELE, P. BRAND and H. SACKMANN

Martin-Luther-Universitat
402 Halle-Saale Sektion Chemie
German Democratic Republic

Received November 27, 1970; *in revised form May* 12, 1971

Abstract—X-ray diffraction patterns of 14 substances have been studied in non-oriented samples in the smectic modification s_A, s_C, and s_B. In all three modifications a sharp reflexion was found at small angles. At large angles a diffuse reflexion was found in the modifications s_A and s_C, and a sharp reflexion in the modification s_B. In all cases the calculated layer separation d is smaller than the molecular length L in the most stretched molecular structure. The X-ray patterns obtained from oriented samples of two substances are described and compared with the results obtained by other investigators. Further the results of the investigation of the equatorial intensity distribution are described.

1. Introduction

Investigations into miscibility relations between liquid crystalline modifications of several substances allow us to distinguish so far, in addition to the nematic (n) and cholesteric (ch) modifications, five types of smectic modifications, which are designated as modifications *A*, *B*, *C*, *D*, *E* (s_A through s_E).[1,2] The variants of polymorphism obtained are summarized in Table 1. In the third column the modifications are named, which originate from the isotropic phase at the clearing point with decrease of the temperature. These proceed then at temperatures T_1, T_2, T_3 to further modifications. More recently systematic caloric[3] and optical[4] investigations have been done on this subject.

X-ray studies on smectic modifications were performed by K. Herrmann[5] and recently by Chistyakov *et al.*[6] on a few substances. The newest results on this subject are reported by de Vries[7]

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

TABLE 1 System of Polymorphism

		T_1	T_2	T_3	Number of investigated cases
(a)	is n				more than 1000
	is chol.				more than 50
(b_1)	is s_A				more than 50
(b_2)	is s_C				about 30
(c_1)	is n	s_A			about 30
	is chol.	s_A			7
(c_2)	is n	s_B			2
(c_3)	is n	s_C			about 30
(d_1)	is s_A	s_B			about 20
(d_2)	is s_A	s_C			about 25
(d_3)	is s_A	s_E			4
(d_4)	is s_C	s_B			4
(d_5)	is s_D	s_C			1
(e_1)	is n	s_A	s_B		about 10
(e_2)	is n	s_A	s_C		2
(e_3)	is n	s_C	s_B		1
(e_4)	is s_A	s_C	s_B		6
(e_5)	is s_A	s_D	s_C		1
(f)	is n	s_A	s_C	s_B	4

and Levelut and Lambert.[8] The important question is whether a structural basis corresponds to the classification given. It is natural to begin with comparative studies of non-oriented samples on a large scale and then to move to a detailed investigation of oriented samples.

2. Experimental

The method of Guinier was used for the investigations on non-oriented samples. A sample-holder, which may be heated, controls the temperature to better than 0.5 °C in the temperature-range from 20 to 200 °C. The sample is melted down in a boring of an aluminum cylinder and is irradiated axially. The pictures of the oriented samples were taken by the flat-film method and a totally reflecting glass capillary was used as the collimator.[9,10] The sample was placed in a heated glass capillary tube and irradiated vertically to

the cylinder axis. The distribution of the intensity and the line profile were recorded with a goniometer.

3. Results and Possible Interpretation

3.1. Investigations of Non-oriented Samples

The substances studied are listed in Table 2. The variant of polymorphism is named in column 3 (in parenthesis the classification in Table 1). References for details, for example on transition-behaviour or transition-temperatures, are found in column 8.

The X-ray diffraction patterns of the non-oriented samples of the *A*-, *B*- and *C*-modifications show the picture described earlier[5] for single smectic modifications. Two interferences exist (apart from the reflexions of higher order), an inner ring at Bragg angles from 1–2° and an outer ring at Bragg angles from 10–11°. Other interferences are not found even with longer exposure-times. The interpretation is known in principle: Layers of molecules exist which are formed by a more or less parallel orientation of the long axes of the molecules. The outer-ring existing at wide angles corresponds with the lateral distances of the molecular axes, the ring at small angles corresponds with the layer separation.

In the *A*-modification the inner ring is sharp and the outer ring diffuse (Fig. 1). Therefore, the lateral distances of the molecules may possess a largely statistical distribution. The phases of the *C*-modifications have more or less the same X-ray pattern. Six substances (Table 2) exhibit an *A*-modification at higher temperatures in addition to the *C*-modification. In these cases a direct comparison is possible of the diffraction patterns of the two phases. The position of the inner ring does not change in transition from the *C*- into the *A*-modification. We have recorded the line profiles of the outer ring with a counter-tube goniometer. The line profiles of the outer ring are generally somewhat more diffuse and flat in the *A*-modification.

In all substances studied in the *B*-modification the inner ring as well as the outer ring is found with sharp profile as compared with the *A*- and *C*-modifications (Fig. 1).

These results substantially verify results from nine substances with smectic polymorphism as given by K. Herrmann. Accordingly

TABLE 2 Substances Investigated by X-ray Diffraction in This Report; d is the thickness of the smectic layers (calculated after Braggs Law); l is the length of the molecules obtained from Stuart–Briegleb models; $\Delta = L - d$; d_w is the intermolecular distance in the smectic layers (calculated after Bragg's Law)

No.	Substance	Polymorphism	d(Å)	L(Å)	Δ(Å)	d_w(Å)	Lit. reference
1.	*n*-amyl-4(4-*n*-octyloxybenzylideneamino)—cinnamate	s_A, s_B (d_1)	31.6	35.5	3.9	4.1	(13)
2.	*n*-amyl-4(4-*n*-nonyloxybenzylideneamino)—cinnamate	s_A, s_C, s_B (e_4)	32.9	37.0	4.1	4.2	(11)
3.	*n*-amyl-4(4-*n*-decyloxybenzylideneamino)—cinnamate	s_A, s_C, s_B (e_4)	33.2	38.5	5.3	4.1	(11)
4.	*n*-amyl-4(4-*n*-dodecyloxybenzylideneamino)—cinnamate	s_A, s_C, s_B (e_4)	36.6	41.5	4.9	4.3	(11)
5.	iso-amyl-4(4-*n*-octyloxybenzylideneamino)—cinnamate	s_A, s_C, s_B (e_4)	30.6	34.0	3.4	4.3	(11)
6.	di-*n*-hexyl-4,4′-azoxy-cinnamate	s_A, s_C (d_2)	30.5	37.5	7.2		(12)
7.	4,4′-di-*n*-undecyloxyazoxybenzene	s_C (b_2)	31.5	46.0	14.5		(12)
8.	4-*n*-hexyloxy-3-nitro-diphenyl-4′-carboxylic acid	*n*, s_A, s_C (e_2)	35.4	22.0	8.6		(2)
9.	di-allyl-4,4′-azoxy-α-methylcinnamate	s_A (b_1)	25.2	28.5	3.3		(12)
10.	ethyl-4(4-methylbenzylideneamino)—cinnamate	s_A, s_B (d_1)	20.1	22.0	1.9	4.1	(3) (12)
11.	ethyl-4(4-ethoxybenzylideneamino)—cinnamate	*n*, s_A, s_B (e_1)	21.4	24.0	2.6	4.1	(3) (12)
12.	ethyl-4(4-methoxybenzylideneamino)—cinnamate	*n*, s_A, s_B (e_1)	21.0	23.0	2.0		(3) (12)
13.	4-(4-*n*-nonyloxybenzylideneamino)—azobenzene	*n*, s_A, s_B (e_1)	29.4	31.5	2.1	4.1	(15)
14.	4,4′-di-*n*-heptyloxyazoxybenzene	*n*, s_C (c_3)					(12) (16) (17)

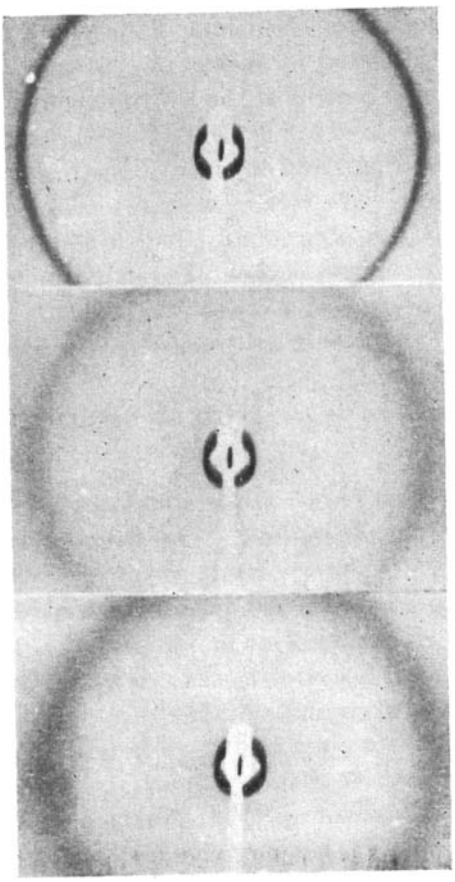

Figure 1. Diffraction patterns of modifications s_B, s_C and s_A of substance No. 4 (from top to bottom).

these modifications should be either from types s_A and s_C or types s_B. This is also the case for the substances included in our investigations of the miscibility.[11,14,15]

The transitions $s_B \rightarrow s_A$ and $s_B \rightarrow s_C$ were found to take place in an interval from 1 to 2 °C in general agreement with microscopic observations and in contradiction to the former investigations by K. Herrmann.[5]

The investigations of the three modifications s_A, s_B and s_C allow us to discern some further details. In column 4 of Table 2 the layer-separation d is written down as calculated from the inner ring

according to Bragg's Law. In column 5 the length L of the molecules is recorded, as estimated by means of " Stuart–Kalotten " in the most stretched arrangement of the hydrocarbon chains. In column 6 the difference $\Delta = L - d$ can be seen. Here the error in the measurement of the inner ring and the error in the estimate of L must be taken into account. We reckon with a total error margin of 2 Å. In all cases $d < L$ has been found. It is a notable feature that the greater ($\Delta > 3.5$ Å) differences are found only in substances with long aliphatic hydrocarbon chains on both sides of the largely inflexible middle part. In the case of substance No. 8 a formation of double molecules is assumed.

Two explanations could be offered for the difference Δ, possibly in combination:

1. The inclination of the considerably stretched molecules to the layer causes the difference Δ. In extreme cases inclinations up to 30° occur. A special arrangement of the molecules is then necessary to guarantee the optical uniaxial character found in the A- and B-modifications in numbers 1, 4, 12.
2. The difference Δ is caused by the existence of other orientations of the hydrocarbon chains, which are possible because of the partial rotation around the C—C bonds. This could explain the great differences in molecules with long hydrocarbon chains. Also, the small increase of the values in the mean lateral distances within the homologous series is thus made intelligible. For this hypothesis it is not necessary to assume an inclination of the molecular axes. Therefore, difficulties do not exist in interpretation of the double-refraction. (i.e. the explanation of the double-refraction in Tl-salts from fatty acids, in which the buckling of the hydrocarbon-chains is also used, see Ref. (21).)

For the discussion of d-values of the substances recorded in Table 2 it is not important in which modification the inner ring is measured. The dependence on the temperature of the inner ring is very small. To what extent this could be detected, is shown in Tables 3 and 4 (these tables can serve as an example for all investigations).

In column 7, d_w is given as calculated from the wide sharp ring of the B-modification using Bragg's Law. Within the homologous

TABLE 3 Position of Inner and Outer Diffraction Ring for Substance No. 4 as a Function of the Temperature (ϑ: Bragg angle)

No.	T(°C)	Type	Inner ring ϑ°	Inner ring d(Å)	Outer ring ϑ°	Outer ring d(Å)
1	77	*B*	1.18	37.4	10.4	4.3
2	84	*B*	1.18	37.4	10.4	4.3
3	89.2	*B*	1.19	37.1	10.3	4.3
4	93	*B*	1.20	36.8	10.3	4.3
5	96	*C*	1.23	36.0		
7	107.2	*A*	1.21	36.5		
8	113	*A*	1.21	36.5		

TABLE 4 Position of Inner and Outer Diffraction Ring for Substance No. 11 as a Function of the Temperature (ϑ: Bragg angle)

No.	T(°C)	Type	Inner ring ϑ°	Inner ring d(Å)	Outer ring ϑ°	Outer ring d(Å)
1	79.5	*B*	2.04	21.6	10.9	4.1
2	84	*B*	2.05	21.5	10.9	4.1
3	90	*B*	2.05	21.5	10.9	4.1
4	99	*B*	2.05	21.5	10.9	4.1
5	114	*B*	2.05	21.5	10.9	4.1
7	115	*B*	2.06	21.4	10.7	4.1
8	115	*B*	2.05	21.5	10.7	4.1
9	116.8	*A*	2.06	21.4		
10	124	*A*	2.07	21.3		
11	131.5	*A*	2.07	21.3		
12	139.5	*A*	2.07	21.3		
13	137.5	*A*	2.04	21.6		
15	147	*A*	2.08	21.2		

series (substances No. 1 to 4, Table 2) a small increase (apart from No. 3) in the lateral distances of the molecules calculated from the wide sharp ring of the B-modification is observed with increasing chain length.

3.2. Investigations on Oriented Samples

Samples of substance No. 5 (Table 2) were oriented in a magnetic field. This substance exhibits all 3 modifications in the sequence s_A, s_C, s_B with decreasing temperature. Oriented samples in the various smectic modifications can be obtained by cooling of the sample, in the magnetic field, from the isotropic phase to the desired temperature. Also, oriented samples of the C- and A-modification with the same X-ray patterns are obtained, if the oriented sample of the B-modification was heated outside the magnetic field.

In Fig. 2 the X-ray pattern of the three modifications are shown. The outer ring is crescent shaped. The broadening takes place at the transition from the B into the C- and A-modifications analogous to the transition in non-oriented samples. The inner ring degenerates to a reflexion lying on the meridian of the pattern (also seen in the second and third order).

The reflexions are more spot-like in the B-modification and become crescent shaped in transition to C- and A-modifications. From this an alignment of the layers is derived vertically to the cylindrical axis of the sample. The rigid alignment of the layer in the B-modifications is progressively removed in the C- and A-modifications. The position of the inner reflexion vertical to the position of the outer reflexion is an expression of the fact that the molecules stand vertical to the layer in the C- and A-modification.

A similar pattern was recorded first in the C-modification of substance No. 14, Table 2 (Fig. 3). The lunar interference maxima of the inner reflexion and of the outer lie again on the meridian or on the equator of the pattern. The repetition of the experiment with samples of smaller diameters (0.9 mm instead of 1.5 mm) yielded the X-ray pattern in Fig. 4. The inner ring is weak. On it two doublet-like interference spots are positioned on the equator line. Several maxima on the outer interference are visible on the original film. The connecting line between the strongest maxima forms an angle of about 45° with the equator.

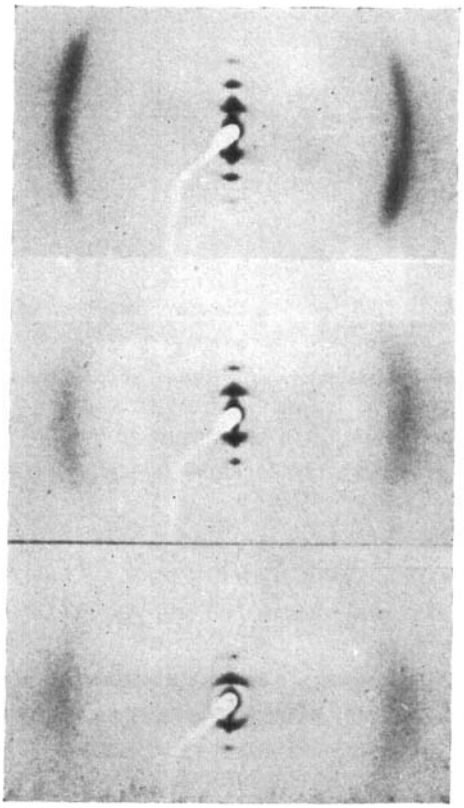

Figure 2. Diffraction patterns of oriented samples of substance No. 5; the modifications s_B, s_C and s_A (from top to bottom).

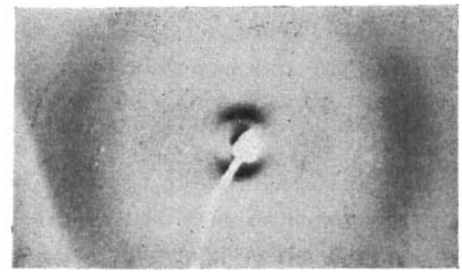

Figure 3. Diffraction patterns of substance No. 14; the modification s_C.

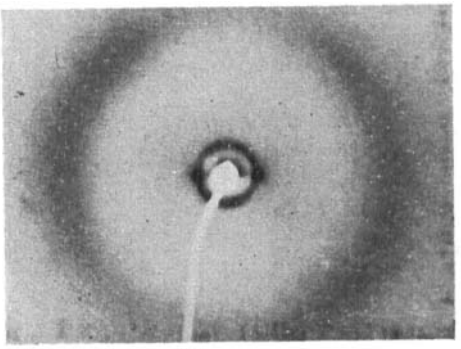

Figure 4. Diffraction patterns of substance No. 14; the modification s_C.

The latter seems to confirm the result given by de Vries[16] in a schematic diagram of the interferences of the same substance in the *C*-modification.

On the other hand Chistyakov and Chaikowsky[17] found a degeneration of the inner ring to four spots. Thus at present three types of X-ray diagrams of oriented samples of the same substance in the *C*-modification exist.

It therefore seems advisable not to discuss further the respective structure suggestions[16,17] but to attempt to make accurate analysis of the influence of the experimental conditions.

3.3. Investigation of the Distribution of Equatorial Intensity

The calculation of cylindrical distribution functions of the distribution of equatorial intensity of oriented samples offers the possibility of obtaining information on the lateral arrangement of the molecular axes.

This method was used with success by Falgueirettes[18] and Delord[19] for the nematic phase and by Chistyakov and his collaborators[17] for the nematic and smectic phases.

It is possible to go two ways[20] which lead basically to the same results:

1. By normalization of the irradiated intensity on one atom you may calculate the distribution of the atoms projected on an area arranged vertical to the molecular axes.
2. By normalization of the irradiated intensity on one molecule you may calculate the distribution of the molecular axes in the layer.

In starting our investigations we have used the first procedure. The specimens had the form of a flat sheet and were oriented as described in Section b. The correction for absorption was negligible. The diffracted intensity was recorded by a goniometer using a proportional counter. The experimental set-up permits recording of the intensity up to a Bragg angle of 30°. The cylindrical distribution functions were calculated in the way described in reference 20.

The distribution functions calculated for substance No. 4, Table 2, in the modifications s_A, s_C and s_B are plotted in Fig. 5. The functions exhibit two maxima ($r_1 = 4.6$ Å; $r_2 = 9.0$ Å), the positions of which scarcely change in transition to another modification.

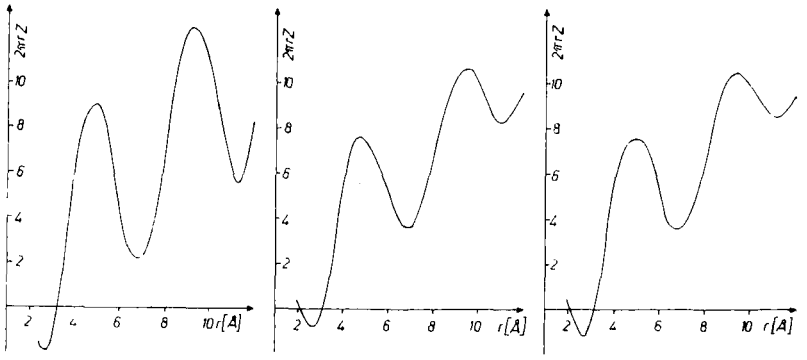

Figure 5. The atomic cylindrical distribution function for s_B, s_C and s_A (from left to right) of substance No. 4.

First, it should be noted that the remarkable difference in the intensity distributions in the distribution functions of the modification s_B on the one hand and on the other, the modifications s_C and s_A are very much reduced. Thus, it seems that only a drop in the statistical fluctuation-width of the lateral molecular distances is connected with the transition from s_A into s_C and s_B. The absence of the other maxima in the distribution function shows that no defined relations of the neighboring molecules exist in the modification s_B. Other statements are made by Levelut and Lambert.[8] They point out the existence of a hexagonal layer lattice in the *B*-modification of two substances which they studied.

The cause for the small number of the maxima in the distribution function by comparison with the calculations of other authors[20]

can be seen in the symmetrical structure of the molecule and in the practical circular cross-section of the substance studied.

REFERENCES

1. Sackmann, H. and Demus, D., *Fortschritte d. chem. Forsch. Berlin*, Heidelberg, New York, **12**, 349 (1969).
2. Demus, D., Kunicke, G., Neelsen, J. and Sackmann, H., *Z. Naturforsch.* **23a**, 84 (1968).
3. Arnold, H., Demus, D., Koch, O., Nelles, A. and Sackmann, H., *Z. Phys. Chem.* **185**, 240 (1969).
4a. Pelzl, G., Dissertation Halle(S) 1969.
4b. Pelzl, G. and Sackmann, H., *Trans. Faraday Soc.*, in preparation.
5. Herrmann, K., *Z. Kristallogr.* **92**, 49 (1935).
6. Chistyakov, I. B., Schabischev, L. S., Jarenov, R. J. and Gusakova, L. A., *Mol. Cryst. and Liq. Cryst.* **7**, 279 (1969).
7. de Vries, A., *Mol. Cryst. and Liq. Cryst.* **11**, 361 (1970).
8. Levelut, A. and Lambert, M., *C.R. Acad. Sci. Paris*, in print (preprint obtained from the authors).
9. Unangst, D. and Zimmermann, B., *Z. Experim. Tech. Phys.* **12**, 320 (1964).
10. Damaschun, G. and Weh, C., *Feingeratemeßtechnik* **17**, 274 (1968).
11. Demus, D., Sackmann, H., Kunicke, G., Pelzl, G. and Salffner, R., *Z. Naturforsch* **23a**, 76 (1968).
12. Arnold, H., Demus, D. and Sackmann, H., *Z. Phys. Chem.* **222**, 15 (1963).
13. Salffner, R., Diplomarbeit Halle, 1967.
14. Arnold, H. and Sackmann, H., *Z. Elektrochem.* **63**, 1171 (1959).
15. Demus, D. and Sackmann, H., *Z. Phys. Chem.* **238**, 215 (1968).
16. de Vries, A., *Acta Crystallogr.* **A25**, S135 (1969).
17. Chistyakov, I. G. and Chaikowsky, W. M., *Mol. Cryst. and Liq. Cryst.* **7**, 269 (1969).
18. Falgueirettes, J., *Bull. Soc. Fr. Mineral Crystallogr.* **82**, 171 (1959).
19. Delord, P., *J. Phys.* (*Paris*) **30**, C 4–14 (1969).
20. Wainstein, B. K. and Chistyakov, I. G., *Dokl. Akad. Nauk SSSR* **153**, 327 (1963).
21. Pelzl, G. and Sackmann, H., *Mol. Cryst. and Liq. Cryst.*, in print.