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X-Ray diffraction study of the smectic I, F, J and G phases of (+)-(4-(2′-methylbutyl)phenyl 4′-*n*-octybiphenyl-4-carboxylate)

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The smectic I, F, J and G phases of the chiral ferroelectric compound (+)-(4-(2′-methylbutyl)phenyl 4′-*n*-octylbiphenyl-4-carboxylate) (+2M4P8BC) were studied by means of optical microscopy and X-ray diffraction. The free-standing film method was used. The films were additionally ordered with a d.c. electric field and true monodomain samples were prepared and examined.

1. Introduction

Smectic phases exhibiting long-range in-plane order have been a subject of increasing interest in recent years. The free-standing film technique which provides samples with perfectly stacked smectic layers seems to be the most suitable for studying these phases. Films as thin as only several (down to two) smectic layers may be prepared and in such films the structure of an individual layer as well as the interlayer correlations are very well pronounced. A number of papers have appeared in which the structures as well as the physical properties of various smectic phases examined with the use of this technique were reported [2–15]. The films are usually reported to be mosaic, i.e. they contain a number of grains disordered about the axis perpendicular to the film. For certain studies such samples are good enough but for others it is essential to prepair mono-domain film. This may be achieved by the application of an external ordering field; either magnetic or electric. Films ordered by a magnetic field were studied by Brock *et al.* [12] as well as Dierker and Pindak [15]. For ferroelectric liquid crystals the use of a d.c. electric field seems to be more appropriate. Electric field ordered bulk samples of the ferroelectric compounds HOBACPC ((R^-)-chloro-2-propyl-*p*-hexyloxybenzylidene-*p*′-aminocinnamate) and +2M4P8BC have already been studied [1, 16]. The free-standing film study of the latter compound was performed by Budai *et al.* [8], but only mosaic films were used. In our recent paper [17] the preparation of perfect single-domain samples of +2M4P8BC by the application of a d.c. electric field to the free-standing film was briefly reported. Here we report a systematic X-ray study of the monodomain samples of the hexatic and the crystalline smectic phases of (+)-(4-(2′-methylbutyl)phenyl 4′-*n*-octylbiphenyl-4-carboxylate) (+2M4P8BC).

2. Experimental

The samples were fixed in a 0·7 mm circular hole made in a 50 μm thick insulating plate. The sample container was placed between electrodes in an oven mounted on a goniometer head. The temperature was controlled to within 0·05°C. In order to obtain a free standing film the sample was heated in to the cholesteric phase (about 137°C) and after cooling the film formed spontaneously. The films used in our study were much thicker than those investigated by other groups [2–15]. Diffraction patterns of good quality were obtained from samples as thick as 10 μm or more, which corresponds to several thousand smectic layers.

When observed between crossed polarizers the films of the I and F phases exhibited a uniform, unaxial structure with the optical axis perpendicular to the film. In the presence of a d.c. electric field the optical axis was tilted with respect to the film normal in the direction perpendicular to the field. After switching the field off the sample relaxed in a few seconds. In a field stronger than about 5 kV/cm the sample started to move and so such fields were not used to align samples for X-ray experiments.

The samples of the J and G phases exhibited a mosaic structure with strong interference colours. We have not noticed any effect of a weak electric field on these phases. When the field was as strong as about 10 kV/cm some grains, presumably those suitable oriented with respect to the field grew in size but the sample remained multidomain. Mono-domain samples could be obtained by cooling the sample slowly starting from the smectic F phase at a rate of 0·25 °C/h. Excellent results were obtained with a small temperature gradient introduced in the oven and with the sample initially ordered with a field of 3 kV/cm. The samples, obtained in this way, could be maintained with the ordering field turned off for more than a week.

A standard X-ray source operating at 34 kV and 30 mA was used for the X-ray experiments. The patterns were recorded on a flat film with copper filtered radiation and a 0·3 mm collimator. A polarizing microscope was fitted to the X-ray camera and the samples were checked for optical perfection before exposure.

3. Results and discussion

The following phase sequence was determined for +2M4P8BC:

$$\mathrm{C} \underset{42^{\circ}\mathrm{C}}{\overset{48^{\circ}\mathrm{C}}{\rightleftarrows}} \mathrm{S_G} \xleftrightarrow{63^{\circ}\mathrm{C}} \mathrm{S_J} \xleftrightarrow{65^{\circ}\mathrm{C}} \mathrm{S_F} \xleftrightarrow{67^{\circ}\mathrm{C}} \mathrm{S_I} \xleftrightarrow{71^{\circ}\mathrm{C}} \mathrm{S_C}$$

$$\xleftrightarrow{81^{\circ}\mathrm{C}} \mathrm{S_A} \xleftrightarrow{136^{\circ}\mathrm{C}} \mathrm{Ch} \xleftrightarrow{139^{\circ}\mathrm{C}} BP \xleftrightarrow{140^{\circ}\mathrm{C}} \mathrm{I}$$

The transition temperatures were determined from the optical study. They were found to decrease slightly during the first few days after preparing the sample. This effect was stronger when the sample was kept in an electric field. The temperatures quoted were measured for a fresh sample.

The X-ray patterns taken from unaligned samples exhibited a sharp continuous outer ring for the smectic I and F phases and spotted ring for the smectic J and G phases. When an electric field was applied to the smectic I or F phase six diffuse maxima appeared, as shown in figures 1 (*a*) and 1 (*b*). The pattern taken from the single-domain samples of the J and G phases consisted of six sharp spots. The pattern presented in figure 1 (*c*) corresponds to the G phase.

The patterns presented in figure 1 clearly display the quasi-hexagonal in-plane arrangement of molecules for all the phases under study. The difference between the hexatic and the crystalline phases can easily be noticed. The existence of two different hexatic phases cannot be questioned. One of these phases, namely the smectic I phase, was studied in details by Budai *et al.* [8]. The occurrence of the second hexatic phase in +2M4P8BC was suggested by Dierker and Pindak [15], but the phase was not characterized. As we shall describe we have determined the direction of the molecular tilt and identified this phase as a smectic I phase.

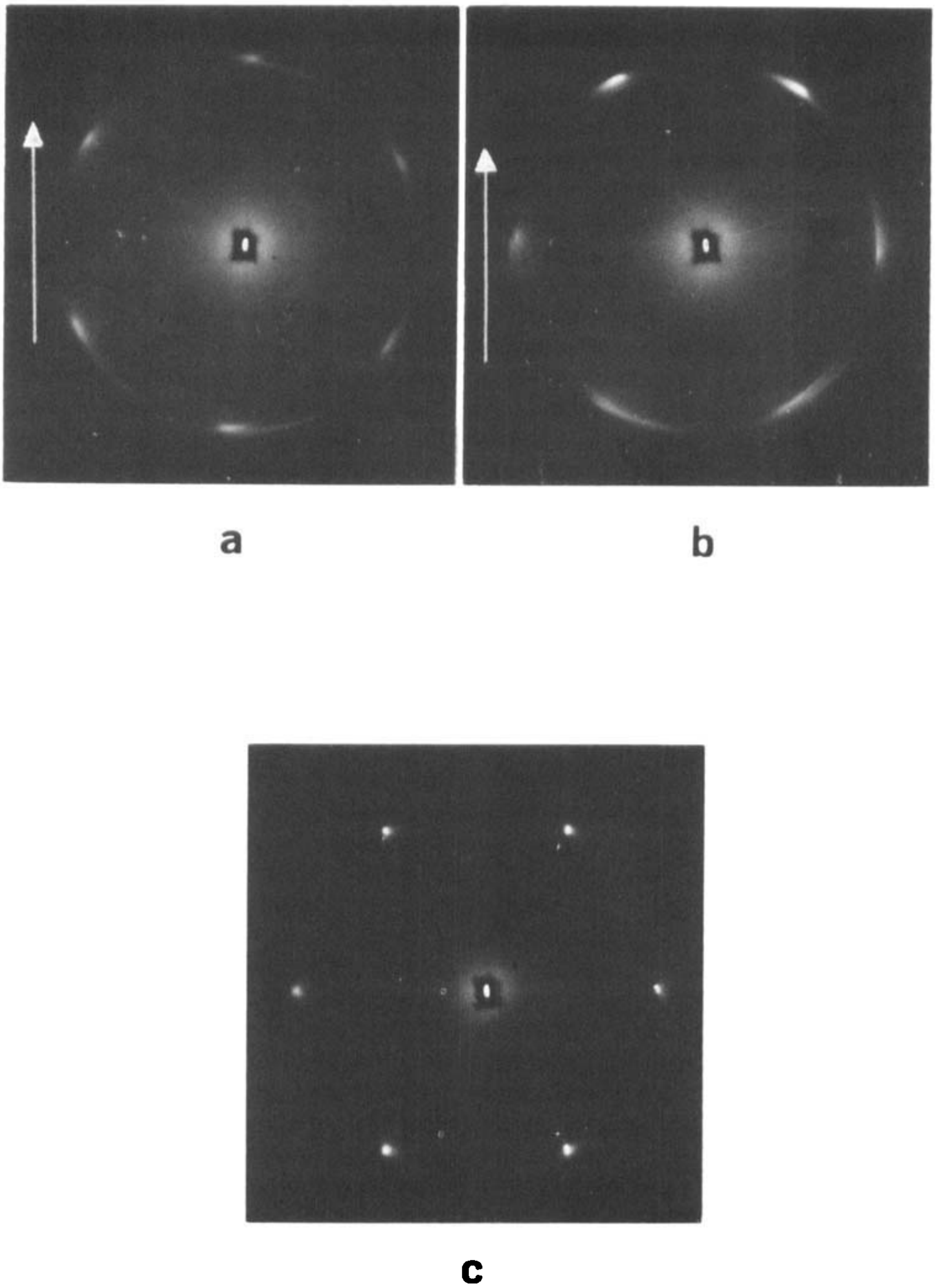

Figure 1. X-ray patterns obtained from the mono-domain samples of $+2M4P8BC$: (*a*) smectic I phase, (*b*) smectic F phase and (*c*) smectic G phase. The diffraction patterns of the smectic I and F phases were obtained with an electric field applied to the sample and the direction of the field is marked with the arrows.

For an arbitrary choice of sample setting some of the six diffraction maxima were weaker than the others or even missing. By adjusting the sample using the goniometer head the respective reflection intensities could be changed and for one well defined setting the pattern had a perfect six-fold symmetry, like that shown in figure 1 (*a*). This effect can be explained in terms of the reciprocal space as follows. The reciprocal lattice of any of the smectic phases under consideration contains six diffuse rods arranged in a hexagon. The intensity has a maximum at the centre of each rod and decreases towards the two ends of the rod. The relative setting of the reciprocal and the real lattice of the smectic F phase viewed along the b^* axis of reciprocal space is shown in figure 2. The reflection sphere is drawn to scale for CuKα radiation. As we can see from figure 2 the reflection sphere intersects the two opposite diffuse rods in points of similar intensities only when the direction of the molecular long axes is precisely parallel to the incident X-ray beam. In consequence we have a method of determining the direction of the molecular long axes in the sample. The method was found to be quite precise. To illustrate this we show in figure 1 (*b*) the diffraction pattern taken with the sample rotated about the horizontal axis by just 1°; as we can see the two upper reflections are significantly stronger.

For the four smectic phases studied the molecules were found to be tilted with respect to the direction normal to the sample surface. For the smectic I and F phases the tilt direction was perpendicular to the electric field. The tilt angle was approximately 18° for both phses which agrees with the value measured for the smectic I phase by Budai *et al.* [8].

A comparison of the determined direction of the long axes with the position of the diffraction spots on the patterns enabled a determination of the direction of the molecular tilt. For the smectic I phase (see figure 1 (*a*)) the molecules are tilted towards the edge of the hexagon in reciprocal space and so the tilt in real space points towards the apex. For the second hexatic phase (see figure 1 (*b*)) the tilt in real space points towards the edge of the hexagon and so this phase is the smectic F phase.

Although the two crystalline phases, smectic J and G, differed in the tilt direction, the pattern did not rotate upon the transition from the smectic J to G as it did at the smectic F to I transition. However, the respective intensities of the reflections did undergo a change; this can be explained as follows. The hexagonal array of the molecular centres does not rotate in space at the transition from smectic J to G. It is the direction of the molecular tilt which undergoes a change; the molecules then precess by an angle of 30° about the layer normal. The reciprocal lattice precesses simultaneously and the reflection intensities change. By adjusting the sample the perfect hexagonal patterns like that shown in figure 1 (*c*) were obtained for both smectic J and G phases and in this way the directions of the molecular long axes were determined. These were compared with the positions of the reflections on the patterns and the molecular tilt in real space was found to be towards the edge of the hexagon for the smectic J phase and towards the apex for the smectic G phase. The tilt angle was equal to approximately 19° for both phases. This agrees with the value given by Budai *et al.* [8].

The effect of the sign of the field on the molecular orientation was studied in the smectic I and F phases. It was found that the direction of the molecular long axes is uniquely determined by the polarity of the field. The molecules are always tilted according to the right-hand screw rule, as shown in figure 2 and they never adopt the opposite position indicated in figure 2 by the dashed line. On changing the sign of the field the molecules do not rotate about their long axes but precess about the layer

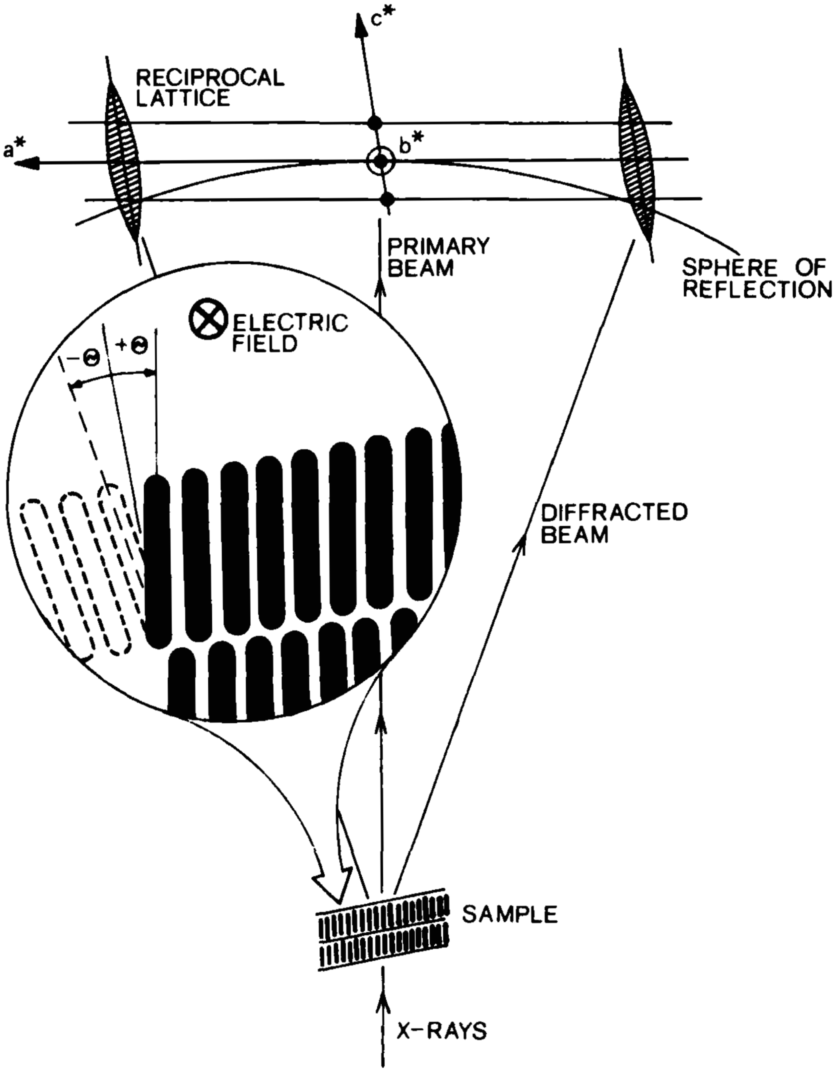

Figure 2. Ewald's construction for a monodomain sample of the smectic F phase. Molecules are marked with black bars. Two of the six diffuse bars in reciprocal space are shaded. The other four bars lying above and below the plane of the paper are not shown. The alternating width of the bars shows the intensity distribution along the direction parallel to the c^*-axis. The electric field is perpendicular to the plane of the paper. The positions of molecules marked with dashed lines are adopted upon changing the sign of the field.

normal by 180°, so that the tilt changes from $+\Theta$ to $-\Theta$. This shows that for both phases the dipole moments of the molecules are strongly coupled and that the molecules cannot rotate either individually or in a collective manner.

4. Conclusions

The structures of the smectic phases of + 2M4P8BC were almost satisfactorily understood before the present work and we have tried to resolve some remaining doubts. Budai *et al.* [8] suggested that two structurally different smectic phases exist.

One of the arguments was that the smectic phases of +2M4P8BC and TBNA (terephthalylidene-bis-4-*n*-nonylaniline) were not continuously miscible. Now it is clear that the smectic F phase was omitted from the phase diagram of +2M4P8BC and so there is only X-ray evidence for the existence of these two smectic I phases. Budai *et al.* [8] also reported the differences in the transition temperatures determined from optical and X-ray measurements. An explanation was given in terms of the slow kinetics associated with the transitions and the high temperature scan rate used in the optical study. We noticed that the transition temperatures undergo a continous decrease in time. This effect is well known for liquid crystals and is due to some chemical processes like decomposition or oxidation of the sample material.

The main aim of the present work was to describe some new possibilities of the free-standing film method. Until now rather thin and still mosaic films were studied. We succeeded in preparing thick and mono-domain films. This enabled photographic recording of the patterns and the use of standard X-ray equipment. So far the structures of the smectic phases were deduced from optical textures or from powder diffraction data (see e.g. [1, 8, 16]). In the present study the molecular tilt for four smectic phases was determined straightforwardly from the single-crystal X-ray diffraction patterns. The way of preparing single crystal samples of the crystalline smectic phases seems to be the most important and promising result reported in this work. Such samples may be studied by means of standard single-crystal X-ray methods which provide much more information than texture or powder methods. An experiment in which the Weissenberg goniometer is utilized is now underway.

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References

[1] Doucet, J., Keller, P., Levelut, A. M., and Porquet, P. 1978, *J. Phys., Paris*, **39**, 548.

[2] Moncton, D. E., and Pindak, R., 1979, *Phys. Rev. Lett.*, **43**, 701.

[3] Pindak, R., Moncton, D. E., Davey, S. C., and Goodby, J. W., 1981, *Phys. Rev. Lett.*, **46**, 1135.

[4] Collett, J., Sorensen, L. B., Pershan, P. S., Litster, J. D., Birgenau, R. J., and Als-Nielsen, J. 1982, *Phys. Rev. Lett.*, **49**, 553.

[5] Pindak, R., Sprenger, W. O., Bishop, D. J., Osheroff, D. D., and Goodby, J. W., 1982, *Phys. Rev. Lett.*, **48**, 173.

[6] Moncton, D. E., Pindak, R., Davey, S. C., and Brown, G. S., 1982, *Phys. Rev. Lett.*, **49**, 1865.

[7] Colett, J., Pershan, P. S., Sirota, E. B., and Sorensen, L. B., 1984, *Phys. Rev. Lett.*, **52**, 356.

[8] Budai, J., Pindak, R., Davey, S. C., and Goodby, J. W., 1984, *J. Phys. Lett., Paris*, **45**, L-1053.

[9] Davey, S. C., Budai, J., Goodby, J. W., Pindak, R., and Moncton, D. E., 1984, *Phys. Rev. Lett.*, **53**, 2039.

[10] Sirota, E. B., Pershan, P. S., Sorensen, L. B., and Collett, J., 1985, *Phys. Rev. Lett.*, **53**, 2039.

[11] Dierker, S. B., Pindak, R., and Meyer, R. B., 1986, *Phys. Rev. Lett.*, **56**, 1819.

[12] Brock, J. D., Aharony, A., Birgenau, R. J., Evans-Lutterodt, K. W., Litster, J. D., Horn, P. M., Stephenson, G. B., and Tajbakhsh, A. R., 1986, *Phys. Rev. Lett.*, **57**, 98.

[13] Smith, G. S., Safinya, C. R., Roux, D., and Clark, N. A., 1987, *Molec. Crystals liq. Crystals*, **144**, 235.

[14] Sirota, E. B., Pershan, P. S., and Amador, S., 1987, *Phys. Rev.*, **A35**, 2283.

[15] Dierker, S. B., and Pindak, R., 1987, *Phys. Rev. Lett.*, **59**, 1002.

[16] Przedmojski, J., Dąbrowski, R., Pura, B., Zickert, K., and Gierlotka, S., 1987, *Molec. Crystals liq. Crystals*, **151**, 171.

[17] Przedmojski, J., and Gierlotka, S., 1988, *Liq. Crystals*, **3**, 409.