X-ray Studies on Layer Stacking and Ordering in a Liquid Crystalline Disubstituted Biphenylcyclohexane

W. Klämke and W. Haase
Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Darmstadt, FRG

Z. Naturforsch. **43a,** 885–888 (1988); received July 27, 1988

X-ray measurements on disubstituted biphenylcyclohexane BCH 52 show a crystalline smectic B phase with an ABCA layer stacking in bulk samples when cooled from the nematic to the smectic phase. No temperature dependence of this stacking can be seen. When cooling freely suspended thin films (below 20 μm) from the nematic to the smectic B phase, the obtained X-ray reflexes indicate an arrangement of the molecules in an orthorhombic F like stacking.

Introduction

Recent studies on thin samples of liquid crystals with crystalline smectic B phase have shown a temperature and thickness dependence of the layer stacking [1, 2]. Especially in thin free standing films of some liquid crystals having a crystalline smectic B phase a rich structural behaviour and also a possible change from crystalline B to hexatic B phase were observed [1–4].

X-ray measurements using conventional flat film techniques on aligned bulk samples of disubstituted biphenylcyclohexanes showed the existence of different (crystalline) smectic B phases with ABCA stacking of the layers [5]. Layer stacking transitions for a certain compound were not observed. So the interest in investigating thin free standing films of this type of compounds was stimulated.

Experimental

The investigated samples were disubstituted biphenylcyclohexane with the general formula

$$C_5H_{11}-C_6H_{10}-C_6H_4-C_6H_4-C_2H_5 .$$

The phases and transition temperatures are [6]:

$$\text{Crystalline} \quad 35\,^{\circ}\text{C} \quad S_B \quad 143\,^{\circ}\text{C} \quad \text{N} \quad 158\,^{\circ}\text{C} \quad \text{I}.$$

The samples were used as obtained from E. Merck Company, Darmstadt.

For the X-ray investigations we used a focussing STOE horizontal 2-circle diffractometer with longer focal length (440 mm) and a curved Ge (111) monochromator giving in conjunction with a long fine focus X-ray source SIEMENS FK 60-04-12 ($\text{Cu}_{K\alpha 1}$ radiation, wavelength: 1.54056 Å) a best resolution in 2 theta of $q = 2.8 * 10^{-3}\,\text{Å}^{-1}$ ($q = 2\pi/d$). The longitudinal resolution is determined by the slits and therefore only $q = 8 * 10^{-3}\,\text{Å}^{-1}$.

In order to get the desired Bragg vector for different angles chi, the sample holder was mounted on a special rotating stage inside the oven with the rotational axis perpendicular to the 2-theta circle, providing the possibility to scan along q_{xy} and q_z (Figure 1). The oven, containing the samples, provides a temperature stability in the investigated temperature range (23 °C to 190 °C) better than 0.01 K.

In order to get well aligned samples, the samples were positioned between the pole caps of two permanent magnets (CoSm_5) inside the oven, giving a field of about 0.8 Tesla.

For a detailed description of our experimental setup cf. [7].

The samples have been aligned homogeneously, that means the smectic layer normal is perpendicular to the normal of the free surface, respectively of the sandwiching foil surface, with help of the two permanent magnets. Without having a magnetic field for alignment, a free standing film would align homeotropically due to the surface tension. If the critical surface tension of the liquid crystal, τ_L, is higher than the critical surface tension of the wall (or solid surface), τ_S, a homeotropic alignment will be obtained [8, 9]. If $\tau_L < \tau_S$, than a homogeneous alignment of the molecules (parallel to the surface, resp. the wall) should happen.

Reprint requests to Prof. Dr. W. Haase, Institut für Physikalische Chemie, Technische Hochschule Darmstadt, Petersenstraße 20, D-6100 Darmstadt.

0932-0784 / 88 / 1000-0885 $ 01.30/0. – Please order a reprint rather than making your own copy.

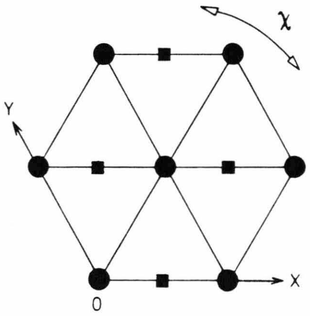

Fig. 1. View of the *xy*-plane with the basic hexagonal arrangement of the molecules in the smectic B phase. The position of the molecules in the adjacent layers for the orthorhombic F like structure is represented by squares.

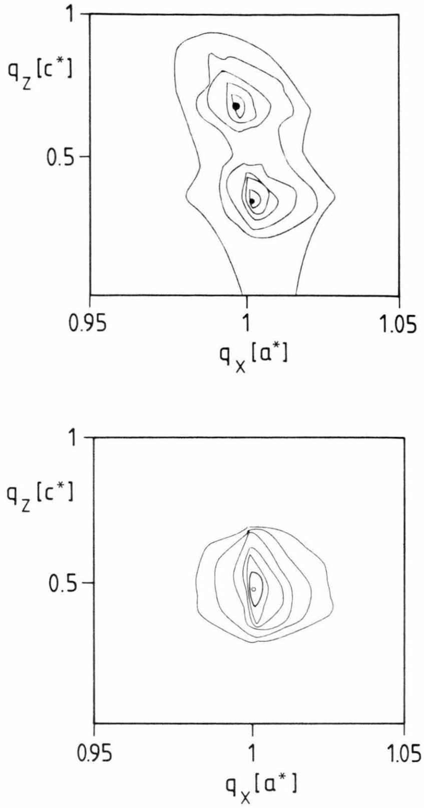

Fig. 2. q_{xz}-plots; (top) sandwiched sample of BCH 52 at 57.6 °C, thickness 25 μm, showing Bragg reflexes refering to an ABC stacking. The Bragg spots are accompanied by an additional diffuse scattering. (bottom) Free standing film of BCH 52 at 58.2 °C, thickness 4 μm, showing one Bragg spot, for an arrangement in an orthorhombic F like stacking.

We used two different ways for preparing the samples:

i) we sandwiched the substance between two foils (Aluminium or Mylar) and managed the thickness by using spacer foils of 1 mm, 50 μm, 25 μm, 7.5 μm and 2.5 μm; and

ii) we tried to get free standing films of liquid crystals by melting a small amount of the liquid crystal material into the isotropic phase and drawing the molten substance with a wiper across a hole of 2 mm diameter in a metal foil (brass, aluminium or copper) with variable foil thickness between 2.5 μm and 50 μm. If a free standing film was established, we cooled the film, like the sandwiched samples before, slowly to the smectic B phase with a cooling rate of 10 K per hour, in the range of 2 K above to 3 K below the transition temperatures T_{ns} (n: nematic, s: smectic) with a rate of 5 K per hour. The film thickness itself was determined by comparing the X-ray intensity absorption I to I_0, according to equation $I = I_0 * \exp.(-\mu x)$ with the absorption coefficient μ and the film thickness x and, additionally, by using a tilting compensator with a Leitz Orthoplan Polarizing Microscope. The error between both methods was up to 10%, so that we could assume to have an error in thickness determination of the same order.

Results

In the way described above, we studied homogeneously aligned sandwiched samples of 1 mm to 2.5 μm thickness and freely suspended films of 1 mm to 0.5 μm thickness. Scanning along q_{xy} and q_z, aligned sandwiched samples of BCH 52, having been cooled from the nematic to the smectic B phase, showed over the whole smectic B temperature range Bragg spots at $(1\ 0 \pm 1/3)$ and $(1\ 0 \pm 2/3)$. According to other authors [1–3], these Bragg spots (Fig. 2a) are typical for ABCA stacking of the layers*.

The linewidth of $q = 1.28 * 10^{-2}$ Å^{-1}, full width of half maximum (FWHM), in q_z-scan of these reflexes leads according to $1/q = \sigma$ to an interlayer correlation length σ of 490 Å. This means that there is a quasi long-range positional order over about 20 smectic layers. (For comparison; a smectic A or C phase has a correlation length of only 60 Å or less.)

X-ray scans on (with help of the magnetic field) homogeneously aligned freely suspended films of

---

* In [5], instead of AB it should read ABC stacking.

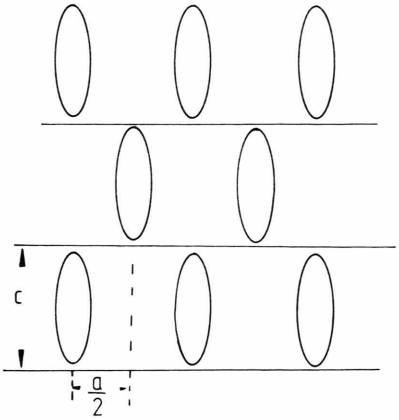

Fig. 3. Projection of the xz-plane of the molecules in the orthorhombic F stacking.

BCH 52, having been also cooled from the nematic to the smectic phase and with less than 20 μm thickness, result in Bragg spots at (1 0 ±1/2) (Figure 2b). According to [1–3], this is assumed to indicate that the molecules have reached an orthorhombic F like stacking (Figure 3).

The linewidth of $q_z = 1.28 * 10^{-2}$ Å^{-1} and the correlation length $\sigma = 490$ Å is in agreement with the value of the ABC stacking. This shows that a quasi long range positional order, the crystallinity of the smectic B phase, is retained.

At small angles in 2-theta, aligned samples of BCH 52 showed also second order reflexes (0 0 2), the intensity of these being 1% of the intensity of the (0 0 1) reflex.

From the small angle reflexes we calculated the layer spacing to be 22.75 Å, and from the large angle reflexes we calculated the intermolecular parameter d to be 5.4 Å.

The in-plane Bragg peaks of sandwiched samples and also free standing films were accompanied by a diffuse scattering; the intensity of this scattering was about 1% to 5% of the maximum of the Bragg peak, but on X-ray photograms with relatively long exposure times this diffuse scattering seemed to be stronger.

Discussion

The in-plane Bragg peaks were accompanied by a (diffuse) scattering, looking like the scattering of a 2-dimensional powder sample. Such scatterings have been found and reported by other authors [2, 11–14] investigating smectic B phases. According to Pershan et al. [14] we conclude this scattering to be originated by acoustic phonons. A possible second origin for the additional diffuse scattering could be nearly 2-dimensional fluctuations, including static or dynamic correlations of parts of the molecules. Normally, the diffuse scattering by phonons would be rather small and would have large linewidths. The shape of the diffuse scattering, being similar to other smectic phases consisting of 2D hexatic layers, lets us suppose that we possibly have 2-dimensional long-range fluctuations, although the intensity of the diffuse scattering is small compared to the Bragg reflexes. (An extended discussion of this diffuse scattering and the 2-dimensional fluctuations will be the subject of a further publication.)

The sharp reflexes of BCH 52 and their position, on the other hand, show undoubtedly the existence of a crystalline smectic B phase with a certain layer stacking.

Concerning the interlayer correlation lengths, it has to be discussed that there is an incompleteness in determining the fully extended correlations, because of the different resolutions in horizontal and vertical scanning direction. The vertical resolution is determined by slits and therefore amounts to only about one third of the horizontal resolution. This means that the shape of the incident beam is not pointlike but more barlike, and therefore the linewidths in q_z are broadened. If we take into account the relation of the horizontal to the vertical resolution, we have to conclude that the real interlayer correlation length is about 30% longer than the resulting length from the uncorrected linewidth. This means that the correlation length σ is ≥ 650 Å and the quasi long range positional order is extended over more than 30 layers.

As it was mentioned, the alignment of liquid crystals by surface effects depends on the critical surface tensions of the liquid crystal and of the wall. Cooling bulk samples of BCH 52, which have been aligned by a magnetic field, from the nematic to the smectic B phase, we saw that the described ABC layer stacking is arranged. Cooling samples of thin free standing films (less than 20 μm) from the nematic to the smectic B phase, a restacking of the layers in an orthorhombic F like stacking takes place. Variations of the temperature of sandwiched samples and freely suspended films of BCH 52 in both conformations gave us no hint to a temperature dependent transition of the layer stacking. That means that the way of restacking the layers at the transition nematic to smectic depends only on the thickness of the free film. We can assume that the cooling process and therefore the transition nematic-smectic B starts at the surface. The arrangement of the molecules to layer stacking would be influenced by the surface energy, and there would be a competition within the sample between bulk and surface energies. The relation of the bulk to the surface energies will be responsible for the way of arranging the layers. For films below 20 μm the contribution of the surface part of the total free energy predominates, so that it results in a different crystalline B structure for thin free films. A similar transition from a crystalline B to a hexatic phase due to a competition between surface and bulk energies in thin free standing films was also described by Collet et al. [2]. This would mean that the surface energy in free standing films tends to lower the molecular order, which is consistent with the fact that in very thin films, at least two layers, 3-dimensional correlation ceases to exist.

Acknowledgement

We thank the BMFT for supporting this work. The samples were a gift from E. Merck, Darmstadt.

[1] J. Collett, L. B. Sorensen, P. S. Pershan, and J. Als-Nielsen, Phys. Rev. A **32,** 1036 (1985).

[2] J. Collett, P. S. Pershan, E. B. Sirota, and L. B. Sorensen, Phys. Rev. Lett. **52,** 356 (1984).

[3] P. A. C. Gane, A. J. Leadbetter, and P. G. Wrighton, Mol. Cryst. Liq. Cryst. **60,** 267 (1981).

[4] G. Albertini, S. Melone, G. Poeti, F. Rustichelli, and G. Torquati, Mol. Cryst. Liq. Cryst. **104,** 121 (1984).

[5] W. Haase, H. Paulus, and H. J. Müller, Mol. Cryst. Liq. Cryst. **97,** 131 (1983).

[6] H. J. Müller and W. Haase, Mol. Cryst. Liq. Cryst. (Lett.) **92,** 63 (1983).

[7] W. Klämke, Z. X. Fan, W. Haase, H. J. Müller, and V. Gallardo, Ber. Bunsengesellschaft Physik Chemie, submitted for publication.

[8] T. Ushida, K. Ishikawa, and M. Wada, Mol. Cryst. Liq. Cryst. **60,** 37 (1980).

[9] F. J. Kahn, G. N. Taylor, and H. Schonhorn, Proc. IEEE **61,** 823 (1973).

[10] L. Walz, F. Nepveu, and W. Haase, Mol. Cryst. Liq. Cryst. **148,** 111 (1987).

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

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

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

[14] P. S. Pershan, G. Aeppli, J. D. Litster, and R. J. Birgeneau, Mol. Cryst. Liq. Cryst. **67,** 205 (1981).