X-Ray Diffraction of Some Biphenylcyclohexanes (BCH's)

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X-ray diffraction measurements have been made on BCH5Cl, BCH5Br, BCH5CN, BCH52 and binary mixture of BCH5CN and BCH52, in the nematic phase. BCH5Cl and BCH5Br are thought to have a weak molecular correlation along the texture axis with repeat unit along that axis of ∼1.1 molecular lengths. Whereas for BCH5CN the repeat unit along the texture axis is about 1.4 molecular lengths implying a strong molecular association.

The d-spacings of the binary mixtures of the strongly polar BCH5CN and the nonpolar BCH52, in the nematic phase, vary roughly linearly between the d-spacing of BCH5CN and that of BCH52.

Introduction

It has become clear that some of the physical properties of liquid crystal molecules with a strongly polar endgroup like $-CN$, $-NO_2$ and $-Cl$ differ from those of the other liquid crystal molecules [1−3]. X-ray and neutron diffraction studies have established an unusual bilayer structure for both the nematic and smectic phases. The mass density fluctuations that exist in the nematic and smectic phases are periodic and can be characterized by a wavelength "d" which is not commensurate with the molecular length "l" and the ratio d/l varies for different compounds from 1.1 up to 1.6 [1−3].

Eidenschink [4] and Eidenschink et al. [5] have reported on the liquid crystalline disubstituted biphenylcyclohexanes (BCH). The diamagnetic properties [6], the densities and the optical properties [7] and the thermal data [8] of a number of these compounds have been studied. Haase et al. [9] have determined the X-ray structures of some BCH's in the solid and liquid crystalline states.

In the present work, the X-ray diffraction investigation of the nematogen structures of the halogen- and pseudohalogen-derivatives of BCH is reported. In addition, X-ray measurements on binary mixtures containing the strongly polar BCH5CN and the nonpolar BCH52 have been made. An interesting point is the question concerning the behaviour of a mixture containing a nematogen with a semi-bilayer structure and that with a monolayer structure.

Experimental

The followings are the compounds which have been studied:
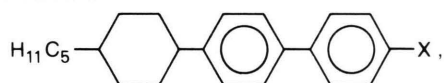
BCH5Cl (X = Cl), BCH5Br (X = Br), BCH5CN (X = CN) and BCH52 (X = C_2H_5).

Samples as obtained from E. Merck, Darmstadt were used without further purification. The transition temperatures and transition enthalpies, measured by the DSC-method, are in a good agreement with those reported in [8].

For X-ray diffraction measurements, the samples were contained in 0.7 mm Lindemann glass capillaries. The capillaries were held in a copper block whose temperature was controlled within about $\pm 0.5\,°C$ and measured with a calibrated thermocouple located near the sample. X-ray diffraction photographs were taken using a flat plate camera with a CuK_α radiation. The photographs were taken in the nematic phase, subsequent to cooling of the samples from the isotropic phase in an electromagnet with a field strength of 1 Tesla. The optical density of the X-ray photographs measured by a Joyce MKIIIC-microdensitometer was used to determine the distances on the X-ray diffraction photographs.

The distance from the sample to the film has been calibrated by measuring the diameter of the (111) reflection of silicon (lattice spacing 5.4306 Å).

Results and Discussions

X-ray diffraction patterns of all the aligned samples are characteristic of compounds having a definite texture axis. The wavelengths of the mass density fluctuations for all the compounds studied are given in Table 1, expressed as Bragg-spacings ($d = \lambda/2 \sin \theta$, where λ is the wavelength of the radiation, 1.5418 Å for our measurements, and θ is the diffraction angle). The wavelengths (or d-spacings) are compared in Table 1 with the maximum molecular lengths "l", as calculated from the X-ray data [9] of some BCH's and the well known bond lengths and the covalent radii of Cl and Br. For BCH5Cl and BCH5Br the d-spacings are approximately equal to the maximum molecular lengths, whereas for BCH5CN they are much larger than "l". On the other hand the d-spacings for BCH52 are smaller than "l".

As it has been experimentally found, we would presume that conformational changes as well as thermal vibrations have taken place in the pentyl chain. Thus the calculated "l" would be, $1-2$ Å, shorter than those values shown in Table 1. In this respect a weak correlation in local order in the case of BCH5Cl and BCH5Br would be suggested, where the repeat unit along the texture axis is about 1.1 molecular lengths. Whereas for BCH5CN the repeat unit along the texture axis is about 1.4 molecular lengths implying a strong molecular association, due to the high dipole moment of the cyano group, which is suggested to be of an overlapping in a head to tail nature. It confirms the suggestion made by Leadbetter et al. [10] for the electron overlap of the cyano groups with the phenylrings in the case of the cyanobiphenyls.

The d-spacings of the binary mixtures of the BCH5CN (semi-bilayer) and BCH52 (monolayer structure), at 150 °C, vary roughly linearly between the d-spacings of BCH5CN molecule and that of BCH52 molecule as shown in Figure 1. This can be interpreted in terms of different amount of overlapping for each mole fraction over the whole range of the nematic mixture. Since both BCH5CN
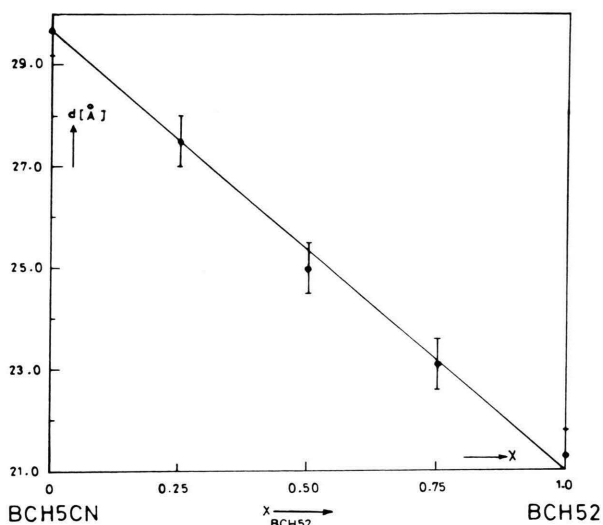

Fig. 1. The d-spacing vs. the mole fraction (x) for the binary mixture of BCH5CN and BCH52, at 150 °C.
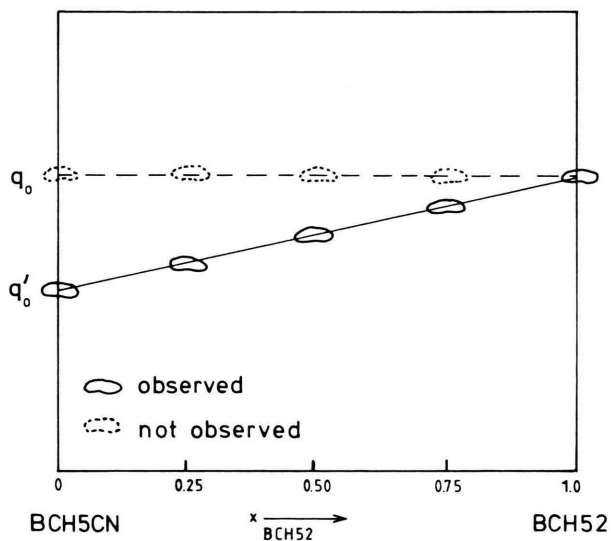

Fig. 2. The wavevectors for the binary mixtures of BCH5CN and BCH52 in the nematic phase vs. the mole fraction (x).

Table 1. Molecular parameters of the compounds studied (d: fluctuation wavelength, l: calculated molecular length, D: intermolecular distance).

Compound	Temperature [°C]	d [Å]	l [Å]	D [Å]
BCH5Cl	150.0	22.7 ± 0.5	22.5	5.4 ± 0.1
BCH5Br	160.0	23.4 ± 0.5	22.8	5.4 ± 0.1
BCH5CN	150.0	29.7 ± 0.5 *	22.9	5.4 ± 0.1 *
BCH52	150.0	21.3 ± 0.5	22.9	5.4 ± 0.1

* These values are in a good agreement with those values in [9].

and BCH52 molecules have the same molecular length (Table 1), the X-ray scattering wavevectors can be illustrated in Figure 2. For BCH5CN only the diffuse vector $q_0' = (2\pi/d')\,\tilde{n}$ with $d' = 1.4\,d$ is observed, where q_0' is the wavevector, $\tilde{n}$ the nematic director, $d' = 29.7\,\text{Å}$ and $d = 21.3\,\text{Å}$. Whereas for BCH52 the vector $q_0 = (2\pi/d)\,\tilde{n}$ is observed. For all mixtures the q-vector is in between q_0' and q_0 using the ideal formula $(q_0)_{\text{mixture}} = \sum_i x_i\,(q_0)_i$, where x_i is the mole fraction and $(q_0)_i$ is the corresponding wavevector. In other words, the binary mixture of BCH5CN and BCH52 behaves like an ideal mixture.

The average intermolecular spacings "D" in the nematic phase are deduced with the formula $D = 1.117\,\lambda/2\sin\theta$ [11]. These D-spacings are also given in Table 1. The D-spacings ($5.5 \pm 0.1\,\text{Å}$) of all the binary mixtures of BCH5CN and BCH52 are identical with those values ($5.4 \pm 0.1\,\text{Å}$) for the pure components of the binary mixtures. Similar D-spacings ($\sim 5.4\,\text{Å}$) have been found for compounds containing phenylcyclohexane cores [9, 12].

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