STRUCTURES OF CYANO-BIPHENYL LIQUID CRYSTALS

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ABSTRACT

The structures of p-alkyl-p′-cyano-bicyclohexanes, $C_nH_{2n+1}(C_6H_{10})(C_6H_{10})CN$ (n−CCH), and p-alkyl-p′-cyano-biphenyls, $C_nH_{2n+1}(C_6H_4)(C_6H_4)CN$ (n−CBP), have been studied. It is convenient to use an x-ray image intensification device to search for symmetric x-ray diffraction patterns. Despite the similarities in molecular structures of these compounds, very different crystal structures have been found. For the smectic phase of 2CCH, the structure is close to rhombohedral with threefold symmetry. In contrast, the structure is close to hexagonal close-packed with two molecules per unit cell for 4CCH. Since intermolecular forces may be quite weak for these liquid crystals systems, it appears that crystal structures can change considerably when the alkyl chain length is slightly altered. Different structures have also been found in the crystalline phases of n-CBP for n=6 to 9. For n=7 to 9, the structures are close to monclinic. The structures are reminiscent of the smectic-A liquid crystal structures with the linear molecules slightly tilted away from the c-axis. In contrast, the structure is quite different for n=6 with the molecules nearly perpendicular to the c-axis.

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p-alkyl-p'-cyano-bicyclohexane (n-CCH), $R(C_6H_{10})(C_6H_{10})CN$, and p-alkyl-p'-biphenyl (n-CBP), $R(C_6H_4)(C_6H_4)CN$, are new classes of liquid cystals[1,2], where C_6H_4 is the phenyl ring, C_6H_{10} is the saturated cyclohexane ring, R may be any alkyl (C_nH_{2n+1}) group, and n is the number of carbon atoms in the alkyl chain. These molecules have long rod-like shapes. Extensive investigations have already been reported for the structures of a variety of these liquid crystals. For the CBP systems, there are stronger interactions between the molecules due to the double bonds in the phenyl rings. The smectic-A structures are commonly observed for these compounds with n=8,10,12 where the CBP molecules are tilted with respect to the smectic layers.[3] The ratio between the smectic layer spacing and the molecular length is about 1.4. In contrast, the molecular interactions are relatively weak for the CCH systems. The smectic phase structures are apparently unstable for 7CCH and higher members. For lower values of n, great varieties of structures have been observed for the smectic phases.[4]

Because of the important roles of both the alkyl chain lengths (n) and the ring systems, we have studied the structures of these systems in our present work. Because of the weak intermolecular forces, the crystallization processes are rather slow. We are able to obtain single-domained samples in capillary tubes by slow cooling from the less-ordered phase at higher temperature. Nevertheless, the spatial orientation of the domain inside the capillary depends on the direction of the initial nucleation and is therefore rather arbitrary. With the sample mounted on a goniometer, we have found it convenient to use an x-ray image intensification device to search for symmetric diffraction patterns visually while the goniometer is rotated.

The x-ray image intensification device was developed by Yin and collaborators at NASA Goddard Space Flight Center.[5,6] The diffracted x-rays are converted into visible light images by a rare-earth phosphor as shown in Fig. 1. The visible light is then coupled via fiber optics to a microchannel-plate

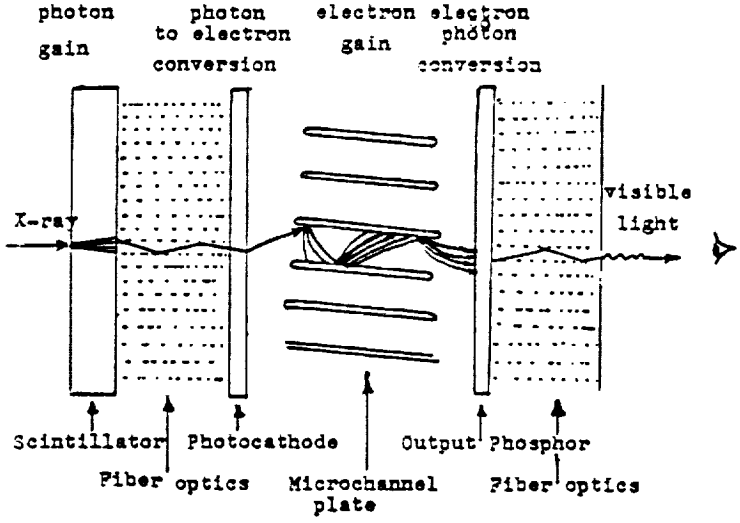

Figure 1. X-ray image intensification system.

image intensifier whic intensifies the visible light signal with a luminous gain of $\sim 10^5$. Because of the high luminous gain, the intensified visible light output can be viewed directly, photographed, or coupled to other video devices. The transmission Laue spots on the output screen can be easily viewed in subdued room light while the sample is being rotated. Hence this is a convenient technique to study the liquid crystals whose molecular alignments inside the capillaries are not known.

The X-rays are produced by a copper anode tube with a nickel filter, usually operating at 22kV and 500 watts. After collimation, the X-ray beam is directed onto the liquid crystal sample which is placed in a thin-walled capillary tube installed on a two-axis goniometer. The goniometer is enclosed in a container so that the sample may be heated or cooled in an air stream with controlled temperature. The X-ray image intensification device, which is small and compact, is placed in the forward scattering direction about 4 cm from the sample. The diffraction pattern displayed on the output screen may be recorded by a Polaroid camera. The calibration is accomplished by placing standard lead grids (with circular and with rectangualr grid patterns) over the scintillation screen. The angular resolution is about 0.03°. It should be noted that the diffraction spots can come from both the characteristic CuKα radiation (wave length of 1.54Å) and the white radiations with shorter wave lengths from the copper anode. The former spots tend to have higher intensities. These two types of spots may be more clearly distinguished by lowering the X-ray tube voltage. There would be much larger reductions in the intensities of white radiation spots as compared to the CuKα radiation spots. Because of the low crystalline orders and large molecular fluctuations in liquid crystals, diffraction spots are observable only in the forward scattering direction within a few degrees of the incident X-ray direction. It is, therefore, necessary to measure several diffraction patterns for various goniometer orientations and then express the scattering vectors of these different orientations in terms of a common set of unit vectors arbitrarily fixed in the crystal.

For the smectic phase of 4CCH, we have used the X-ray image intensification device to search for symmetric diffraction patterns. These patterns are shown on the left side of Fig. 2. Patterns of sixfold symmetry are shown in (a) and (b). Changing the goniometer angles resulted in patterns with twofold symmetry as shown in (c) and (d) where the incident X-ray direction is perpendicular to the c-axis with sixfold symmetry. These results indicate a hexagonal close-packed structure for the smectic phase of 4CCH with c=31Å and a=b=5.7Å. The packings of the molecules are sketched on the right side of Fig. 2. The unit cell parameters a and b are nearly the same as the molecular diameter. The parameter c is slightly less than twice the molecular length (~ 17Å).

It is surprising to find that the smectic phase structure of 2CCH is quite different from 4CCH despite the similarities in their molecular structures. Again, we have used the X-ray image intensification device to search for symmetric diffraction patterns. A diffraction pattern with threefold symmetry is sketched in Fig. 3(a). The incident X-ray direction is coincident with the direction of the threefold axis. At other goniometer angles, the diffraction patterns shown in Figs. 3(b), (c) and (d) have been observed. The incident X-ray directions for these patterns are tilted about 16° from the threefold axis and are distributed symmetrically about the threefold axis. These results indicate that the smectic phase structure of 2CCH is close to rhombohedral with a=b=c=12.5Å and the common angle of 28° between pairs of these units' cell vectors. These vectors are 17° away from the threefold axis direction.

These experiments indicate that the liquid crystal structures can change considerably even when their molecular structures are only slightly altered. This may be a consequence of the weak intermolecular forces in these systems. The effects of the alkyl chain length n may also be important.

Different structures have also been found for the crystalline phases of n-CBP for n=6 to 9. For 8CBP, several typical diffraction patterns are shown in Fig. 4. After some searching with the X-ray image intensification device, a clean symmetric pattern of four spots has been found as shown in Fig. 4(a) (the

shaded circle is the beam stop). This pattern demonstrates the monoclinic symmetry of the lattice. When the X-ray beam is more than 3° away from the monoclinic c-axis, the diffraction spots are usually observed in pairs only, as shown in Figs. 4(b), (c) and (d). These results indicate that the crystalline phase structure of 8CBP is close to monoclinic with a=b=5.5Å, c=37Å, $\alpha=\beta=90°$ and $\gamma=99°$. There are two molecules per unit cell. The unit cell parameters a and b are comparable to the molecular diameter. The parameter c is slightly less than twice the molecular length ~21Å. This structure is similar to the hexagonal close-packed structure except that the angle γ is 99° instead of the standard value of 120°. Similar structures have been found for 9CBP (a=b=4.9Å, c=27Å, $\gamma=110°$) and 7CBP(a=7Å, b=6Å, c=30Å, $\gamma=133°$). These structures are reminiscent of the smectic-A liquid crystal structures with molecules tilted slightly away from the c-axis. In contrast, the structure is quite different for 6CBP with a=19Å, b=9Å, c=6Å, $\gamma=148°$. The molecules are nearly perpendicular to the c-axis. Our experimental results have demonstrated that the crystal structures can change considerably when the alkyl chain length n is altered.

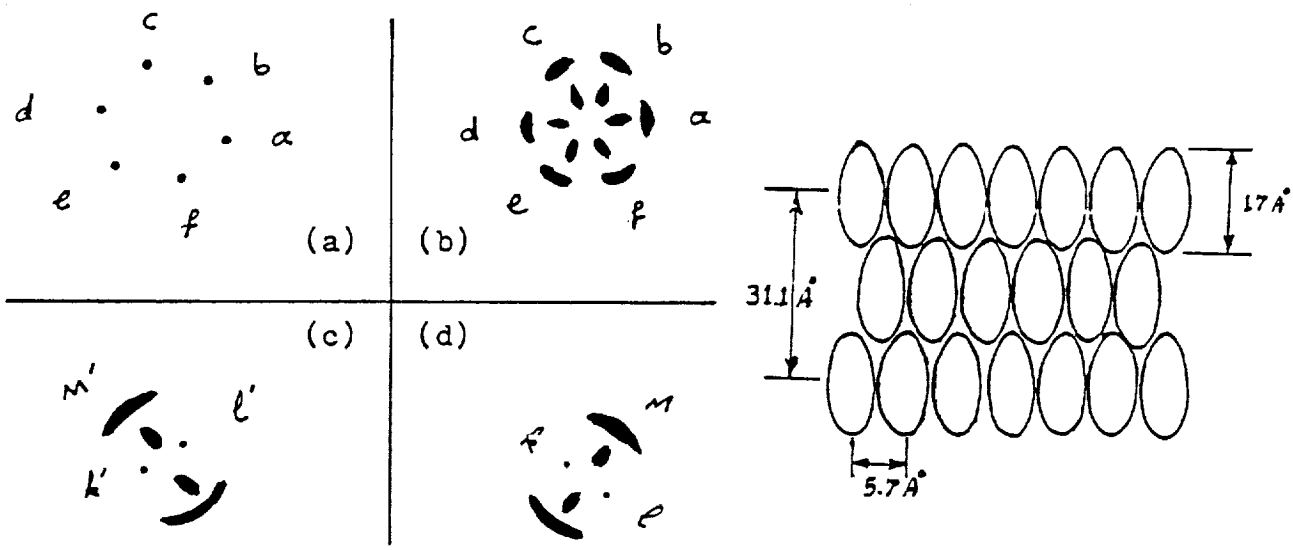

Figure 2. Left: Sketch of diffraction patterns of smectic phase of 4CCH.
(a)(b) X-ray beam along the sixfold c-axis., (c)(d) X-ray beam perpendicular to sixfold axis.
Right: Sketch of the molecular packing (c-axis in the perpendicular direction).

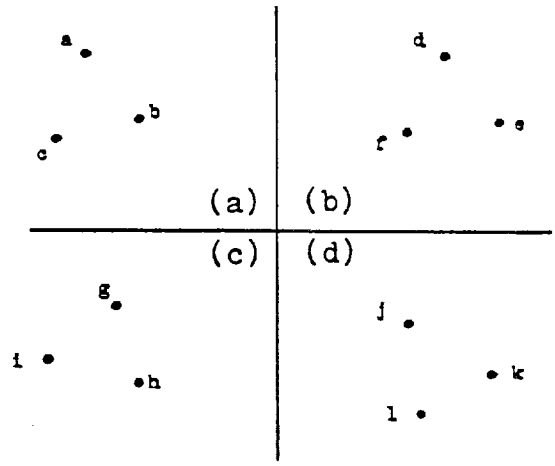

Figure 3. Diffraction patterns of smectic phase of 2CCH from CuKα X-rays. (a) X-ray beam along threefold axis; (b)(c)(d) X-ray beams 16° away from the threefold axis and 120° apart azimuthally.

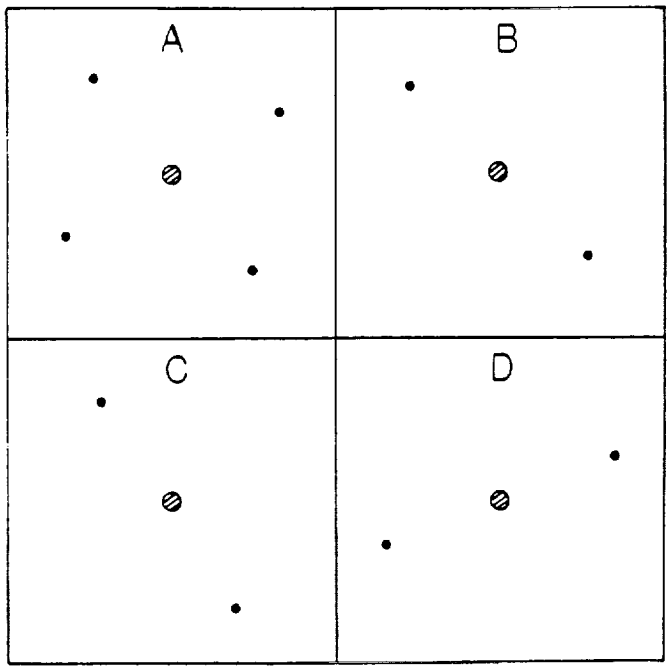

Figure 4. Diffraction patterns of the crystalline phase of 8CBP from CuKα X-rays. (a) incident X-ray along monoclinic c-axis, (b)(c)(d) incident X-rays 3°, 16°, 14° away from c-axis.

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