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X-RAY ANALYSIS OF THE STRUCTURE OF LIQUID CRYSTALS BY MEANS OF DISTRIBUTION FUNCTIONS

All substances known at the present time that are capable of passing into the liquid-crystalline state are built of sharply anisometric elongated molecules. These molecules are, as a rule, of low symmetry or asymmetric (Fig. 1).

A feature characteristic of both nematic and smectic liquid crystals is the parallel arrangement of molecules within certain microregions, domains*. With such an arrangement a denser packing of molecules of elongated shape is achieved than with their chaotic orientation, characteristic of a liquid. Thus, it is precisely this geometric factor that permits the existence of certain minima of packing energy, intermediate between the true liquid and the true crystalline state, which correspond to the liquid-crystalline state. In nematic liquid crystals there is no correlation whatever between the projections onto the z axis (the principal axis of the domain) of the distances between the centers of molecules. Any displacements of molecules along z relative to one another are equally probable; this may be written as the presence of an infinitely small statistical translation $\tau_\infty(z)$–an axis of continuous translations (2). If the molecules are polar (and in many cases this is so), then, generally speaking, their parallel and antiparallel packings are possible. In the latter case an additional symmetry operation statistically transforming the molecules into one another is a twofold axis perpendicular to the principal axis of the liquid crystal. In projection along the z axis, the packing of molecules in a nematic liquid crystal possesses a certain degree of ordering. It may be described statistically if one considers the lateral environment of each molecule and then compiles statistics over all the molecules. Then we obtain a two-dimensional distribution function $W(\mathbf{r})$ ($\mathbf{r}$ is the radius vector in the plane perpendicular to the principal axis), giving the probability of finding the vector $\mathbf{r}$ between the axes of molecules. With such a packing, owing to the presence of nearest-neighbor order oriented in the plane and to the constancy of the coordination number, the function $W(\mathbf{r})$ possesses periodically located but damped maxima, so that when a certain distance r_M is exceeded all

Fig. 1

Figure 1: Fig. 1

Fig. 2. Possible arrangement of molecules in a smectic layer of BT

Figure 2: Fig. 2. Possible arrangement of molecules in a smectic layer of BT

values of $|\mathbf{r}|$ become equiprobable. Thus there is two-dimensional translational statistical symmetry at short distances.

Fig. 1. Shape of the molecules of some substances that give liquid crystals:
a—α-azoxybenzene (anisal-α'-naphthylamine) (BAN);
b—*p*-N-dimethylaminobenzalamino-naphthalene-4-azobenzoic ethyl ester (DBAE);
c—n, n'-nonoxybenzaltoluidine (BT);
d—cholesteryl caprinate (ChK)

* Here we shall consider only the packing of molecules inside domains, leaving aside the extensive range of questions connected with the mutual orientation of domains.

If the cross section of the molecules changes strongly with height, then the coordination number for the molecular axes may vary (on average it tends to 6), and in that case statistical periodicity is hardly possible. In this case the mutual arrangement of the axes can be described by the cylindrically symmetric function $z\,(r)$ of the probability of distances between axes, whose maxima give the value of the number of neighbors located at a distance r.

Let us note that the function $W(r)$ is oriented azimuthally in its plane only at distances smaller than r_M, whereas over the domain as a whole all its orientations occur. Therefore (as is also self-evident in the case of $z\,(r)$) the principal axis of a nematic domain is (statistically) an axis of infinite order ∞.

As a result, the structural symbol (symmetry) of nematic liquid crystals may be written as $\infty \tau W(r)$. This symbol may be refined by taking into account the intrinsic symmetry of the molecules, the presence or absence of antiparallel packing, twisting for the cholesteric variety σ_∞, etc.

Fig. 2. Possible arrangement of molecules in a smectic layer of BT.

In smectic liquid crystals the molecules are arranged in layers. The relatively higher ordering of the smectic phase also follows from the fact that, in those cases where a given substance forms both smectic and nematic phases, the latter is the higher-temperature one. For example, BT (Fig. 1) gives smectic liquid crystals in the temperature interval 71—73.5°C, and nematic ones in the interval 73.5—76°C. Apparently, the absence of protruding lateral groups favors the formation of smectic layers. For example, BAN and DBAE (Figs. 1 , 1) form only nematic liquid crystals, whereas two other substances (BT and KhK in Figs.

Figure 3

Figure 3: Figure 3

1 and 1) form both smectic and nematic liquid crystals. Analyzing the shape of the molecules, we arrive at the conclusion that the main cause of the formation of smectic layers is the convenience of antiparallel packing of the molecules (Fig. 2). Thus, in smectic liquid crystals there is a correlation of displacements of molecules along the axis relative to one another, described by the function $\tau(z)$, and the layers are arranged with some period c, close to the length of the molecule. Within the layers the arrangement of the molecules is characterized, analogously to nematic liquid crystals, by the function $W(r)$ or $z\,(r)$ and, apparently, almost always by the presence of "statistical" axes 2 (specifying antiparallelism) lying in the layer perpendicular to the principal molecular axis. Consequently, in the general case the structural symbol (symmetry) of smectic liquid crystals may be written in the form $\infty c\tau(z)W(r):2$.

Information about the functions describing the structure of both varieties of liquid crystals can be obtained from an X-ray experiment. If a liquid-crystal specimen is not oriented (the domains are arranged chaotically), then the method of radial distribution may be applied (^{5}), which reduces to inversion of the corrected intensity curve

$$i(s) = \frac{I}{f^2(s)} - 1 \tag{1}$$

according to the Fourier integral formula

$$4\pi r^2\rho(r) = 4\pi r^2\rho_0 + \frac{2r^2}{\pi}\int_0^{s_{\max}} s^2 i(s)\,\frac{\sin sr}{sr}\,ds, \tag{2}$$

Here I is the normalized experimental intensity curve, $f(s)$ in (1) is the mean atomic scattering factor of these atoms, practically close to the $f(s)$ of carbon. The radial distribution function $4\pi r^2\rho(r)$ determines the number of atoms in a spherical layer of thickness dr at a distance r from

of the initial atom, ρ_0 is the mean atomic density of the substance. This quantity can be found from the expression

$$\rho_0 = \rho/(A\cdot 1.65), \tag{3}$$

where ρ is the density in g/cm^3, A is the atomic weight of carbon.

As an example, Fig. 3A and 3B show, respectively, the intensity curves and the radial distribution for unoriented vitrified liquid-crystalline DBAE samples.

Fig. 3. Normalized curves of the scattering intensity of a vitrified liquid-crystalline DBAE sample (left) and the distribution functions obtained from them (right). A detailed explanation is given in the text.

More interesting and complete data can be obtained if the liquid-crystal sample is oriented mechanically, by an electric field, or by some other action, and forms a texture. In this case the X-ray pattern is a set of equatorial and meridional diffuse arcs. From the intensity of the equatorial arcs one can extract information on the cylindrically averaged distribution function of atoms in the sample and on the distribution of molecular axes $z_{\|}(r)$.

The function of the cylindrical distribution of projections of atoms is calculated by means of the Fourier–Bessel integral (^{6},^{7} ,^{2})

$$2\pi r z(r) = 2\pi r z_0 + 4\pi^2 r \int i(R) J_0(2\pi r R)\, R\, dR. \qquad (4)$$

Here $R = s/2\pi = 2\sin\nu_{\mathrm{eq}}/\lambda$; $J_0(2\pi r R)$ is the Bessel function of zero order; z_0 is equal to the number of atoms in the projection per square angstrom. Obviously, $z_0 = \rho_0^{2/3}$, where ρ_0 is found from (3). The distribution curve of intensities along the equator of the photograph from an oriented DBAE sample is shown in Fig. 3B, and the function of the cylindrical distribution of projections of atoms onto the base plane is shown in Fig. 3G. The magnitudes of the peaks of the function $2\pi r z(r)$ are proportional to the products of the numbers of atoms located in the projection at a distance r. From Fig. 1b it is seen that the main contribution should be made by projections of the "axial" atoms of the molecule. Therefore we may interpret the curve in Fig. 3G as a curve mainly due to intermolecular distances.

That this is indeed so is confirmed by another treatment of the equatorial intensity curve.

It can be used to construct the function of the cylindrical distribution of molecular axes onto the base plane $2\pi r z_{\|}(r)$. The expression for this function is completely analogous to the expression for the function of cylindrical distribution of projections of atoms (4). However, now the function $i(s)$ entering into (4) must be found by normalizing the intensity I_{eq}^{n} to the scattering of indi-

molecule, and not an atom, as in (1). In this case

$$i(R) = \frac{I_e^H - \overline{|F_M|^2}}{\overline{|F_M|^2}}. \qquad (5)$$

With cylindrical averaging,

$$|\overline{F_M}|^2 = \left[\sum_{j=1}^{N} f_j(R) J_0(2\pi r_j R)\right]^2 ; \qquad (6)$$

Fig. 4. Most probable contacts of DBAE molecules

Figure 4: Fig. 4. Most probable contacts of DBAE molecules

$$\overline{|F_M|^2} = \sum_j \sum_k f_j f_k J_0(2\pi r_{jk} R). \tag{7}$$

The curve $i(R)$ (5) is shown in Fig. 3D, and the function $2\pi r z_c(r)$ in Fig. 3E. Using model representations and the curve in Fig. 3E, one can establish the most probable arrangement of molecules in the sample (Fig. 4). The area under the peak at 3.65 Å is equal to 5. The number of neighbors found from model representations is most often equal to 6; however, configurations with 5 neighbors are also often realized.

The study of the intensity distribution along the meridian (Fig. 3Zh) should yield chiefly interatomic intramolecular distances, since in the nematic state there is no correlation in the mutual axial displacements of molecules. The linear distribution of atoms along the axis of the sample, $\rho_{\text{lin}}(r)$, is calculated by means of a one-dimensional Fourier integral

$$\rho_{\text{lin}}(r) = \rho_{0\,\text{lin}} + \frac{1}{\pi} \int_0^{s_{\max}} i(s) \cos sr \, ds. \tag{8}$$

Fig. 4. Most probable contacts of DBAE molecules

The form of the curve $\rho_{\text{lin}}(r)$ is shown in Fig. 3Z; it is consistent with the intramolecular interatomic distances.

Similar calculations were carried out for BAN and for a mixture of cholesteryl benzoate with cholesteryl acetate. This made it possible to draw conclusions about the nature of the mutual packing of molecules in these liquid-crystalline samples. In particular, in constructing the cylindrical distribution function for the smectic phases, peaks were found that are due to antiparallel packing of the molecules.

For the smectic phases of BT and KhK, small-angle photography showed the presence of a period c between the smectic layers. For BT the period c proved to be 25.2 Å, and for KhK, 31.9 Å. This is somewhat smaller than the molecular lengths L found by constructing their models on the basis of covalent-radius values (27 Å for BT and 34.5 Å for KhK). The fact that the period of the smectic layers is smaller than the molecular length can be explained by a coordinated (and possibly also statistical) inclination of the molecules within these layers, as well as by "interpenetration" of the ends of the molecules of a given layer into neighboring layers.

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REFERENCES

1. E. Alexander, K. Herrmann, *Zs. Kristallogr.*, **69**, 285 (1928).
2. B. K. Vainshtein, *Diffraction of X-rays by Chain Molecules*, Publishing House of the Academy of Sciences of the USSR, 1963.
3. R. Hosemann, *Zs. Phys.*, **128**, 1, 465 (1950).
4. R. Hosemann, S. N. Bagchi, *Direct Analysis of Diffraction by Matter*, Amsterdam, 1962.
5. J. Zernike, J. A. Prins, *Zs. Phys.*, **41**, 184 (1927).
6. G. Oster, D. P. Riley, *Acta Cryst.*, **5**, 272 (1952).
7. I. S. Andreeva, V. I. Iveronova, *Biofizika*, **2**, 281 (1957).

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