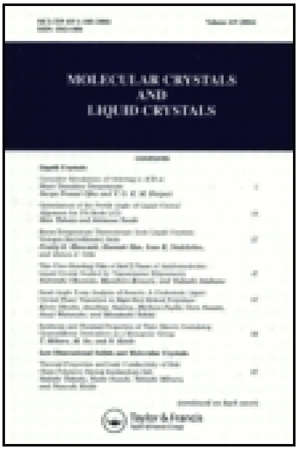

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Structure of Nematic *p*-Azoxyanisole in Electric and Magnetic Fields‡

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The structure of *p*-azoxyanisole in electric and magnetic fields was investigated. The observations were made in both constant and alternating fields. In order to show the structural characteristics of *p*-azoxyanisole use was made of the stastical distribution function.

1. The Influence of a Constant Electric Field on Nematic *p*-azoxyanisole

p-azoxyanisole is a typical example of substances forming liquid crystals of the nematic type. It gives a nematic mesophase in the range from 116° to 135 °C. In an unoriented nematic mesophase dark threads can be observed. When an external electric field is applied to the liquid crystal, the threads are seen to be arranged along the field. This suggests an idea that the long molecular axes lie perpendicular to the field.[1]

A model of the *p*-azoxyanisole molecule is shown in Fig. 1. The $N = O$ side group creates a dipole moment $\mu = 2.48 \times 10^{-18}$ GGSE which makes an angle of 58° 31′ with the long axis of the molecule.[2] This is strong evidence for the normal orientation of the long molecular axis with respect to the field.

The negative dielectric anisotropy (minimum dielectric constant along the long axes of the molecules[3–6]) favors the normal orientation.[4–7]

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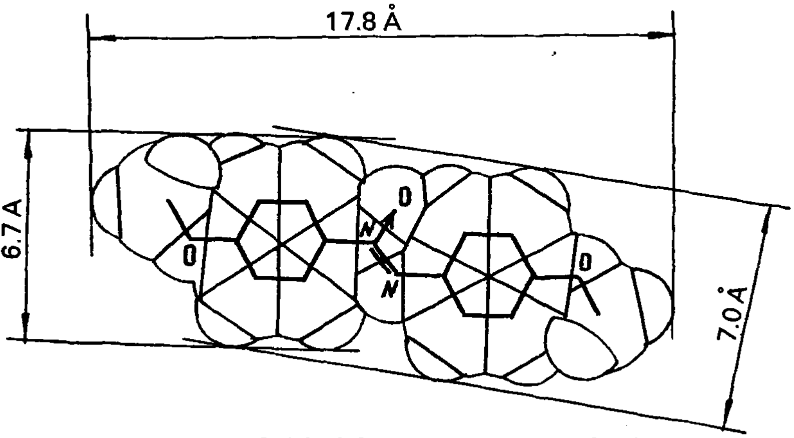
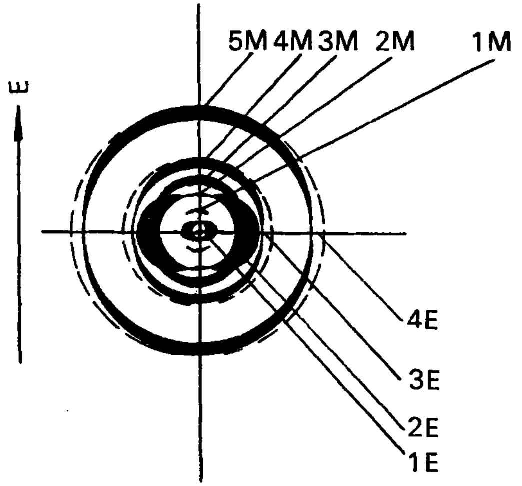


Figure 1. Model of the *p*-azoxyanisole molecule

On the other hand, the X-ray patterns taken in constant fields show the parallel orientation of the molecules relative to the field.[8,9] The motion of the liquid crystal along the electric field may, apparently, account for these contradictory data. It is thus possible to conclude that the long axes of the molecules are oriented along the field.[9] Optical observations show that the molecules appear to be normal to the field only near the threads which are arranged parallel to the field and behave as something independent. In the remaining mass of the substance the molecules are oriented by the flow parallel to the field. It is thus clear that due to the dielectric anisotropy in the liquid crystal the applied electric field appears to be inhomogeneous, which gives rise to the motion of the liquid crystal.[10–12] The X-ray patterns of nematic *p*-axoxyanisole taken at a temperature of 123° in a constant electric field of different strengths showed[21,22] that the diffuse rings characteristic of the preparation in the absence of a field are transformed into arcs in the field of 50 v/cm. This points out to a partial orientation of the molecules which occurs across the field. Consequently, at this field strength only the orientation effect manifests itself in an electric field, the long molecular axes being oriented normal to the field. In a field of 100 v/cm liquid-crystal flow begins to exert influence. The orientation by the flow partially compensates the orientation by the field. This leads to the change of the position of the reflections on the X-ray picture. In a field of 200 v/cm (and higher) the movement of the liquid crystal intensifies. The orientation by the flow starts prevailing over the orientation by the field, and the X-ray patterns show the orientation of the long molecular axes along the electric field. The schematic representation of the X-ray pattern in an electric field, the values of the angles θ, and interplanar spaces are given in Fig. 2.



	CuK$_\alpha$		MoK$_\alpha$			CuK$_\alpha$		MoK$_\alpha$		
	1E	2E	3E	4E		1M	2M	3M	4M	5M
θ	4°10	9°33	10°30	17°12		6°	8°33	14°15	10°30	17°12
d,Å	10,73	4,64	1,96	1,23		7,36	5,18	3,28	1,96	1,23

Figure 2. Schematic representation of the X-ray pattern; values of the angles and interplanar spaces of *p*-azoxyanisole oriented by an electric field are given. Characteristics of *p*-azoxyanisole.

Apparently, the strongest equatorial reflections 1E and 2E are due to intermolecular interference. As the field strength increases the reflections 1E and 2E intensify. This corresponds to the increase in the degree of ordering of the molecules; at the same time the meridional reflection 2M becomes weaker. This suggests that the 2M reflections are also due to some extent, to intermolecular interference. At the same time the sharpening of the meridional reflections 1M, 3M and 4M appears clearly.

The X-ray photographs taken in MoK$_a$ radiation show the extra reflections 3E, 4E, 4M and 5M. In fact, these reflections can be described as rings which are seen to be sharper along the meridian and more diffuse along the equator of the X-ray picture. We thus come to the conclusion that the reflections 1E, 2E (2M) can appear due to intermolecular interference, whereas the reflections 1M, 3M, 4M (3E) and 5M (4E) owe their origin to intramolecular interference.

Inversion of the intensity curves along the equator by means of a Fourier–Bessel integral enables us to find the cylindrical distribution functions of the projections of the long molecular axes on the basal plane[13–22]

$$2\pi r Z_M(r) = 2\pi r Z_0 + r \int_0^{s_{\max}} i(s) s j_0(sr)\, ds$$

in this equation j_0 is the Bessel function, $s = (4\pi \sin\theta)/\lambda$, $i(s) = (i^{n}_{\text{exp}} - \overline{|F_m|^2})/|\overline{F_m}|^2$ $|\overline{F_m}|^2$ and $|\overline{F_m}|^2$ are the square of the average structural amplitude of the molecule and its root-mean-square value respectively. The curves of cylindrical distribution $2\pi r Z_M(r)$ can be seen in Fig. 3.[21] The comparison of the curves giving the cylindrical distribution $2\pi r Z_M(r)$ shows that an increase in the field strength is accompanied by the reduction of the number of peaks. This is connected with the fact that the molecules are packed in a simpler arrangement due to the stronger orientation by the flow. It is known that the values of the areas under the peaks are equal to the number of neighbors surrounding the molecules. The total areas under the 3.6 Å and 5.3 Å peaks characterizing the first coordination sphere equals:

4.35 in a field of 200 v/cm
4.79 in a field of 500 v/cm
4.84 in a field of 4000 v/cm

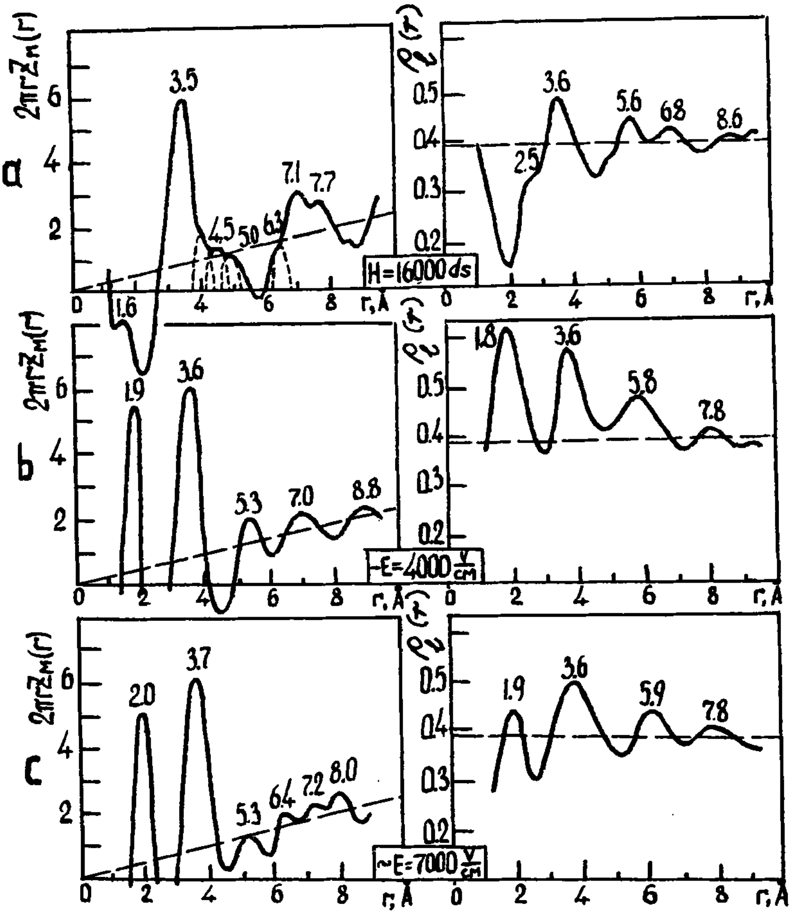


Figure 3. Cylindrical distribution function of the molecular axes (on the left); Linear distribution function of the atoms along the z-axis (on the right). (a) in a magnetic field; (b) in a constant electric field; (c) in an alternating electric field.

A certain increase in the area with increasing field points to a closer packing of molecules in high fields. This is also evidenced by the sharpening of the 7 Å and 8.8 Å peaks as the field strength increases. A probable model of the liquid–crystal structure is shown in Fig. 4a. The distances between the molecules are

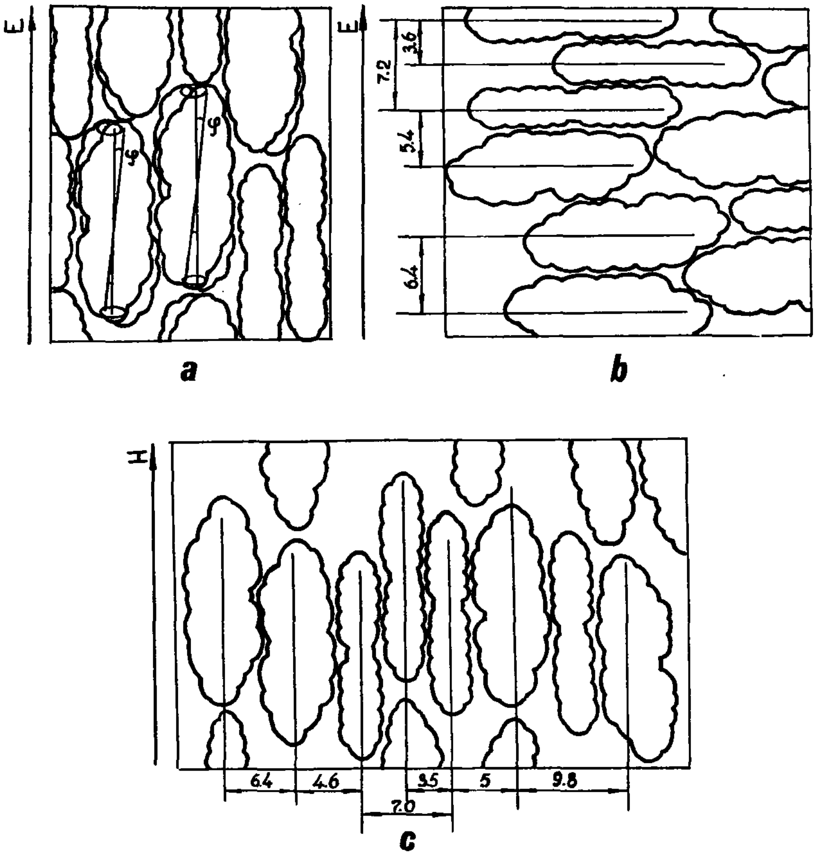


Figure 4. Probable model of the liquid-crystal structure of *p*-azoxyanisole in (a) constant electric field: (b) in an alternating electric field; (c) in a magnetic field.

obtained on the assumption that the long molecular axes precess at an angle ϕ to the direction of flow. The precession may be either real or statistical.

The cylindrical distribution functions, $2\pi r Z_M(r)$, were plotted against various temperatures in a field of 200 v/cm (Fig. 5). We notice a displacement of the principal peaks into the region of large intermolecular distances. The molecular packing becomes more " loose " with increasing temperature.[21,23]

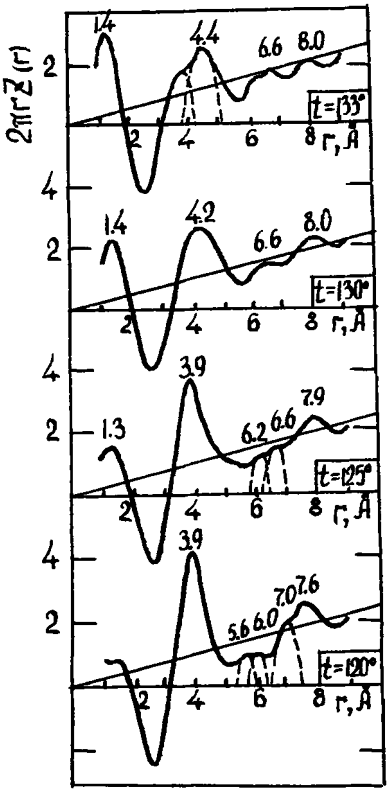


Figure 5. Cylindrical distribution function of the molecular axes at various temperatures.

Inversion of the curves giving intensity along the meridian by means of a one-dimensional Fourier integral enables us to find the linear distribution functions of the atoms along the texture axis:

$$\rho(r) = \rho_0 + \frac{1}{\pi}\int_0^{s_{\max}} i(s)\cos(sr)\,ds, \qquad i(s) = \frac{i^{n}_{\text{exp}}}{f_c^2} - 1$$

The linear distribution curves of the atoms are shown in Fig. 3.

If all the atoms in the molecule are projected on the long molecular axis, the average periods will correspond well enough to the values of the peaks on the $\rho(r)$ curves.

a.	1.9; 1.8	3.7; 3.6	5.9; 5.8	7.8 Å
b.	1.8	3.73	5.92	7.8 Å

Here " a " identifies the position of the peaks on the distribution curve, and " b "—the values of the interatomic distances in the *p*-azoxyanisole molecule.

The estimated periods can be interpreted as the average-value distances between various atoms, and groups of these in projections on the long axis.

2. The Influence of Alternating Electric Fields on Nematic *p*-azoxyanisole

X-ray studies of nematic *p*-azoxyanisole oriented by an alternating electric field were first carried out by Kast.[8] The arcs on the X-ray patterns indicated that in low-frequency fields the molecules were oriented along the field. At a definite critical oscillation frequency of about 3000 00 c.p.s. the orientation would appear to be disrupted. Therefore, it seems reasonable to conclude that 1/600 000 sec. is the period of time necessary for particles to rotate through 180°. At higher frequencies (600 000 c.p.s.) the molecules were found to be oriented perpendicular to the field. This is explained by the fact that the orientation of the molecules parallel to the field could no longer be attained during the period corresponding to the reversal of the field. Kast[24] also found that *p*-azoxyanisole prepared by different methods yielded different values of critical frequencies. Herrmann, Krummacher and May[9] reported, however, that this was due to the fact that in a low-frequency field a parallel orientation of the molecules was produced by the flow of the liquid crystal.

On the other hand, Naggiar[25] found that the motion of the liquid crystal was no longer to be observed at 4000 c.p.s. (E–750 v/cm).

We made studies of nematic *p*-azoxyanisole in fields of

7000 v/cm with frequencies of 50 c.p.s. to 12 mc.[21,26] The X-ray photographs of *p*-azoxyanisole in a field of strength 7000 v/cm were taken at temperatures 119°, 121°, 123°, 128° and 133°. The final results are given in Fig. 6. The region of parallel molecular orientation is isolated on the top of the photograph by curve 1. The zone of normal molecular orientation is located above curve 2,

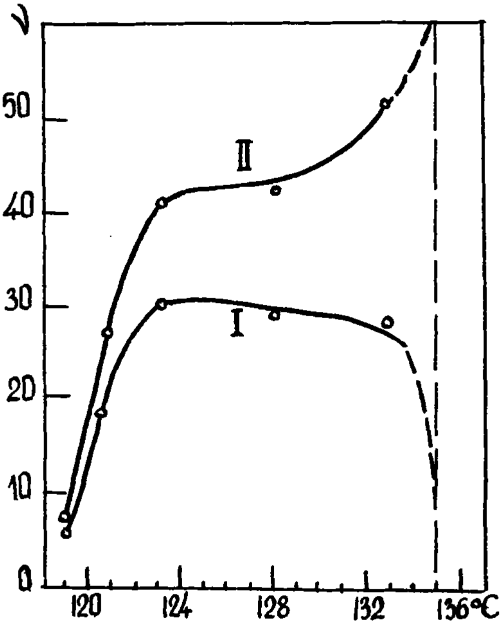
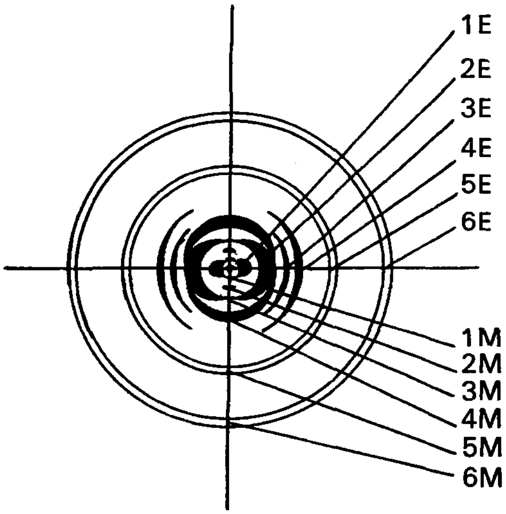


Figure 6. Boundaries between the regions of parallel and perpendicular orientations of *p*-azoxyanisole in alternating electric fields.

and the region where the molecules are not oriented at all lies between curve 1 and curve 2. Let us note that the change of parallel molecular orientation to perpendicular orientation will take place at a more or less broad frequency band, and not at a definite critical frequency. This band becomes significantly broader with increasing temperature. For example, at a temperature of 123 °C a parallel orientation of the molecules along the field is found to occur up to 30 Kc frequency. With increasing temperature a decrease in the degree of orientation can be observed, while in the region of 30 to 40 Kc orientation is completely absent. Above 40 Kc a perpendicular orientation of the molecules starts appearing.



	CuK_α		MoK_α				CuK_α				MoK_α	
	1E	2E	3E	4E	5E	6E	1M	2M	3M	4M	5M	6M
θ°	5,7	10	16	19,5	24,2	41	2,8	6,2	8,8	14,3	25	42
d(Å)	7,82	4,4	2,8	2,31	1,88	1,18	16,25	7,18	5,07	3,13	1,83	1,15
	2	1	5	5	5	5	2	2	3	4	5	5

Figure 7. Schematic representation of the X-ray photograph of *p*-azoxyanisole in a magnetic field with an induction of 12 000 G at 122.3 °C. Values of the angles θ and interplanar spacings d in Å are given.

Undoubtedly, one can use the mean value of the band, which according to Kast may be called critical frequencies. In this case Kast's conclusion regarding a decrease in the critical frequency with decreasing temperature is in accord with our own data. However, the numerical values of critical frequencies as well as of the entire frequency band in our experiments appear to be much smaller when compared with those obtained by Kast.

As already remarked by Kast himself, this is apparently due to different methods of substance purification.

Optical observations showed that in the region below curve 1 there occurs movement of liquid crystal. Thus, a parallel orientation of the molecules is produced by the flow in the field direction. An increase in the average critical frequency with increasing temperature is, apparently, caused by intensification of movement as the texture becomes less viscous. It should be noted that as the temperature rises the region between curve 1 and curve 2 where orientation does not occur becomes broader, which is associated with an increase of the thermal fluctuations of the molecules; this leads to the undersaturation of the orientation effect in both field and flow. This region is larger, the smaller the distance to the clear point, evidently, owing to the fact that at this stage the thermal fluctuations begin to exert predominant influence.

The cylindrical distribution functions of the projections of the axes of the *p*-azoxyanisole molecules $2\pi r Z_M(r)$ in alternating fields, and linear distribution functions of the atoms (Fig. 3c) along with the texture axis differ little from distribution functions in constant electric fields. The molecular packing of a nematic liquid crystal in an alternating field of strength 7000 v/cm with a frequency of 0.5 mc is shown in Fig. 4b.

3. The Influence of External Magnetic Fields on Nematic *p*-azoxyanisole

Liquid crystals of the nematic type are known to be oriented by magnetic fields. The long axes of the molecules are arranged along the field. The X-ray patterns show diffuse maxima along the meridian and equator.[27–35] The X-ray pattern taken in a magnetic field of induction 12 000 G at a temperature 122.3° revealed a larger number of details than that taken in an electric field.[21–36] This pattern is schematically represented in Fig. 7. Six meridional reflections IM and 6M, and four equatorial reflections 3E to 6E owe their origin to intramolecular interference.

Two equatorial reflections IE and 2E are due to intermolecular interference. The Bragg angles for the reflections depend on the temperature of liquid crystal (Fig. 8). The angles for the reflections IE and 2E decrease with increasing temperature. The interplanar spaces correspondingly increase. For the meridional reflections IM and 4M these angles increase as temperature rises.

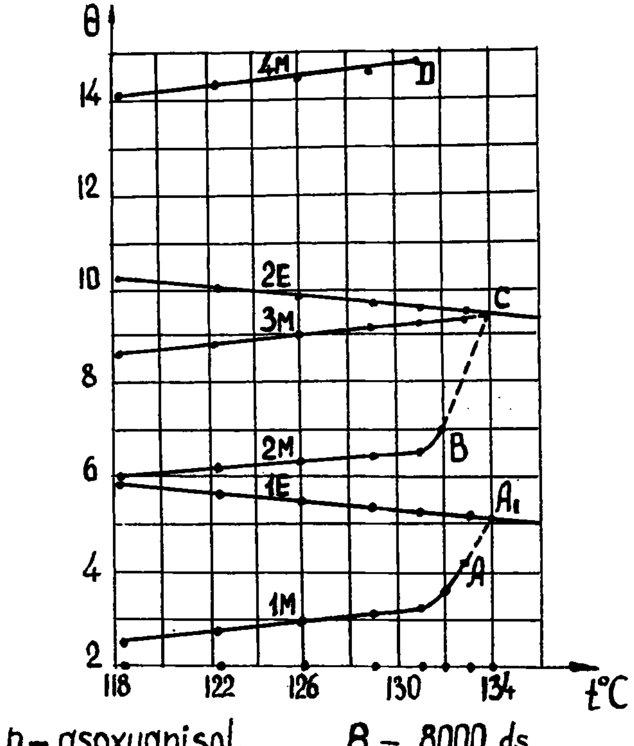


Figure 8. Temperature dependence of the angular distance of the reflections of *p*-azoxyanisole in a magnetic field.

Let it be noted that the reflections IE and IM are found to draw together tending to the value 5°, whereas the reflection 2E, 2M, 3M—to the angle 9° 20′ characteristic of the isotropic melt of *d*-azoxyanisole.[36]

The cylindrical distribution functions and linear distribution functions were calculated for various fields at a temperature of 122.3 °C (Fig. 3a). All these distribution functions depend only slightly on the intensity of a magnetic field. This points to saturation of the orientation effect in the fields of about 1000 gauss.[21,36]

4. Comparison of X-ray Data Obtained in Electric Magnetic Field

The cylindrical distribution functions and linear distribution functions of *p*-azoxyanisole in permanent electric and magnetic fields as well as in alternating fields are plotted for well oriented samples. We can see that these functions differ very slightly from each other. We still notice the displacement of the principal peaks in the low-value direction for magnetic fields. A closer molecular packing in magnetic fields may account for this phenomenon. For the case of magnetic fields we notice a large number of details on the curve $2\pi r Z_M(r)$, which characterize the packing of the molecules. The analysis of the liquid–crystal structures in electric and magnetic fields shows that a certain difference in the molecular packing has no effect on the general symmetry properties. For all these cases the structure of nematic *p*-azoxyanisole is designated by the symmetry symbol $\tau_\infty(Z)w(xy)$. Here $\tau_\infty(Z)$ is the translation axis of infinite order which denotes the equally probable and arbitrary displacements of molecules along the principal axis z of the texture, $w(x, y)$ being the statistical function of second sort characterizing the distribution of particles in the basal plane of the texture.[13]

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