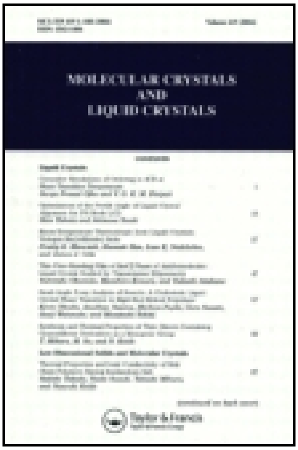

Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

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To cite this article: I. G. Chistyakov & W. M. Chaikowsky (1969): The Structure of p-Azoxybenzenes in Magnetic Fields, Molecular Crystals, 7:1, 269-277

To link to this article: http://dx.doi.org/10.1080/15421406908084877

Molecular Crystals and Liquid Crystals. 1969. Vol. 7, pp. 269–277

Printed in Great Britain

The Structure of *p*-Azoxybenzenes in Magnetic Fields‡

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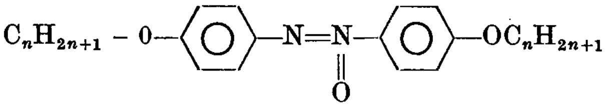
Abstract—A systematic X-ray diffraction study of the 10 homologues of *n*-azoxybenzenes has been performed. The structures of nematic and smectic mesophases as a function of the strength of the magnetic field and the temperature have been established.

Up to the present time the properties of the liquid crystalline phases in the homologous series of *p*-azoxybenzenes have been investigated in some detail.



The systematic investigation of the structure and properties of the mesophases of this homologous series have been made primarily on the first two members of this series. The lower members (n = 1–6) give only the nematic phase, the middle members (n = 7–10) give both the smectic and nematic mesophases, and the higher members of this series ($n > 10$) give only smectic mesophases. It should be noted that the temperatures at the clear-points vary regularly from member to member in the homologous series (Table 1, Fig. 3). that is, the clear-point rises with the transition from every even member of the series to the next uneven member.

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‡ Paper presented by title at the Second International Liquid Crystal Conference.

TABLE 1

No.	Alkyl Group	Substance	Temperature, °C		
			Melting Point	Smectic-Nematic Point	Clear Point
1	CH_3	4,4′-di-*n*-methoxyazoxybenzene	116	—	134
2	C_2H_5	4,4′-di-*n*-ethoxyazoxybenzene	135	—	162
3	C_3H_7	4,4′-di-*n*-propoxyazoxybenzene	114.7	—	122
4	C_4H_9	4,4′-di-*n*-butoxyazoxybenzene	101.5	—	134
5	C_5H_{11}	4,4′-di-*n*-pentoxyazoxybenzene	73.5	—	122
6	C_6H_{13}	4,4′-di-*n*-hexoxyazoxybenzene	77	—	127
7	C_7H_{15}	4,4′-di-*n*-heptoxyazoxybenzene	74.5	95	123
8	C_8H_{17}	4,4′-ci-*n*-octoxyazoxybenzene	79	107	125
9	C_9H_{19}	4,4′-di-*n*-nonoxyazoxybenzene	74.5	113	121
10	$C_{10}H_{21}$	4,4′-di-*n*-decoxyazoxybenzene	78	120	125

It is interesting to establish the influence of changes of molecular configuration, within the limits, of this series, on the structure of liquid crystals. At the same time this experiment made it possible to estimate the " sensitivity " of existing methods of X-ray analysis to a small change in the structure of liquid crystals with an increase of CH_2 groups in the molecular skeleton. We investigated the members of the homologous series of *p*-azoxybenzene with *n* from 1 to 10. The samples were oriented by magnetic fields. The method of the experiment has been described before.[1,2] The X-ray diagrams of the nematic phases were obtained at temperatures 5° above the transition point from the solid to the nematic mesophase or from the smectic mesophase. Similarly, the smectic mesophases were investigated with temperature 5° above the transition point of the solid into the smectic state.

The X-ray diagrams and schemes of collection of reflections for nematic and smectic states are shown in Fig. 1. It is a matter of interest to establish the change of the meridional reflection 1 M, for which Bragg's spacing corresponds roughly to the length of a molecule, with an increase in the number of carbon atoms in an homologous series.

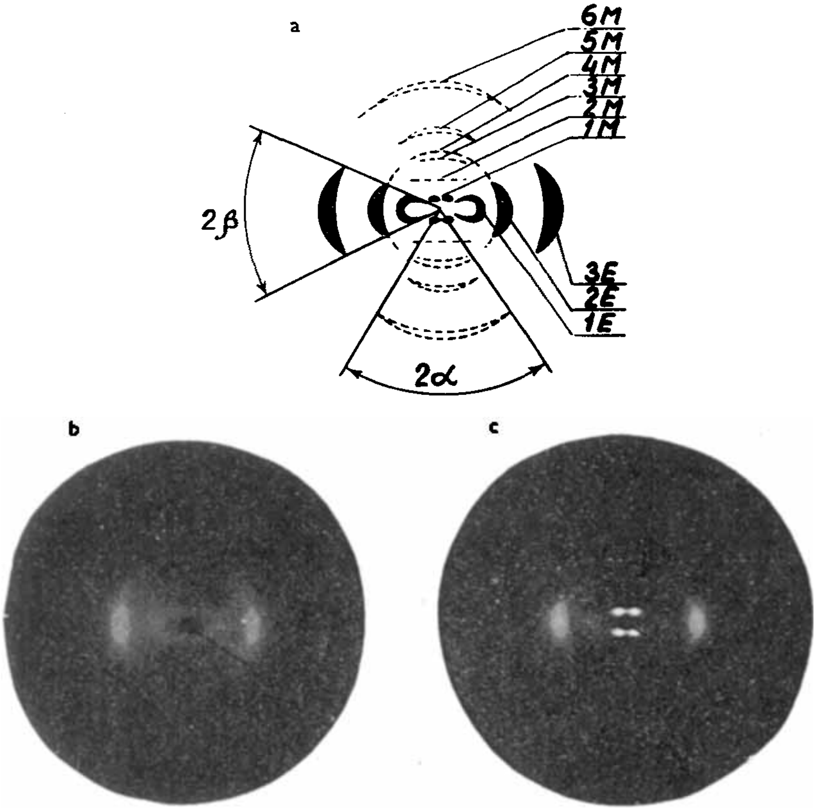

Figure 1. The X-ray diagrams (Cu K_α) and their scheme (Fig. 1 a.) (Cu K_α, Mo K_α) for nematic phase: b. 1, 3 members of series; c. 2, 4–10 members of series; a. The scheme of X-ray diagram on Fig. 1b.

If for *p*-azoxyanisole this reflection corresponds to a reflection representing flat discs in reciprocal space, then for homologous members with molecules of the greatest length, this reflection corresponds to discs in reciprocal space with less thickness approaching the center of the disc (reflections has form of dumbbell). With an increase in temperature, this disc changes first into a disc with uniform thickness; with the transition of the sample into the isotropic state, it changes into a crescent, which

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corresponds with the appearance of a diffusion ring in the X-ray diagram. Apparently this reflection is in the form of dumb-bells due to the fact that the molecules are lined up in the magnetic field, not parallel, but as a certain quite definite angle with respect to the lines of field forces, the angle depending on the diamagnetic anisotropic particle (the molecule, swarm, domain). Naturally, such a distribution of molecules possesses a cylindrical symmetry, which carries the dumb-bell form of the reflection.

With the transition of the substance into the smectic state (decrease of temperature) the dumb-bell reflection, which is peculiar to the nematic states, divides into two spots (their intensity is often different). Clearly, the parallel planes in the smectic sample must correspond in reciprocal space to rods with spots having the period $C^* = 1/C$.

On the X-ray diagrams this reflection divides into two spots. This may result from two main causes:

1. The molecules are inclined with respect to the smectic planes. Taking into account the frequent appearance of spots with different intensity, it may be presumed that it is purely by chance the molecules are inclined predominantly on one side with respect to the principal axis Z (different numbers of swarms of molecules with parallel and anti-parallel packing).
2. A statistical rotation of reciprocal space takes place at an acute angle with respect to C^*-axis.

The first case is difficult to explain, if we take into consideration the presence of the equatorial diffusion reflection $1E$, which falls symmetrically with respect to meridional direction. Evidently this arrangement of molecules in planes must give rise to the splitting of these two equatorial reflections into four, which are situated at angle $\propto$ to the meridian.

Hence, case 2 is more likely, as it corresponds to the incline of planes at angle α with respect to the principal axis Z and is peculiar to statistical inclinations of molecules in planes, which causes the smearing of the reflection $1E$ into arcs (meridional reflection $1M$ is very sharp, which indicates the strictly parallel position of the smectic planes). It was very interesting to determine the regularity of change of the angle formed by the directions of maximum darkening for this reflection. We designate its angle 2α (Fig. 1). In the nematic phase, this angle remains constant (as far as we were able to determine) with variations of temperature. Approaching the clear-point, reflection 1*M* smears out and the measurement of angle 2α loses its meaning. With the transition from the nematic to the smectic phase, angle 2α increases two or three degrees. Fig. 2a shows this dependence for 4,4′-di-*n*-heptoxyazoxybenzene. For other members of the series the dependence is analogous. The angle 2α varies with the transition from one member of the homologous series to another. With increase in the number of carbon atoms in the alkyl chain this angle markedly decreases (Fig. 2b). Obviously in future investigations it will be interesting to compare the variation of the diamagnetic properties of the compounds in the homologous series.

From meridional reflection 1*M* it is possible to get additional interesting information.

If we assume that in smectic phases, the interplanar dimension spacing *d* corresponds to the reflection 1*M*, we can obtain the dimension between smectic planes. For nematic phases the

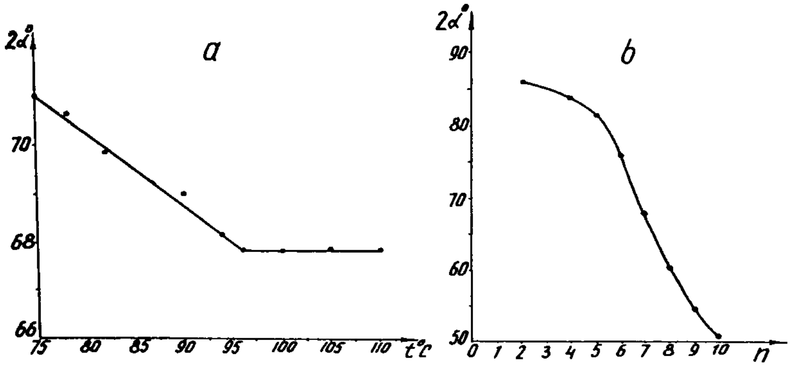

Figure 2. a. The temperature dependence of angle 2α for 4,4′-di-*n*-heptoxyazoxybenzene; b. Angle 2α against number of carbon atoms in alkyl chain.

reflection gives the mean space between centers of molecules along the axis of texture.

According to the general principles of crystallochemistry,[3] a model of a molecule can be constructed and its approximate length l determined. A comparison of " d " and " l " shows convincingly that for all members of the series the estimated length of a molecule is always less than the interplanar spacing d (Table 2).

TABLE 2

No.	Alkyl Group	t °C Exposit‡	d Å (1M)	l Å	$\beta = \arccos(d/l)$	β_{exp}	S
1	CH_3	121	15.80	18.80	28° 36′	29°	0.65
2	C_2H_5	140	18.20	20.1	25° 12′	25°	0.75
3	C_3H_7	116	19.38	22.7	31° 30′	32°	0.59
4	C_4H_9	110	22.78	25.4	26° 24′	27°	0.69
5	C_5H_{11}	80	22.55	28.0	28° 48′	29°	0.65
6	C_6H_{13}	80	27.00	30.4	27° 00′	28°	0.68
7	C_7H_{15}	98	28.80	33.0	29° 12′	30°	0.64
8	C_8H_{17}	110	31.45	33.5	27° 30′	28°	0.68
9	C_9H_{19}	118	32.20	38.00	32° 00′	33°	0.57
10	$C_{10}H_{21}$	120	33.75	40.5	38° 24′	34°	0.54

‡ The temperature at which were made X-ray diagrams of liquid crystal.

These facts indicate that the molecules are inclined to the principal texture axis Z. From the relation $d/l = \cos\beta$ it is possible to calculate the mean angle of incline β (Table 2). It is clear that the approximate value of this angle may be determined by measuring the angle within the limits of which the principal equatorial reflection $2E$ lies (Fig. 1). As shown in Table 2, the values for angle β determined by these two methods coincide sufficiently with one another. Without making any claims to great accuracy, it is nevertheless possible to attempt an evaluation of the degree of orientation in liquid crystals, using the mean angle of incline of the molecules to the axis of texture:

$$S = 1 - \frac{3}{2}\sin^2\beta$$

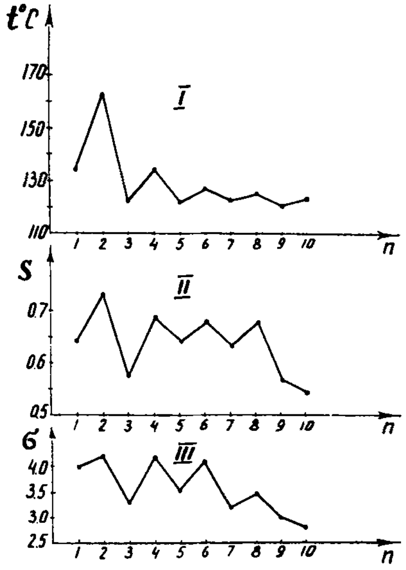

Figure 3. The clear-point (1), the degree of orientation S (II), and the area under peak β(III) against number of carbon atoms in alkyl chain.

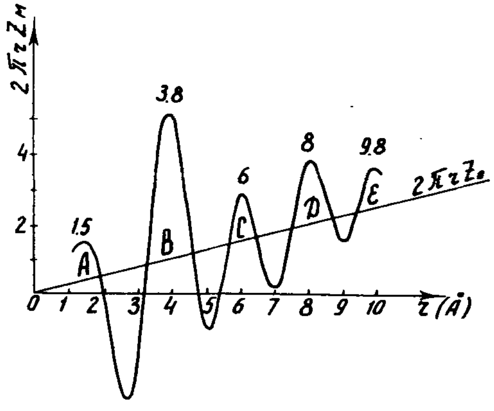

Figure 4. The function of cylindrical distribution for nematic phase of 4,4′-di-n-butoxyazoxybenzene.

(t = 110 °C, H = 17,200 gauss)

The values S are given in Table 2 and Fig. 3. The regularity of the change of the degree of orientation of S in the homologous series is clearly observed. It is greater for even and less for uneven members of the series. This regularity is accounted for by the regularity of change of the clear-point in the homologous series. The evaluation of S was made from the X-ray diagrams which were obtained at temperatures 5° above the transition point from solid crystal to nematic liquid crystal, or from smectic liquid crystal to nematic mesophase. The degree of orientation S turns out to be greater in those cases where the temperature of transition into the isotropic liquid for certain homologous members (even numbers of carbon atoms) is higher than for neighboring members (uneven number of carbon atoms). It is natural that

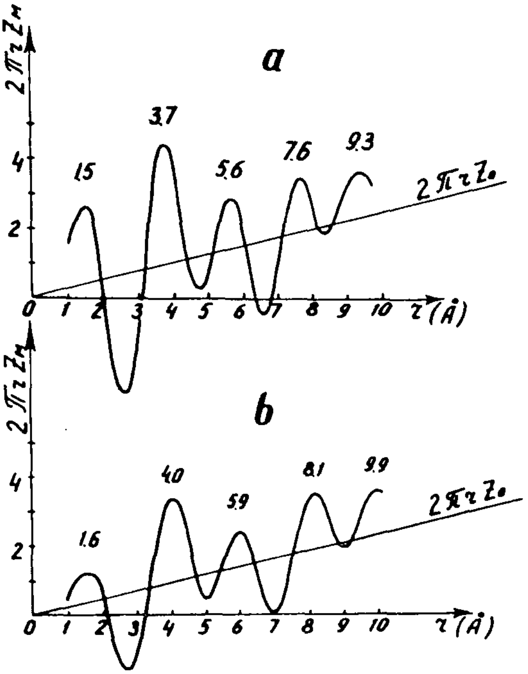

Figure 5. a. The functions of cylindrical distribution for smectic (a) (t = 80 °C) and nematic (b) phases (t = 110 °C) of 4,4′-di-n-octoxyazoxybenzene in magnetic fields 17,200 gauss.

under comparable conditions (strength of magnetic field) the degree of orientation S of a liquid crystal is greater in the case where it is situated farther from the temperature of the transition into isotropic liquid.

The functions of the cylindrical distribution of the axis of the molecules, $2\pi r Z_m(r)$,[4,5,6] were calculated. The form of these functions for nematic phases of all homologous members is approximately identical (Fig. 4). Only the displacement of the peak toward greater values of the dimension for the higher members of the homologous series (from 3.8 Å to 4 Å) is observed. It is interesting that the area under this peak and its height show the same regularity of change during the transition from one homologous member to another as is found for the degree of orientation S (Fig. 1) of members of the series.

In comparing the function $2\pi r Z_m(r)$ for nematic and smectic phases, a displacement of peaks to greater values for the nematic phase is clearly observed (Fig. 5). This is indicated in the decrease of the degree of orientation S with the transition into the nematic phase.

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