

## XRay Diffraction Intensity of the Two Liquid Phases of ParaAzoxyanisol

G. W. Stewart

Citation: [The Journal of Chemical Physics](#) **4**, 231 (1936); doi: 10.1063/1.1749827

View online: <http://dx.doi.org/10.1063/1.1749827>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/4/4?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Recover the phases from intensity data of x-ray diffraction](#)

Appl. Phys. Lett. **73**, 909 (1998); 10.1063/1.122034

[Bibliography on X-Ray Diffraction Studies of Liquids](#)

Am. J. Phys. **40**, 1343 (1972); 10.1119/1.1986833

[Apparatus for XRay Diffraction Studies of Liquids](#)

Rev. Sci. Instrum. **36**, 449 (1965); 10.1063/1.1719596

[The Diffraction of XRays by Liquid Oxygen](#)

J. Chem. Phys. **10**, 504 (1942); 10.1063/1.1723757

[XRay Diffraction in Liquid Ethyl Alcohol](#)

J. Chem. Phys. **7**, 878 (1939); 10.1063/1.1750336

---



# THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 4

APRIL, 1936

NUMBER 4

## X-Ray Diffraction Intensity of the Two Liquid Phases of Para-Azoxyanisol

G. W. STEWART, *University of Iowa*

(Received January 31, 1936)

Further experiments with greatly improved conditions show that the liquid crystal swarms or groups of molecules at 125°C give an x-ray diffraction intensity distribution curve which is similar to but not exactly like that of the transparent liquid at 150°C. The former has a greater intensity at the peak, and a narrower peak with a steeper slope on the zero angle side. The group in the liquid crystal, about  $10^6$  molecules, does not have the same structure as the very much smaller and less stable cybotactic

group in the liquid. The latter does not need to contain more than 25 to 50 molecules to account for the experimental evidence. The liquid crystal swarms may be descriptively regarded as a regimentation of modified cybotactic groups. A new temperature effect is strongly suggested by the apparent orientation of swarms in the liquid crystal with molecular axes perpendicular to the temperature gradient.

**D**IFFERENCES in experimental results for the x-ray diffraction intensity of liquid crystalline para-azoxyanisol, as reported by two observers,<sup>1, 2</sup> have rather required the additional experiments which are here reported. The question to be answered by experiment is: What is the change, if any, in the x-ray diffraction intensity in passing from the liquid crystalline to the transparent liquid state? An interpretation from the facts is of importance in a consideration of the difference between the two phases.

### EXPERIMENTAL METHOD

The experimental method has been to place the sample in a thin-walled cylindrical blown glass tube having a diameter of 0.7 to 1.0 cm and a transmission of Mo  $K\alpha$  radiation of approximately 80 percent. The orientation of the liquid crystal by the walls of the container would be effective for a distance not greater than 0.02

mm<sup>3</sup> and may be neglected. This container was placed in a cylindrical electric oven, internal diameter 7.3 cm, height 16.0 cm, with each of the two openings for the x-rays covered with two separated pieces of writing paper. The exit was kept small by attaching it to the rotating ionization chamber arm of the spectrometer. The apparatus was of the type described elsewhere,<sup>4</sup> spectrometer, methylbromide ionization chamber, zirconium and strontium filters for Mo  $K\alpha$  radiation, but with the electrometer replaced by a vacuum tube amplifying circuit.<sup>5</sup> The specimen tube, 9 cm high, was enclosed in a cylindrical writing paper jacket. This prevented the air convection currents caused by oven circulation and produced a very steady temperature condition within. Two thermocouple junctions were

<sup>3</sup> Ornstein and Kast, *Trans. Faraday Soc.* **29**, 931 (1933).

<sup>1</sup> G. W. Stewart, *Phys. Rev.* **38**, 931 (1931) and *Trans. Faraday Soc.* **29**, 982 (1933).

<sup>2</sup> W. Kast, *Ann. d. Physik* **19**, 571 (1934).

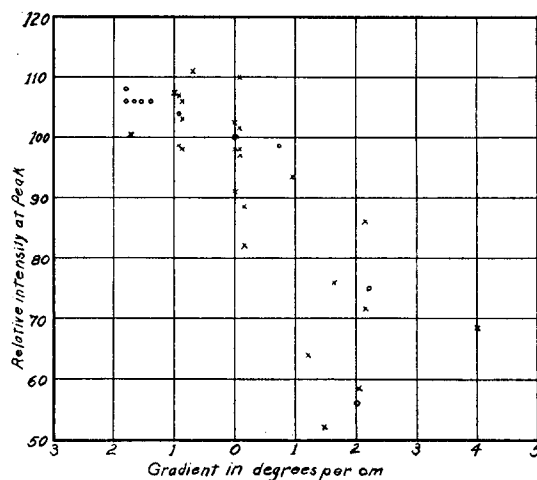
<sup>4</sup> Stewart, *J. Chem. Phys.* **2**, 147 (1934), except that one of the Soller slits was 20 cm in length and the other 12 cm the dimensions of a single slit being  $1.5 \times 0.8$  cm. A crystal diffraction curve showed a line width of  $36''$ .

<sup>5</sup> An FP-54 (G.E. Co.) tube was employed with a balanced circuit as described by DuBridge and Brown, *Rev. Sci. Inst.* **4**, 532 (1935).

inserted through the jacket to within 2 mm of the wall of the tube and separated vertically by 1.5 cm, being within the level of the x-rays but not in the beam. A fan for vertical circulation was placed at the bottom of the oven. So effective was the surrounding paper cylinder that in practically all adjustments of temperature gradient at the tube, no change was produced by the operation of the fan. The presence of the paper made the production of temperature change in the liquid a very slow one indeed and it became necessary to wait at least three hours for a reasonably steady condition to be reached after the current in the heating coils was finally adjusted.

### EXPERIMENTAL RESULTS

In the case of the liquid phase the constancy of temperature was of no importance, for convection currents in the liquid did not alter the x-ray diffraction. On the other hand, as is well known, currents in the liquid crystalline phase do alter the orientation<sup>6</sup> of the liquid crystalline swarms or groups. The x-ray diffraction is very sensitive to this orientation as is shown by experiments<sup>7</sup> with an imposed magnetic field. In fact, it is just in the effect of convection currents that the difference between the results of the author and of Kast, referred to above, can be explained. With all the care exerted in the present experiment it is doubtful if convection currents in the liquid crystal were at any time entirely eliminated. As may be supposed, the absence of temperature gradient as shown by the thermocouples, together with the constancy of diffraction intensity, might be used to determine when the optimum nonconvection condition of the liquid crystal was obtained. Nonrotation of the glass container was necessary<sup>8</sup> because even a small constant rotation produced an alignment of liquid crystal groups or swarms. A reduction in peak intensity of 16 percent was produced by a rotation about the vertical axis of the container of 18 r.p.m. This effect corresponds



different times, for each one is an average of several measurements which differed among themselves by only 1 to 4 percent. The points are separated in time by at least several hours, and usually a day or more. The ones represented by circles were reduced to the same standard by assuming the value 100 zero temperature gradient. The remainder were adjusted assuming the transparent liquid to give a maximum of 85. On each occasion one or the other of these practically equivalent checks was employed. Apparently great care would not always produce the same intensity diffraction for the same temperature condition. This indicates that the same degree of preferred orientation, even randomness, could be only approximated and not obtained at will.<sup>9</sup> With reference to the depressed value of the maximum with the top at a higher temperature as shown in Fig. 1, an interpretation of the preference for horizontal orientation will later be discussed. For the moment attention is called to the fact that zero gradient may be accepted as a satisfactory condition of randomness of orientation, for it is at least the best obtainable. Throughout the work, the steadiness of the deflection with the transparent liquid as well as the apparent immunity from effect of a temperature gradient, caused one to accept the interpretation that, in the liquid phase, there was no preferential orientation in the body of liquid,

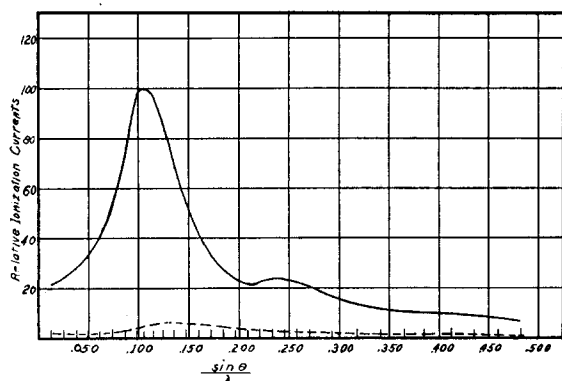


FIG. 2. Relative total intensity diffraction curve for the transparent liquid at approximately 150°C.

<sup>9</sup> Naturally the liquid crystal swarms are not all of the same size. Even the average size may not be independent of the direction of approach to a given temperature. Moreover Herrman (*Zeits. f. Krist.* 92, 49 (1935)) has recently found differences in diffraction of certain liquid crystals which depends upon the direction in which temperature has changed.

0.2 cc in volume. Obviously the thermocouples just outside the thin-walled tube only approximated the temperature of the liquid on the interior, and this may be the cause in part of the irregularities in Fig. 1. But no interpretations are vitiated by this approximation.

### Transparent liquid diffraction

In Fig. 2 is represented a mean curve for the transparent liquid at 150°C. Observations, not less than twelve, were made at each point indicated by the short vertical lines at zero ordinate. The maximum occurs at  $(\sin \theta)/\lambda = 0.105$  ( $2\theta = 8.55$ ) and minor peaks at  $(\sin \theta)/\lambda = 0.248$  and  $0.420$  ( $2\theta = 20.3$  and  $34.6$ , respectively).  $2\theta$  is the diffraction angle read on the spectrometer. As indicated in the foregoing the diffracted intensity was always found to be independent of convection currents. The dotted curve is the effect of the glass container which has not been subtracted from the observed intensity.

In all the diffraction curves in this report corrections have been made for the stray radiation in the neighborhood of  $2\theta = 0^\circ$ , this being of noticeable magnitude from  $2\theta = 1^\circ$  to  $5^\circ$  or  $6^\circ$ . Correction for absorption, incoherent radiation and shape of vessel are not necessary for the comparisons to be made of the two phases.

### Liquid crystal diffraction

In Fig. 3 is represented a mean diffraction curve for the liquid crystal at 125°C. The maximum occurs at  $(\sin \theta)/\lambda = 0.109$  ( $2\theta = 8.84^\circ$ ), a minor peak at  $(\sin \theta)/\lambda = 0.248$  and possibly another at  $0.420$ . Fig. 3 was obtained by no less

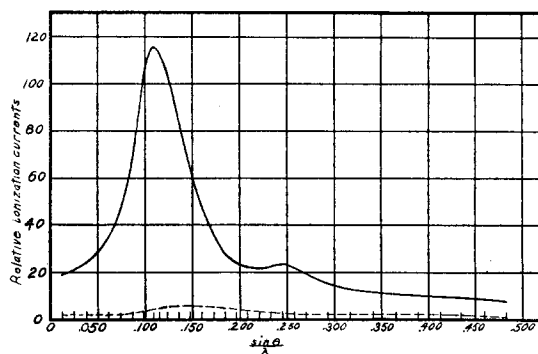


FIG. 3. Relative total intensity diffraction curve for the liquid crystal at approximately 125°C.

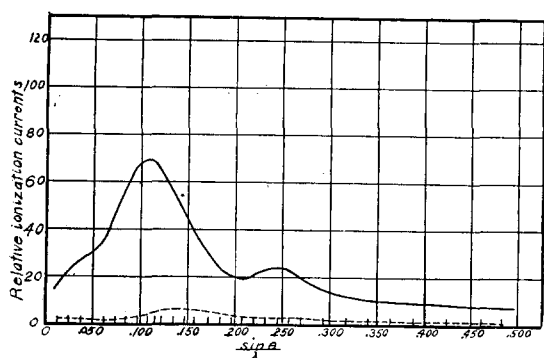


FIG. 4. Relative total intensity diffraction curve for the liquid crystal at approximately 125°C with a temperature gradient of 2.07°/cm, temperature increasing upward.

than five complete series over the entire range, each with four observations at angles indicated by the short vertical line on the zero coordinate. Also there were three additional partial checks at different times. In the five, one had a negative gradient (meaning higher temperature at the bottom) of 1.73°/cm, another of 1.00°/cm and the remaining three have less than 0.1°/cm. The degree of similarity of intensity of scattering at the peak angle in the five series, taken at different times is shown by the respective relative values 117.5, 113.5, 112, 113.5, 117.5 in the five complete series, and 117, 113 and 117.5 in the three partial checks. It is thought that even in these experiments where, for the most part, the temperature gradient is less than 0.1°/cm, there is a residue of convection currents which prevents random orientation of the swarms. This opinion arises from the fact that on three occasions a less intensity of the peak was observed, but in each of them the series was not regarded as satisfactory. Nevertheless the peak intensity was always greater than that with the transparent liquid and the peak was always narrower. Thus, the only error in adopting Fig. 3 as correct for the liquid crystal would be quantitative and not qualitative. The interpretations drawn would remain.

In Fig. 4 is shown the diffraction curve for the liquid crystal at a positive gradient of 2.07°/cm, the higher temperature at the top. The maximum is at  $(\sin \theta)/\lambda = 1.082$  ( $2\theta = 8.84^\circ$ ), a minor peak at  $(\sin \theta)\lambda = 0.248$  and possibly another at 0.420. Fig. 4 is not a mean, using varied conditions, but a measurement made on a single day with four

observations at each angle used. It is presented to indicate a case of non-random orientation.

In Figs. 2, 3 and 4 the ordinate scales have been chosen so that the curves represent the correct relative experimental peak intensities.

### Fluctuations in preferred orientation

The constancy of the galvanometer deflection for a given spectrometer angle was greatest with the liquid and least with the liquid crystal, the fluctuations in the latter being about twice those in the former. These fluctuations were noticeable from reading to reading, taken 10 sec. apart. In the liquid crystal phase there were also fluctuations of a longer time duration, sometimes 10 minutes in magnitude. The stability in the "depressed" state of liquid crystal was almost as good as that in the liquid phase.

### Areas of diffraction curves

The areas under the curves plotted with relative intensities as ordinates but with the angle of the spectrometer,  $2\theta$ , as abscissae, varying from  $0^\circ$  to  $40^\circ$ , are as follows:

Fig. 2	55.2 liquid
Fig. 3	58.7 liquid crystal
Fig. 4	48.8 liquid crystal

It is assumed that the difference in interference effects in the two phases would be intermolecular and hence would occur within the angular range chosen. If the orientation of the molecular groups were, in all three cases, without a preferred direction, then the areas would be the same differences in density being disregarded. Difference in areas may be used as indicative of difference in preferred orientation, for the magnetic experiments with liquid crystals show that an alignment of swarms (and molecules) perpendicular to the incident x-ray beam, reduces the magnitude of the diffraction intensity or increases it depending upon whether this alignment is in the plane of the incident and diffracted beam or perpendicular thereto (or, in these experiments, horizontal or vertical). Assuming that, in the liquid phase, the cybotactic groups are without preferred orientation, then the comparison of areas and intensities shows that, in Fig. 3, the molecular swarms have a slightly preferred vertical orientation and in Fig. 4 a larger preferred horizontal orientation.

### Width of diffraction peak

The width of the liquid crystal peak is less than that of the liquid. The width at 0.6 of the maximum height for Fig. 3 is 8 percent narrower for the liquid crystal than for the liquid in Fig. 2. In Fig. 4, with a distinct preferred horizontal orientation, the width is perhaps 20 percent greater.

### Steepness of slope on inner side of diffraction peak

Measurements of the slopes of the curves at 0.6 the heights of peaks show that on the inner side this angle for the liquid crystal, Fig. 3, is 2 percent greater than for the liquid. This is also true for the additional measurements above mentioned in which the peak value was not so great. In the "depressed" liquid crystal curve, Fig. 4, the slope is approximately 14 percent less.

### Temperature effect

The temperature difference, 25°C, and the corresponding change in density, 1.159 to 1.131<sup>10</sup> requires consideration in the comparison of the above diffraction curves. The ratio of the scattered intensities at any angle may be expressed as  $I_1/I_2 = (\rho_1/\rho_2)e^{\exp(\mu_2 - \mu_1)t}$  wherein  $I$  refers to intensities,  $\rho$  to densities,  $\mu$  to the absorption coefficients, and the subscripts 1 and 2 to temperatures, 125°C and 150°C, respectively. Because the samples are at practically the optimum thickness for each, the correction for the difference in densities proves to be about 0.5 percent and is therefore omitted from consideration.

### Position of diffraction peaks

The major peak values of  $(\sin \theta)/\lambda$ , liquid and liquid crystal, differ by three to four percent. It is believed that the accuracy of the location of the peaks is at least sufficient to negate any thought that the difference is caused by expansion. There is probably no significance in the differences in magnitudes of the two minor peaks in Figs. 2, 3 and 4, for the accuracy in the curve for the liquid was somewhat greater. These diffraction peaks at  $(\sin \theta)/\lambda = 0.248$  and 0.420 are found in approximately the same positions as those in liquid benzene as shown by Katzoff<sup>11</sup>  $(\sin \theta)/\lambda = 0.255$  and 0.425 and by Wierl<sup>12</sup> using

electron diffraction ( $(\sin \theta)/\lambda = 0.227$  and 0.421). One would anticipate that these minor peaks are caused by atomic arrangement in the benzene ring in the molecule of para-azoxyanisol.

### DISCUSSION

As already described, sufficient corrections have been made in the curves Figs. 2–4 to enable direct comparison to be made. The results are accurate enough to be used as a basis for the following interpretations and conclusions.

1. A general consideration of x-ray diffraction in liquids and of the constitution of liquid crystals, coupled with these and other x-ray diffraction experiments in para-azoxyanisol, leads to the conclusion that "structure" exists in both phases. In the liquid crystal it may be described as a swarm, consisting of about  $10^5$  or  $10^6$  molecules<sup>13</sup> with axes parallel and with mobility of the molecules within the swarm much less than in the very much smaller cybotactic groups in the liquid state.

2. A conclusion as to the exact relative scattered intensities at the diffraction-intensity-curve peaks of the liquid crystal and of the liquid, both with randomness of orientation of molecular groups, is not possible. The temperature conditions would lead one to claim Fig. 3 as representing this case for the liquid crystal. Here the peak intensity is 15 percent higher than that of the liquid. But both the greater area of the curve in Fig. 3 as compared with Fig. 2, and the occasional lesser intensity of the former found by experiment, lead one to conclude that the peak intensity with the liquid crystals in random orientation is greater than that with the liquid, the difference being of the order of five to fifteen percent. But one can say with certainty that the greater sharpness of the diffraction peak and steeper inner slope with the liquid crystal show more regularity of structure in that phase.

3. The differences in preferred orientation of the molecular grouping in the two phases, the liquid having no such preference, also indicates a difference in structure. In a liquid crystal, convection and temperature gradient (see below) cause orientation. The susceptibility in this

<sup>10</sup> Jaeger, *Zeits. f. anorg. Chemie* **101**, 152 (1917).

<sup>11</sup> Katzoff, *J. Chem. Phys.* **2**, 841 (1935).

<sup>12</sup> Wierl, *Ann. d. Physik* **8**, 521 (1931).

<sup>13</sup> For evidence for this value Ornstein and Kast, *Trans. Faraday Soc. Discussion* **29**, 931 (1935).

respect may be explained by the very great difference in magnitude of regions or groups in which noticeable orderliness or molecular arrangement occurs.

4. The depression and greater width of the depressed curve peak of the liquid crystal, and the discussion of areas are in harmony with the conclusion that a small temperature gradient produces a preferred orientation of the liquid crystal "swarms" or groups with their longitudinal axis perpendicular to the direction of the maximum temperature gradient. One hesitates to adopt this conclusion without reservation, for a detectable turning moment caused by the scattering of the elastic waves with such a small gradient seems surprising. The experiments were so carefully performed, however, that one may emphasize the striking agreement of this interpretation with the results of the numerous experiments reported in Fig. 1. Something certainly occurs that is, in our experiments, equivalent to this interpretation. At any rate these experiments may be regarded as adding confirmatory evidence to that from magnetic and electric studies, in emphasizing the relatively large size of these liquid crystal swarms.

5. The range of temperature in the liquid crystalline experiments would, with greater

refinement, be of importance. The temperatures for the present observations varied from 122°C to 130°C without any noticeable effect on the location of the peak of the intensity diffraction curve or its magnitude. This does not mean that there can be no gradual alteration in structure in the liquid crystalline state, but only that it is small.

6. The size of the liquid crystalline groups must be quite large, as already stated. In the transparent liquid one has no definite measure of the size of the cybotactic groups. Experience in computation of diffraction intensity curves of liquids by using a density function leads one to expect that the size of the striking regularity in liquid groups of para-azoxyanisole would not need to be over 30Å in its longer dimension with a gradual fading of regularity with distance. Thus one would anticipate no noticeable optical scattering. The large liquid crystal group is not merely an orderly aggregate of the small liquid groups for there is a definite change in structure. But the much larger aggregation of closely similar groups is a prominent characteristic of the change of phase.

I wish to acknowledge with thanks the research assistance of Dr. W. D. Phelps and Mr. B. J. Miller in the experiments herein recorded.

APRIL, 1936

JOURNAL OF CHEMICAL PHYSICS

VOLUME 4

## X-Ray Diffraction Study of Liquid Sodium

L. P. TARASOV AND B. E. WARREN, *George Eastman Laboratory of Physics, Massachusetts Institute of Technology*

(Received January 17, 1936)

The x-ray scattering curve for liquid sodium is obtained photographically with Mo  $K\alpha$  radiation, monochromatized by reflection from rocksalt. By a Fourier analysis of the corrected scattering curve, one obtains directly the radial distribution of atoms about any atom in the liquid.

The distribution curve shows a first concentration at about 4.0Å, followed by a dip at 5.0Å, and a second concentration at about 7Å. The significance of the curve as giving a picture of a simple monatomic liquid is discussed.

### INTRODUCTION

IT has been shown<sup>1,2</sup> that from a Fourier analysis of the x-ray scattering curve of a liquid, one gets directly the radial distribution of atoms surrounding any average atom. It is of

considerable interest to apply the method to a monatomic liquid, and get directly and uniquely a picture of this simplest type of liquid. Debye and Menke have successfully applied the method to liquid mercury. While mercury is an excellent example of a simple liquid, it is not however well suited to x-ray study, since the absorption co-

<sup>1</sup> Zernike and Prins, *Zeits. f. Physik* **41**, 184 (1927).

<sup>2</sup> Debye and Menke, *Erg. d. tech. Röntgenkunde*, II.