

## The Diffraction of X Rays by Liquid BenzeneCyclohexane Mixtures

A. Eisenstein and N. S. Gingrich

Citation: *J. Chem. Phys.* **10**, 195 (1942); doi: 10.1063/1.1723706

View online: <http://dx.doi.org/10.1063/1.1723706>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v10/i4>

Published by the AIP Publishing LLC.

---

### Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: [http://jcp.aip.org/about/about\\_the\\_journal](http://jcp.aip.org/about/about_the_journal)

Top downloads: [http://jcp.aip.org/features/most\\_downloaded](http://jcp.aip.org/features/most_downloaded)

Information for Authors: <http://jcp.aip.org/authors>

## ADVERTISEMENT

**SHARPEN YOUR  
COMPUTATIONAL  
SKILLS.**



Subscribe for  
**\$49** | year



**computing**  
in **SCIENCE & ENGINEERING**

Scientific  
Computing  
with GPUs

# THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 10

APRIL, 1942

NUMBER 4

## The Diffraction of X-Rays by Liquid Benzene-Cyclohexane Mixtures

A. EISENSTEIN AND N. S. GINGRICH  
*University of Missouri, Columbia, Missouri*  
(Received February 2, 1942)

The x-ray diffraction pattern of a liquid mixture of benzene and cyclohexane is investigated, using both the photographic method and the Geiger-Mueller tube counter method. The fine structure on the main peak, and a secondary peak as reported by Bell and Davey, cannot be obtained. It is concluded that these features do not exist in this pattern.

### INTRODUCTION

IN a recent article, Bell and Davey<sup>1</sup> reported that they found some very unusual fine structure in the main diffraction peak from benzene-cyclohexane mixtures. A repetition of this work is highly desirable for three reasons: first, no liquid x-ray diffraction pattern has heretofore shown fine structure of this type; second, this particular mixture has been worked upon by Ward,<sup>2</sup> by Murray and Warren,<sup>3</sup> and by Bell and Davey,<sup>1</sup> and all three reports of these workers are in disagreement; third, the extent of succeeding arguments based on the results of Bell and Davey is so great that it is desirable to examine critically the experimental basis for these arguments. The present authors have made an experimental study of the diffraction of x-rays by benzene, by cyclohexane, and by one mixture of these liquids, using both the photographic and the Geiger-Mueller counter methods of detection of the x-rays. Particular attention was given to the controversial matter of fine structure in the main peaks of the mixture.

<sup>1</sup> P. H. Bell and W. P. Davey, *J. Chem. Phys.* **9**, 441 (1941).

<sup>2</sup> H. K. Ward, *J. Chem. Phys.* **2**, 153 (1934).

<sup>3</sup> G. E. Murray and B. E. Warren, *J. Chem. Phys.* **7**, 141 (1939).

### EXPERIMENTAL

Benzene and cyclohexane of high purity were purchased, and no further purification of the liquids was attempted. The index of refraction of the benzene used here was measured and found to be 1.5008 at 20°C while that used by Bell and Davey was given as 1.5009. The index of refraction of the cyclohexane used here was measured and found to be 1.4263 at 20°C, and that used by Bell and Davey was given as 1.4263. The mixture studied was approximately 50 percent benzene—50 percent cyclohexane by volume, and its index of refraction was 1.4597. The cell holder consisted of a brass cylinder 1.1 cm long and 1.9 cm diameter with thin Cellophane windows clamped on the ends. After the various liquids were contained in the cell for several days, tests on the index of refraction were made. In the cases of benzene and of cyclohexane alone, no difference in the index of refraction was ever obtained. In the case of the mixture, no difference greater than 0.0001 was obtained when adequate care in rinsing the cell was taken and when precautions were taken against evaporation through the filling tube.

Two cameras were used in the photographic studies here reported, a small camera of 9.20-cm

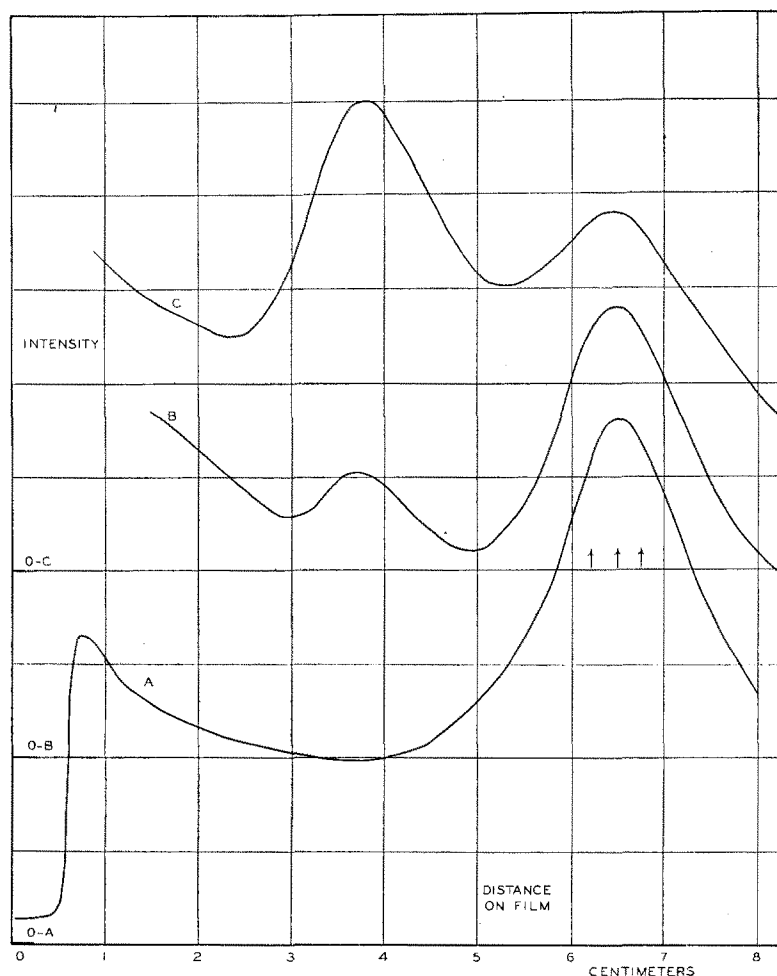


FIG. 1. X-ray diffraction patterns of a 50-50 mixture of liquid benzene and cyclohexane, showing intensity as a function of distance on the films in cm. One cm corresponds to about  $1^{\circ} 16'$ . Curve *A* taken with Mo  $K\alpha$  radiation; curve *B* with Mo radiation filtered through 0.08 mm Zr equivalent; curve *C* with Mo radiation filtered through the above Zr and 0.132 cm Al.

radius and a large camera of approximately 44.6-cm radius. Using the small camera, no indication of fine structure on the main peak could be obtained with either pure liquid or with the mixture, but it was observed that in pictures taken with filtered radiation a weak peak appeared at nearly half the angle for the main peak whereas with crystal reflected Mo  $K\alpha$  radiation, no secondary peak could be observed. Further work on the mixture was done using the large camera and three different types of radiation, first, crystal reflected Mo  $K\alpha$ , second Zr filtered Mo radiation, and third, Zr and Al filtered Mo radiation. Intensity curves obtained from micro-

photometering typical films are shown in Fig. 1. The intensity, computed in the usual manner, is plotted as a function of distance on the film from the center of the film. In the lower curve, taken with Mo  $K\alpha$  crystal reflected radiation, it is to be noted, first, that no fine structure appears on the main peak, and second that no secondary peak at roughly half the distance (or angle) of the main peak can be detected. This is in contradiction to the results of Bell and Davey who state that in all cases a small intensity peak was observed at about  $4^{\circ}$ , and which had an intensity approximately one-eighth of the high intensity peaks.

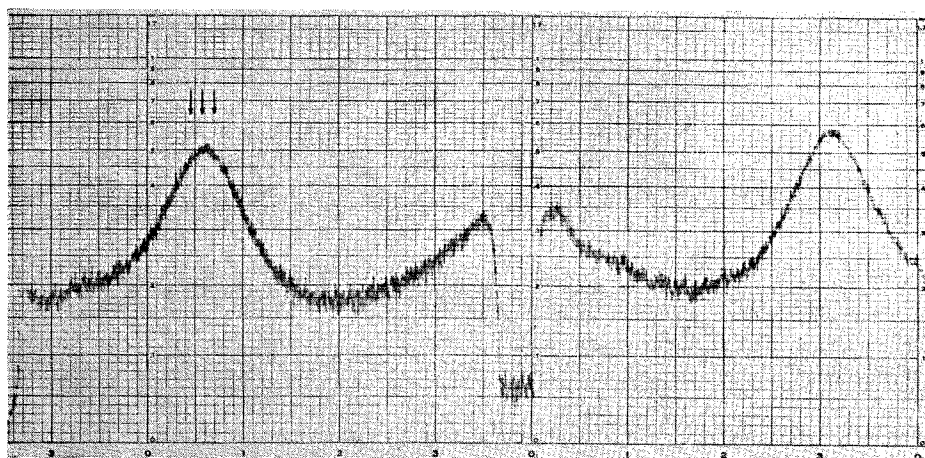


FIG. 2. A microphotometer trace for the benzene-cyclohexane mixture, using  $Mo K\alpha$  radiation, showing the main diffraction peak on each side of the direct x-ray beam. The three arrows indicate the approximate position of the three fine structure peaks as reported by Bell and Davey.

The total horizontal angular divergence of the incident beam was measured photographically to be slightly less than 7 minutes, a value which compares favorably with that of Bell and Davey. The density of the film at the peak was of such value that the fine structure as reported could easily have been detected. Furthermore the region of the film over which the fine structure should have appeared is more than half a centimeter, the general location of the three peaks being indicated by the three spurs in Fig. 1. Both the film and the microphotometer are easily capable of showing up structure of this type. Figure 2 shows a portion of a microphotometer trace typical of the one from which the lower intensity curve of Fig. 1 was obtained. The gradual increase of intensity at small angles is due to air scattering, and the cut-off at still smaller angles is due to a lead strip to suppress the direct beam.

In an attempt to find a possible explanation for the secondary peak at about half the angle of the main peak, two other patterns were obtained. These are shown in Fig. 1, the middle curve being taken with  $Mo$  radiation filtered with  $ZrO_2$  of 0.08 mm  $Zr$  equivalent thickness, the upper curve with  $Mo$  radiation filtered with the same  $Zr$  filter and 0.132 cm of  $Al$ . In both cases, the total horizontal angular divergence of the incident beam was measured photographically to be 10 minutes, and the same camera was

used for all three curves of Fig. 1. The origin of the extra peak at nearly half the angle of the main peak is unquestionably that which is given in detail elsewhere.<sup>4</sup> Residual continuous radiation forming the spurious peak in the  $Zr$  filtered pattern is greatly enhanced in the  $Zr+Al$  filtered pattern due to the greater absorption of 0.710A as compared to that of the continuous radiation at about 0.4A. This rough effective wave-length is that obtained with the x-ray tube operated at about 40 kv peak, whereas Bell and Davey, operating their tube at 59 kv peak, obtained the secondary peak at an angle smaller than that obtained in the present work. This is qualitatively in accord with the above possible explanation of the origin of their secondary peak. In the use of the balanced filter method, extreme care must be taken to be sure that a perfect balance is obtained over the entire region studied, especially when compounds of the balancing elements are used.

Using a Geiger-Mueller tube counter, an amplifier, a scale of sixteen and a Cenco counter, a further study was made of the diffraction of x-rays by the same liquid benzene-cyclohexane mixture as was used above. Rocksalt reflected  $Mo K\alpha$  radiation was passed through two slits as shown in Fig. 3. The total horizontal angular divergence of the incident beam, determined

<sup>4</sup> R. Q. Gregg and N. S. Gingrich, *Rev. Sci. Inst.* **11**, 305 (1940).

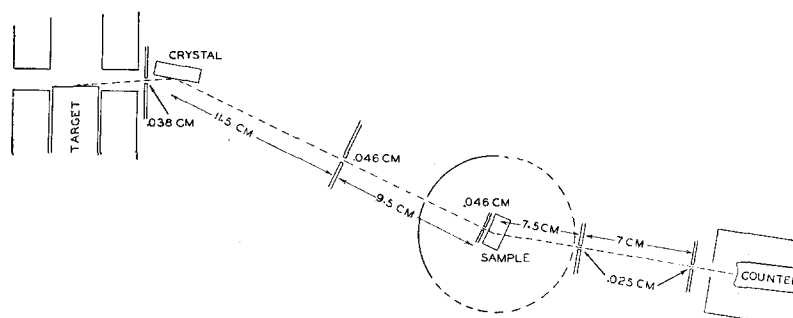


FIG. 3. Geometrical arrangement using the Geiger-Mueller counter method.

largely by the crystal, was measured photographically and found to be 10 minutes. The maximum possible divergence of the diffracted beam through the last two slits is 26 minutes or about the same as that of Bell and Davey's Soller slit system. Many runs were taken, particularly over the top of the main peak and the average of these runs is shown in Fig. 4, together with a reproduction of one of Bell and Davey's curves at roughly the same temperature and mixture. The maximum counting rates in the two cases are roughly 120 per minute in the previous work, and 470 per minute in the present work. The total number of counts per point in the present work is from 12,000 to 16,000. The probable error in the determination of each point was calculated according to the expression

$$\text{p.e.} = \pm 0.67N/(NT)^{1/2}$$

where  $N$  is the rate of counting, and  $NT$  the total counts. This probable error is indicated on the lower curve of Fig. 4. It is seen that though the points do not fall on a perfectly smooth curve, the curve drawn does pass through some portion of the limits of the probable errors. In no case could the results here obtained show a fine structure anywhere near as large as that reported by Bell and Davey. In preliminary runs in which only a few hundred counts per point were taken, irregularities were obtained which, if no further work was done, might conceivably have been interpreted as fine structure, though never, in the present work, as great as that in question. Furthermore, these irregularities appeared quite at random. It was found, for example, that reliable curves could be taken only after midnight and before 7 A.M., during which

time the line voltage was most steady. Even assuming ideal experimental conditions, however, the results, using a Geiger counter, can only be statistical in nature, and fluctuations always appear more prominent on a flat or nearly flat portion of the curve.

### CONCLUSIONS

In a photographic method of recording the x-ray diffraction pattern of a liquid benzene-cyclohexane mixture, especially designed to show any possible fine structure, no significant trace of fine structure could be observed such as

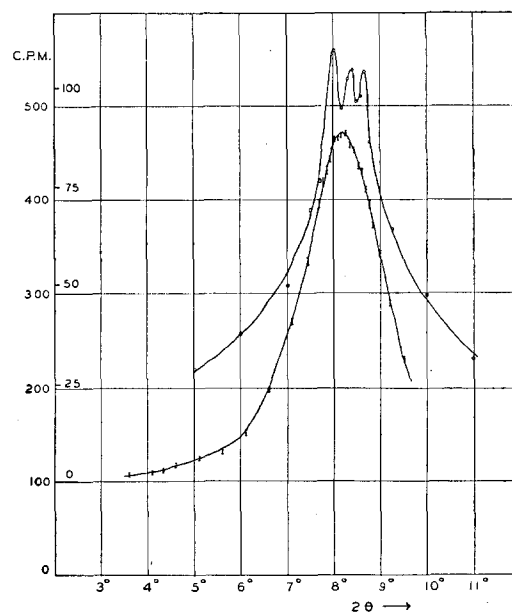


FIG. 4. Lower curve shows counts per minute as a function of scattering angle,  $2\theta$ , as determined in the present work. The probable error is indicated by vertical arrows. Upper curve is one reproduced from Bell and Davey's work.

was reported by Bell and Davey. Further studies were made, demonstrating the fact that impure radiation can give rise to a secondary peak at small angles. It is suggested that it may be possible that this is the origin of Bell and Davey's secondary peak, caused by a slight unbalance of their balanced filters.

Using the Geiger-Mueller counter method, as Bell and Davey did, but with pure radiation and with geometrical conditions at least as good as in their work, no fine structure could be obtained. Slight fluctuations of the observed points about a smooth curve are not large enough to establish

fine structure, and these fluctuations are considered to be wholly statistical.

It is concluded, further, that the extensive deductions made by Bell and Davey are without experimental foundation.

#### ACKNOWLEDGMENTS

It is a pleasure to acknowledge that this work was supported in part by grants from the Rumford Fund of the American Academy of Arts and Science, the American Association for the Advancement of Science, and the Elizabeth Thompson Science Fund.

APRIL, 1942

JOURNAL OF CHEMICAL PHYSICS

VOLUME 10

### The Infra-Red Absorption of Silver Cyanide

W. DAVID STALLCUP AND DUDLEY WILLIAMS

*University of Florida, Gainesville, Florida*

(Received January 17, 1942)

The spectrum of powdered AgCN has been studied in the region  $2500\text{--}1800\text{ cm}^{-1}$ . Intense absorption at  $2178\text{ cm}^{-1}$  is attributed to an oscillation involving the CN group. The CN frequency for AgCN is almost  $100\text{ cm}^{-1}$  higher than the CN frequencies of NaCN and KCN.

INVESTIGATIONS of the infra-red and Raman spectra of the organic cyanides have revealed the existence of a vibrational frequency of approximately  $2245\text{ cm}^{-1}$  which is characteristic of the CN groups, while similar studies of the organic isocyanides indicate that the NC group has a characteristic frequency of  $2146\text{--}2161\text{ cm}^{-1}$ . The simpler inorganic cyanides, NaCN and KCN, have CN frequencies of approximately  $2080\text{ cm}^{-1}$ , while in the complex cyanides such as  $\text{KAg}(\text{CN})_2$  and  $\text{K}_3\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$  the characteristic frequencies are in the neighborhood of  $2150\text{ cm}^{-1}$ .<sup>1,2</sup> It has been suggested by several workers<sup>3</sup> that in inorganic cyanides the CN frequency increases when there

is an increase in the homopolar nature of the M-CN binding.

It seemed desirable to test this hypothesis by determining the CN frequency for a simple cyanide in which the M-CN bond possesses some homopolar properties. As the existing data provide only comparisons of NaCN and KCN with double cyanides and with complex cyanides of the type mentioned above, the study of the infra-red spectrum of AgCN for comparison with NaCN immediately suggested itself, since the homopolar properties of the silver salts are well known.<sup>4</sup>

The silver cyanide used in the present work was prepared by adding an equimolecular amount of potassium cyanide solution to an approximately  $0.1M$  solution of silver nitrate with constant and vigorous stirring. After precipitation was complete, the supernatant liquid was decanted and the precipitate was placed in a two

<sup>1</sup> Summary of the Raman data: K. W. F. Kohlrausch, *Der Smekal-Raman Effekt* (J. Springer, Berlin, 1931), p. 320; J. H. Hibben, *The Raman Effect and Its Chemical Applications* (Reinhold, New York, 1939), p. 452.

<sup>2</sup> Infra-red data: W. Gordy and D. Williams, *J. Chem. Phys.* **3**, 664 (1935); **4**, 85 (1936); F. K. Bell, *J. Am. Chem. Soc.* **57**, 1023 (1935).

<sup>3</sup> P. Krishnamurti, *Ind. J. Phys.* **5**, 651 (1930); R. Samuel and M. J. Khan, *Zeits. f. Physik* **84**, 87 (1933); Volkenshtein, *Acta Physicochim.* (U. S. S. R.) **7**, 315 (1937).

<sup>4</sup> L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, 1940), p. 73.