

X-RAY STRUCTURAL STUDIES OF LIQUIDS AND THEIR SOLUTIONS*

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The method of analysis of experimental intensity distribution curve of X-ray scattered radiation is presented on the example of liquid 1,3,5-triphenylbenzene $C_6H_3(C_6H_5)_3$. The experimental curve obtained for 1,3,5-triphenylbenzene was normalized with respect to two theoretical curves of radiation intensity distribution derived for two different models of the molecule. The curve of reduced radiation intensity was analysed by the reduction method. In the present study, we conducted X-ray diffraction experiments for the first time on 1,3,5-triphenylbenzene, in combination with the method of Blum and Narten. The mean amplitudes of vibration were studied in detail. For the first time, the theoretically predicted model of the 1,3,5-triphenylbenzene structure was experimentally confirmed. The structural data obtainable by X-ray analysis for the studied liquid were discussed. Conclusions concerning the most correct interpretation of experimental data were pointed out.

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1. Motivation and introduction

The conformation of organic compounds is of interest to many structural chemists and physicists who have applied a wide variety of experimental and theoretical methods in their investigations. The present article deals with the structural study of 1,3,5-triphenylbenzene $C_{24}H_{18}$ at 473 K. Studies of 1,3,5-triphenylbenzene in the liquid phase have been very difficult because of its sublimation properties.

The structure of liquid 1,3,5-triphenylbenzene was studied by diffraction of strictly monochromatic X-ray radiation. The measurements of scattered radiation intensity were performed in a wide range of wave vector

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($S_{\min} = 0.925 \text{ \AA}^{-1}$ to $S_{\max} = 14.311 \text{ \AA}^{-1}$). An elementary cell of a crystalline 1,3,5-triphenylbenzene belonging to the orthorhombic system ($a = 7.610(2)$, $b = 19.765(2)$, $c = 11.258(2) \text{ \AA}$, space group $Pna2_1$; $D_v = 1.22$, $D_c = 1.20 \text{ g cm}^{-3}$) contains 4 molecules [1]. However, to the best of our knowledge, diffraction study of liquid 1,3,5-triphenylbenzene was not performed yet.

A value of the packing coefficient was proposed to be a criterion of correctness of the liquid structure model determined. For the proposed model of 1,3,5-triphenylbenzene molecule, the theoretical function of the reduced intensity was calculated and compared to the experimental one.

The studied liquid is an important aromatic compound. The study of structure of 1,3,5-triphenylbenzene may be helpful in the explanation of the mechanism of intermolecular interactions in synthetic polymers [2]. Aliphatic synthetic polymers are added to various aromatic compounds which act as antioxidants. The presence of such compounds often results in morphological changes in the crystal structure and the polymer matrix. It appeared that 1,3,5-triphenylbenzene was also an interesting compound to study the conjugation potential by molecular packing analysis [3]. Triphenylbenzene samples of 99% purity were purchased from Aldrich-Chemie (Germany).

2. Experimental procedure

X-ray scattering in liquid 1,3,5-triphenylbenzene (melting point 444 K) was measured by applying MoK_α radiation, Å . The radiation was monochromatized by reflection from the (002) planes of flat graphite with the angle of monochromatization of $\alpha = 6^\circ 00'$. The angular distribution of the X-ray scattered intensity was measured for the angles $6^\circ \leq 2\theta \leq 120^\circ$ at every 0.2° , where 2θ is the scattering angle. The measurements were performed using the transmission technique. The method is described in detail in [4, 5].

An important problem was the divergence of the primary beam and that diffracted in the vertical direction. In the path of the diffracted beam, there was a system of Soller slits composed of a few thin metallic plane-parallel plates whose separation determined the vertical divergence of the diffracted beam. The divergence of the primary beam in the vertical direction was restricted by a set of collimation slits. The voltage on the probe was optimised to be 1.85 kV. The deviation in intensity due to instability of the diffractometer work were of about 1% in the whole range considered.

The liquid 1,3,5-triphenylbenzene was placed in an electrically heated cell [5] closed on both sides with windows made of Bengal mica of $0.015 \pm 0.001 \text{ mm}$ in thickness. The high temperature camera was previously used to study the structure of naphthalene derivatives [5].

3. Correcting the experimental data

The experimentally obtained function of the angular distribution of the scattered X-ray intensity was corrected to include the background [6], polarization [7], absorption [8] and anomalous dispersion [9]. The scattered X-radiation was normalized to electron units [e.u.] according to the Krogh-Moe [10] and Norman [11] method.

The experimental values of scattered radiation intensity were corrected by the Renninger and Kaplow computer program [12] according to the scheme:

$$I = \left(I^{\text{exp}} - I^{\text{inc}} - I^{\text{mult}} - T \right) PA, \quad (1)$$

where I^{exp} is the experimentally obtained intensity of scattered radiation, I^{inc} intensity of incoherent radiation, I^{mult} intensity of multiple scattering, T apparatus background and noise of the analysing system, P polarizing factor, and A absorption factor.

4. Determination of the structure of 1,3,5-triphenylbenzene. Mean amplitudes of vibration

To determine the conformation of the molecule, we use the modified Debye equation [13]

$$i_m(S) = \left[\sum_{uc}^N \sum_{i \neq j}^N f_i f_j A_{ij} \frac{\sin(S\bar{r}_{ij})}{S\bar{r}_{ij}} \right] \left[\sum_i^N f_i(S) \right]^{-2}. \quad (2)$$

In this equation, \bar{r}_{ij} is the distance between two atoms i and j (which may or may not be linked by a chemical bond), and A_{ij} is an exponential term which allows for the fact that the atoms within the N — atomic molecule — are not strictly at rest but are vibrating with respect to each other. A_{ij} has the form of $\exp \left[-\frac{\langle u_{ij} \rangle}{2} S^2 \right]$, where $\langle u_{ij} \rangle$ is the root-mean-square variation in the distance \bar{r}_{ij} between pairs of atoms. From the best values of these damping factors, the average amplitudes of vibration of the different pairs at atoms may be obtained. In Eq. (2), f_i and f_j are the atomic scattering factors for the i^{th} and j^{th} atoms.

The sum of atomic scattering factors is determined by the expression

$$\sum_{j=1}^n f_j(S) = 3f_{\text{C}_6\text{H}_5} + 3f_{\text{CH}} + 3f_{\text{C}}, \quad (3)$$

and then

$$i_m(S) = [3f_{C_6H_5} + 3f_{CH} + 3f_C]^{-2} \times \left[\sum_{uc}^n \sum_{i \neq j}^n f_i f_j \exp\left(-\frac{\langle u_{ij} \rangle S^2}{2}\right) \frac{\sin(S\bar{r}_{ij})}{S\bar{r}_{ij}} \right]. \quad (4)$$

In molecular liquids whose molecules consist of atoms of various species and atomic factors, one considers as scattering centres not the atoms as such but rather certain functions describing the electron distribution in the liquid. For different atomic species i, j, \dots, k , one has different electron scattering functions *i.e.* different atomic factors f_i, f_j, \dots, f_k [14]. For example, the expression: $3f_{C_6H_5}$ can be represented as follows: $3[6f_C + 5f_H]$. The values of the atomic scattering factors are tabulated [15]. Computer techniques [16, 17] were used to minimise the effects of experimental errors, uncertainties in the scattering factors, and termination errors.

For calculation of mean amplitudes of vibrations $\langle u_{ij} \rangle$ of different pairs of atoms of a liquid studied, the empirical formula of Mastyukov and Cyvin was applied [18].

The curves of reduced radiation intensity were analysed by the method of Blum and Narten [19]. The reduced intensity $i(S)$ function, defined as

$$i(S) = i_m(S) + i_d(S), \quad (5)$$

where

$$i(S) = \frac{\bar{I}_{eu}(S)/N - \sum_{uc} f_i^2(S)}{g^2(S)}, \quad (6)$$

is the structural-sensitive part of the total coherent intensity $\bar{I}_{eu}(S)/N$ in electron units per molecule, $g(S) = \sum_{uc} f_i / \sum_{uc} Z_i$ is a sharpening factor, $i_m(S)$ is the molecular structure function describing the scattering by a single molecule and $i_d(S)$ is the distinct structure function providing the information about intermolecular correlations from the experimental data.

There are two possible different values of the angles of twist phenyl rings (relative to the center) for the conformations of 1,3,5-triphenylbenzene. Farag [1] reported the twist angles of the phenyl rings in this compound as $+34^\circ$, -27° , and $+24^\circ$. The second conformation of the compound was presented by Lin and Williams. According to them, angles of rotation are phenyl rings, respectively, $+40.7^\circ$, -37.2° , and $+36.1^\circ$ [20]. Determining the conformation was essential for the analysis of mutual positions of molecules.

The normalized function $\bar{I}(S)$ of scattered radiation intensity obtained for the liquid studied is presented in Fig. 1. The positions of the maxima on these functions were found using the Lagrange polynomials method. Using the experimental values of $\bar{I}(S)$ presented in Fig. 1 and Eq. (6), the values of $i(S)$ and the total functions of the structure were calculated.

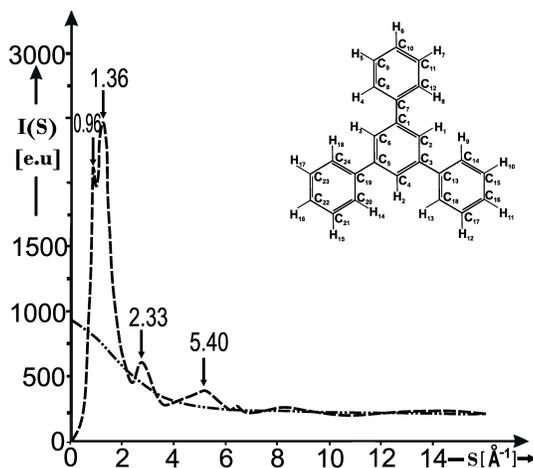


Fig. 1. The normalized, experimental curve of angular distribution of X-ray scattered intensity in liquid 1,3,5-triphenylbenzene using high-temperature camera.

The courses of the dependencies $i(S)$ and $i_m(S)$ for the studied liquid are shown in Fig. 2. For the properly chosen values of molecular parameters \bar{r}_{ij} and thermal factor, the molecular function describing the structure of

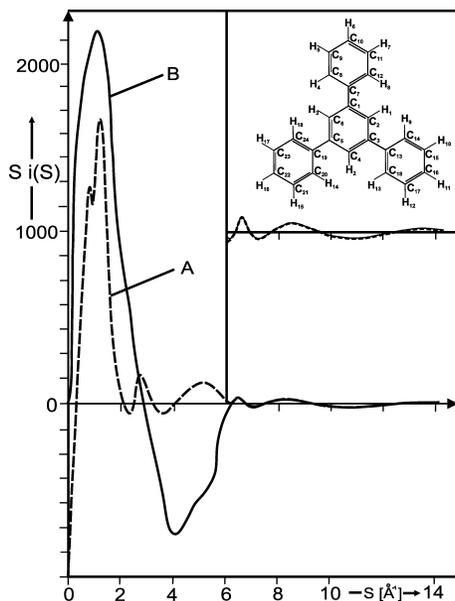


Fig. 2. Dashed line (A), the experimental structure function $S_i(S) \exp(-\alpha^2 S^2)$; $\exp(-\alpha^2 S^2)$ is convergence factor with coefficient $\alpha = 0.06$. Solid line (B), the molecular structure function $S_{i_m}(S)$ calculated according to Debye for 1,3,5-triphenylbenzene.

studied liquid was fitted to the experimental function of reduced intensity of scattered X-ray radiation for $S \geq 5 \text{ \AA}^{-1}$. Molecular parameters \bar{r}_{ij} have been fitted by a testing method [13, 19] assuming that $i(S) \approx i_m(S)$ for values of S ($S \geq 5 \text{ \AA}^{-1}$).

Determining the conformation 1,3,5-triphenylbenzene turned out to be a very difficult task. The model assumes a conformational analysis of the test molecule on the basis of crystal X-ray data for organic compounds (interatomic distances, angles of rotation, the radius of the atomic van der Waals) and the selected test values of internuclear distances \bar{r}_{ij} .

Distances characteristic for the 1,3,5-triphenylbenzene molecule are summarized in Table I. The determined intramolecular distances compared to the corresponding results obtained by Lin and Williams are within the measurement uncertainty ($\Delta\bar{r} \in < 0.01 \div 0.02 > \text{ \AA}$). The mean distance between carbon atoms in the central benzene ring was: $C_1-C_2 \equiv C_3-C_4 \equiv C_5-C_6 = 1.37 \pm 0.01 \text{ \AA}$. Such a value for these bonds was given during the fit of the function $i(S) \exp(-\alpha^2 S^2)$ to the function $i_m(S)$ of the wave vector $S \geq 5 \text{ \AA}^{-1}$. The most probable value of the packing coefficient of the molecules was found to be $k = 0.53$. This value falls in the range of k values permissible for the liquid phase [19].

TABLE I

The values of parameters of 1,3,5-triphenylbenzene molecule model applied in Debye formula Eq. (4).

Type of intramolecular interactions	Intramolecular distances \bar{r}_{ij} [Å]	Mean amplitude $\langle u_{ij} \rangle$ [Å]
C ₂ -H ₁	1.10	0.07 ₇
C ₁ -C ₂	1.37	0.04 ₆
C ₁ -C ₇	1.49	0.03 ₈
C ₃ -C ₁₃	1.50	0.04 ₃
C ₅ -C ₁₉	1.50	0.04 ₃
C ₁ -C ₃	2.38	0.06 ₉
C ₁ -C ₄	2.73	0.07 ₇
C ₁ -C ₉	3.68	0.06 ₈
C ₁ -C ₁₀	4.20	0.06 ₈
C ₁ -C ₁₁	3.80	0.09 ₅
C ₃ -C ₁₅	3.80	0.09 ₅
C ₃ -C ₁₆	4.20	0.06 ₇
C ₃ -C ₁₇	3.80	0.09 ₅
C ₅ -C ₂₁	3.70	0.06 ₈
C ₅ -C ₂₂	4.20	0.06 ₇
C ₅ -C ₂₃	3.70	0.06 ₈

Experimental distributions of scattered X-radiation intensity were compared with theoretical results (Fig. 2) predicted for a proposed model of 1,3,5-triphenylbenzene molecule (Fig. 3). X-ray structural analysis of the liquid 1,3,5-triphenylbenzene confirmed the model of molecule proposed by Lin and Williams for crystal [20].

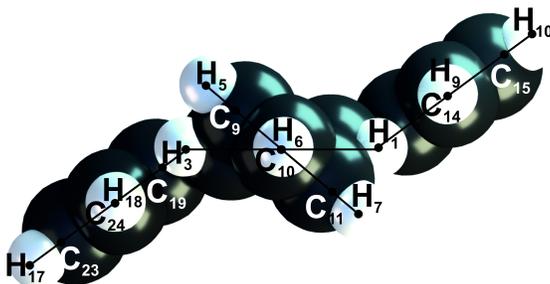


Fig. 3. A model of 1,3,5-triphenylbenzene molecule structure: the angles of rotation of phenyl rings are as follows: $+40.7^\circ$, -37.2° , $+36.1^\circ$.

5. Conclusions

The most important results of this paper are listed below.

- New experimental data on the structure of 1,3,5-triphenylbenzene $C_6H_3(C_6H_5)_3$ at 473 K. From the shape of the angular distribution function $I(S)$ and in particular from the positions of their maxima, we can conclude about the most probable model 1,3,5-triphenylbenzene molecule structure.
- The appearance of clear maxima on the functions of angular-distributions of X-ray radiation indicates the presence of short-range ordering in liquid 1,3,5-triphenylbenzene up to the distance of about 20 Å. The function $I(S)$ and $Si(S)$ are sensitive to the shape of molecules of the liquid studied, so they bring information on molecular structures in them and thus also on intramolecular interactions.
- X-ray structural analysis of liquid 1,3,5-triphenylbenzene (the theoretical and experimental functions were in good agreement) confirms the model of molecule proposed by Lin and Williams for crystal.
- The proposed method research of 1,3,5-triphenylbenzene in high-temperature can be used in investigation of structure and conformations other of liquids.

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REFERENCES

- [1] M.S. Farag, *Acta Crystallogr.* **7**, 117 (1954).
- [2] G. Champetier, L. Monnerie, «Introduction à la Chimie Macromoléculaire», Masson et C^{ie} Editeurs, Paris 1989.
- [3] D.E. Williams, *Acta Crystallogr. A* **28**, 629 (1972).
- [4] D.M. North, C.N.J. Wagner, *J. Appl. Cryst.* **2**, 149 (1969).
- [5] H. Drozdowski, *J. Mol. Struct.* **595**, 83 (2001).
- [6] B.E. Warren, R.L. Mozzi, *J. Appl. Cryst.* **3**, 59 (1970).
- [7] B.D. Cullity, «Elements of X-Ray Diffraction», Addison-Wesley, Massachusetts 1978.
- [8] R.J. Samuels, «Structured Polymer Properties», Wiley, New York 1974.
- [9] D.T. Cromer, D. Libermann, *J. Chem. Phys.* **53**, 1891 (1970).
- [10] J. Krogh-Moe, *Acta Crystallogr.* **9**, 951 (1956).
- [11] N. Norman, *Acta Crystallogr.* **10**, 370 (1957).
- [12] A.W. Renninger, R. Kaplow, «Computer Programs for Radial Distribution Analysis of X Ray», Massachusetts Institute of Technology, Cambridge, MA 1997.
- [13] H. Drozdowski, *Chem. Phys. Lett.* **351**, 53 (2002).
- [14] D.T. Cromer, J.T. Waber, *Acta Crystallogr.* **18**, 104 (1965).
- [15] «International Tables for X-Ray Crystallography. Vol. IV», Kynoch Press, Birmingham 1974, p. 73.
- [16] G. Licheri, G. Piccaluga, G. Pinna, *J. Appl. Cryst.* **8**, 73 (1975).
- [17] F. Hajdu, T. Radnai, *J. Appl. Cryst.* **8**, 488 (1975).
- [18] V.S. Mastyukov, S.J. Cyvin, *J. Mol. Struct.* **29**, 16 (1975).
- [19] L. Blum, A.H. Narten, «Diffraction by Molecular Liquids», in: I. Prigogine, S.A. Rice (Eds.) «Advances in Chemical Physics», 1976.
- [20] Y.C. Lin, D.E. Williams, *Acta Crystallogr. B* **31**, 318 (1975).