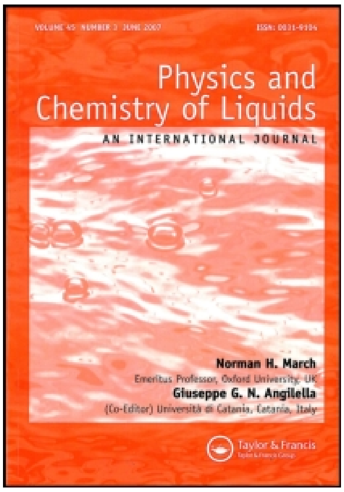

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Vibrations in atoms in liquid 1,4-dimethylbenzene

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Vibrations in atoms in liquid 1,4-dimethylbenzene

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The structure of 1,4-dimethylbenzene $C_6H_4(CH_3)_2$ at 293 K was investigated using the X-ray diffraction method. The observable range of scattering angles was $6 \le 2\Theta \le 120°$. Monochromatic radiation MoK_α enabled determination of the scattered radiation intensity between $S_{\min} = 0.430\,Å^{-1}$ and $S_{\max} = 14.311\,Å^{-1}$. Mean amplitudes of vibrations $\bar{u}_{ij}$ as a function of CC internuclear distances in 1,4-dimethylbenzene molecule were calculated. Analysis of intramolecular interactions between pairs of atoms has been made, taking into account the values of the temperature factors $\exp(-\bar{u}_{ij}/2 \cdot S^2)$. Experimental distribution of scattered X-radiation intensity $i(S)$ was compared with theoretical results predicted for a proposed model of 1,4-dimethylbenzene molecule. The best fitting theoretical curve $i_m(S)$ for the function $i(S)$ was obtained. Also for the first time, the method of reduction proposed by Mozzi–Warren with modifications introduced by the author has been applied to verify the assumed model of the molecule studied and to separate the intra- from inter-molecular interactions. The mean distances between the neighbouring molecules and the packing coefficient of liquid 1,4-dimethylbenzene were found.

Keywords: Molecular function of Debye; Mean square amplitudes; Reduction method of Blum and Narten; X-ray scattering in liquids

1. Introduction

The interest in the thermal motion in the area of the X-ray structural studies of liquids follows mainly from the fact that this motion significantly affects the atoms' positions [1,2]. Studies of liquid bicyclohexyl at 293 and 363 K [3] have shown that the least intramolecular distances C_1–C_2, $C_1 \cdots C_3$, $C_1 \cdots C_4$ (for $\Delta T = 70$ K) have shortened by 0.03 Å. Taking into regard the fact of variations in the interatomic distances, and knowing that the admissible deviation from the mean values usually is from ±0.01 to ±0.03 Å [4], the interference function $i(S)$ was calculated for a molecule studied and compared with the experimental curve in order to verify the assumptions made in the structural model proposed.

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With increasing temperature the amplitudes of thermal oscillations and librations increase. For the cubic metal lattices [5], it has been established that when the amplitude of oscillations reaches about $0.2a$ (where a is interatomic distance), the metal melts. When the angular amplitude of molecular librations reaches a certain critical value the molecules lose their orientational ordering or start rotating and the crystal undergoes a phase transition.

The structures of monoatomic liquids have been determined [6]. The molten sodium and potassium have been found to preserve their structure (regular lattice type I) even on heating to a temperature by 573 K higher than the melting point. At still higher temperatures, liquids of monoatomic molecules most often show hexagonal arrangement distorted by Brownian motions.

The temperature factor must be taken into account because the thermal vibrations of the atoms cause a decrease in the atomic scattering factors [7], and consequently a weakening of the scattered radiation intensity. Exact determination of the temperature factor, the so-called Debye–Waller, is possible only in the crystals of the regular system composed of one type atoms [8]. In analysis of molecular liquids, it is possible to apply the formula [8]:

$$T(2\Theta) = \exp\left[-B\left(\frac{\sin\Theta}{\lambda}\right)^2\right], \tag{1}$$

where $B(\sin\Theta/\lambda)^2$ is the molecular factor, B, a constant dependent on the thermal oscillations of atoms whose value increases with increasing temperature.

The aim of the article was to determine the most probable model of the molecule of 1,4-dimethylbenzene by the modified method of Mozzi–Warren reductions [9] and to establish interrelations of the thermal motions of different atoms. The earlier reported structural data for liquid 1,4-dimethylbenzene have prompted the study of intermolecular interactions in diluted binary mixtures of benzene nitroderivatives: o-nitroanisole and o-anisidine in 1,4-dimethylbenzene or in benzene [10].

Biswas [11] reported the elementary cell parameters of the 1,4-dimethylbenzene crystal $a = 7.56$ Å, $b = 8.45$ Å, $c = 11.11$ Å, and $\beta = 98°57'$. The compound crystallizes in the monoclinic system in the space group $C_{2h}^2(P2_1/m)$, and contains 4 molecules in the elementary cell.

The values of the structural and physical parameters of liquid 1,4-dimethylbenzene are collected in table 1. Dimethylbenzene samples of 99% purity were purchased from Aldrich-Chemie (Germany).

Table 1. Physical and structural parameters of liquid 1,4-dimethylbenzene ($\sum_j Z_j$ denotes the sum of the atom numbers in one molecule).

Macroscopic density d [g cm^{-3}]	0.866
Molecular mass M [g mol^{-1}]	106.17
Mean electron density ρ_0 [el Å^{-3}]	0.285
Mean effective number of electrons per hydrogen atom $\bar{K}_H$	0.431
Mean effective number of electrons per carbon atom $\bar{K}_C$	6.734
Total effective number of electrons in one molecule $\sum_j \bar{K}_j$	58.000
Total of atom numbers in one molecule $\sum_j Z_j$	58

2. Experimental

X-ray scattering in liquid 1,4-dimethylbenzene $C_6H_4(CH_3)_2$ (melting point, 286 K and boiling point, 411 K) was measured by applying MoK_α radiation, $\lambda = 0.71069$ Å. The radiation was monochromatized by reflection from the (002) planes of flat graphite with the angle of monochromatization of $\Theta_m = 6°00'$ ($\Delta\Theta_m = 2.2'$). The applied experimental technique was presented in the previous paper [12].

The diffracted X-ray pulses were counted in the time of 40 s, for the diffraction angle ranging from $3 \le \Theta \le 60°$, measured with the accuracy $0.005 \le \Theta \le 0.1°$. The measurements were carried out at a temperature of 293 K.

The liquid studied was placed in a plane-parallel cell of adjustable thickness and with windows of thin mica layer. The measuring chamber was dynamically thermostated within the range from 293 to 473 K. Temperature inside the cuvette was measured by a probe made by Testoterm GmbH & Lenzkirch, Germany.

The angular distribution of the scattered X-ray intensity was measured up to $S_{\max} = 4\pi \sin\Theta/\lambda = 14.311\ \text{Å}^{-1}$. The corrections for the background, polarization, absorption and Compton scattering were made over a mean angular distribution of the scattered X-ray intensity, which was next normalized according to Norman's method [13].

3. Calculations

The experimental function $i(S)$ is defined [14] as:

$$i(S) = \frac{\bar{I}_{eu}(S) - N\sum_j^n n_j f_j^2}{N f_e^2(S)}, \tag{2}$$

where the function $\bar{I}_{eu}(S)$ represents the experimental averaged values of the angular distribution of scattered intensity in electron units, n_j is the number of j-th type atoms in the molecule, f_j the atomic scattering factor, N the number of molecules, and $f_e(S)$ is the mean value of the atomic factor for a molecule per a single electron, often written in the form: $\sum_{uc} f_j / \sum_{uc} Z_j$. The reduced intensity $i(S)$ is a structurally sensitive part of the total experimental coherent intensity $\bar{I}_{eu}/N$ per molecule, and represents the so-called total function of structure because it involves both intra- and intermolecular scattering effects.

The molecular function of structure was calculated from the modified Debye formula:

$$i_m(S) = \left[\sum_{uc}^{n}\sum_{i\neq j}^{n} f_i f_j \exp\left(-\frac{\bar{u}_{ij}}{2}S^2\right)\frac{\sin(S\bar{r}_{ij})}{S\bar{r}_{ij}}\right]\left[\sum_{j}^{n} f_j(S)\right]^{-2}, \tag{3}$$

which describes the scattering by a single molecule.

For calculations of mean amplitudes of vibration $\bar{u}_{ij}$ of different pairs of atoms of a liquid studied, the empirical formula of Mastryukov and Cyvin was applied [15]

$$\bar{u}(\mathrm{CC}) = 0.013837 + 0.023398r - 0.000147r^2, \tag{4}$$

where r is the internuclear distance in the molecule (r and $\bar{u}_{ij}$ are both in Å). This formula was proposed by Mastryukov and Cyvin on the basis of a large body of data from electron diffraction laboratories in the USA, Norway, Japan and England [15]. Molecular parameters $\bar{r}_{ij}$ (the distance between two atoms i and j) and the coefficients $\bar{u}_{ij}$ have been fitted by a testing method [16] assuming that $i(S) \approx i_m(S)$ for high values of S. The procedure of fitting $i_m(S)$ to the experimental curve $i(S)$ for $S \geq 5\,\text{Å}^{-1}$ was carried out for the most probable model of the dimethylbenzene molecule. In equation (3), 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:

$$\sum_{uc} f_j(S) = 2f_{\mathrm{CH_3}} + 4f_{\mathrm{CH}} + 2f_{\mathrm{C}}. \tag{5}$$

The Warren–Krutter–Morningstar method [17] was applied to obtain the electron-density radial-distribution function $\sum_{j,k} \bar{K}_j 4\pi r^2 \rho_k(r)$. The application of Fourier transforms to the experimental curve $i(S)$ gave the total and differential functions of electron density distribution. The distribution function was interpreted by the Warren method [17]. The numerical integration was carried out by Simpson's method with integration steps of 0.20°. The parameter $\bar{r}$ was varied in steps of 0.05 Å. The maximum experimental error $\Delta(\bar{r})$ of the radial distribution curve was estimated to be 3% [18].

4. Results

The molecular structural function $i_m(S)$ was calculated from equation (3) for the Bragg angle Θ changing in the range 0–60°. Having determined $i(S)$ and $i_m(S)$, the so-called distinct structure function [19] was obtained from equation:

$$i_d(S) = i(S) - i_m(S), \tag{6}$$

where $i_m(S)$ is the molecular structure function describing the scattering by a single molecule and $i_d(S)$ is the distinct structure function providing the information abort intermolecular correlations from the experimental data. The dependencies of $i(S)$, $i_m(S)$, and $i_d(S)$ on S are presented in figure 1. The values of the function $Si(S)$ were calculated from the equation [17]:

$$Si(S) = \frac{1}{r}\int_{S_1}^{S_2}\left(\sum_{j,k}^{n} \bar{K}_j 4\pi r^2 \rho_k(r) - \sum_{j}^{n} \bar{K}_j 4\pi r^2 \rho_0\right)\sin(Sr)\,\mathrm{d}r, \tag{7}$$

where r is the distance from an atom or molecule selected as scattering centre, $\rho_k(r)$ is the function of radial electron density and $\bar{K}_j$ is the effective mean atomic numbers. The calculations were performed for a finite range of S values from $S_1 = 0.430\,\text{Å}^{-1}$ to $S_2 = 14.311\,\text{Å}^{-1}$.

The values of $i_m(S)$ shown in figure 1 were calculated from the modified Debye formula assuming the rigid model of the 1,4-dimethylbenzene molecule. This model is shown in figure 2, and table 2 gives the values of the Debye equation parameters.

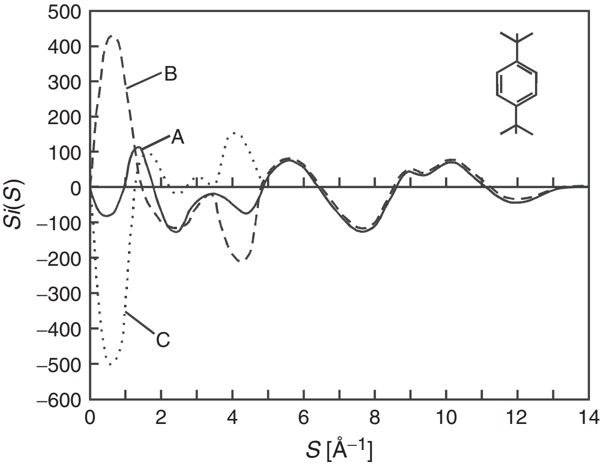

Figure 1. Curve A (continuous line), the experimental structure function $Si(S)$. Curve B (broken line), the molecular structure function $i_m(S)$ calculated according to Debye. Curve C (dotted line), subtraction of the calculated curve B from the curve A.

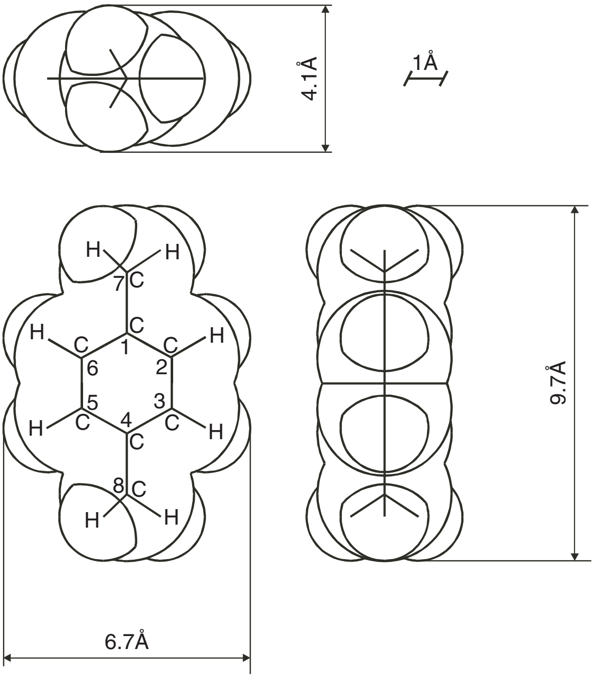

Figure 2. A model of 1,4-dimethylbenzene $C_6H_4(CH_3)_2$ molecule structure.

Table 2 presents 8 types of interatomic distances C–C and C···C for which mean amplitudes of vibrations $\bar{u}_{ij}$ were calculated. The mean amplitudes of vibration ($\bar{u}_{ij}$) for bonded C–C and non-bonded C···C distances in 1,4-dimethylbenzene molecule are shown in figure 3.

Table 2. The values of parameters of 1,4-dimethylbenzene molecule model applied in Debye formula equation (3). Atom notations the same as in figure 2.

No.	Type of intramolecular interactions	Intramolecular distances $\bar{r}_{ij}$ (Å)	Mean amplitudes $\bar{u}_{ij}$ (Å)
1	C_1–C_2, C_1–C_6, C_2–C_3, C_3–C_4, C_4–C_5, C_5–C_6	1.40	0.034
2	C_1–C_7, C_4–C_8	1.54	0.037
3	$C_1 \cdots C_3$, $C_1 \cdots C_5$, $C_2 \cdots C_4$, $C_2 \cdots C_6$, $C_3 \cdots C_5$, $C_4 \cdots C_6$	2.40	0.057
4	$C_2 \cdots C_7$, $C_6 \cdots C_7$, $C_3 \cdots C_8$, $C_5 \cdots C_8$	2.55	0.060
5	$C_1 \cdots C_4$, $C_2 \cdots C_5$, $C_3 \cdots C_6$	2.79	0.066
6	$C_2 \cdots C_8$, $C_6 \cdots C_8$, $C_3 \cdots C_7$, $C_5 \cdots C_7$	3.85	0.089
7	$C_1 \cdots C_8$, $C_4 \cdots C_7$	4.43	0.101
8	$C_7 \cdots C_8$	5.87	0.134

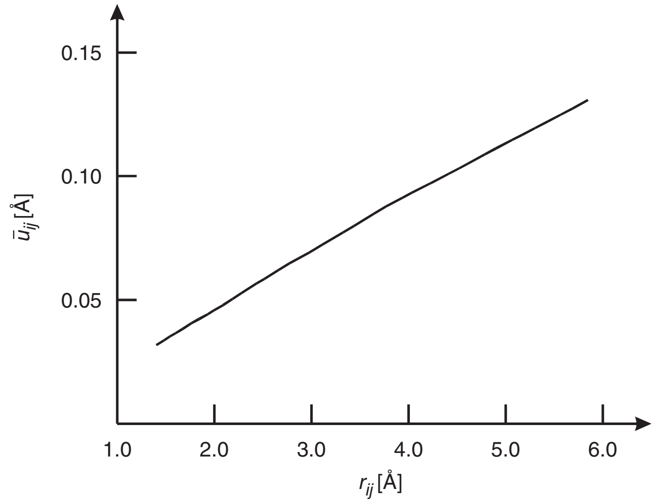

Figure 3. Mean amplitudes of vibration as a function of CC internuclear distances in 1,4-dimethylbenzene molecule.

The exponential damping function in the form $\exp(-\bar{u}_{ij}/2 \cdot S^2)$ is the temperature factor [20]. The function takes into regard the fact that within the n-atomic molecule the atoms are not at rest but perform vibrations with respect to one another. The temperature factors calculated for 8 particular types of the C–C and C···C distances within the molecule studied are shown in figure 4.

The function of $4\pi r^2 \sum_{j,k} \bar{K}_j[\rho_k(r) - \rho_0]$ is presented in figure 5. The maxima in the radial distribution function correspond to the intra- and inter-molecular distances for the liquid 1,4-dimethylbenzene.

5. Discussion

The modified method of Blum–Narten reductions was applied to verify the correctness of the assumed model of the molecule and to permit a separation of the intra- and intermolecular interactions. Analysis of the functions of the experimental $i(S)$ and the calculated $i_m(S)$ for the proposed model (table 2, figure 2) shows that these two curves

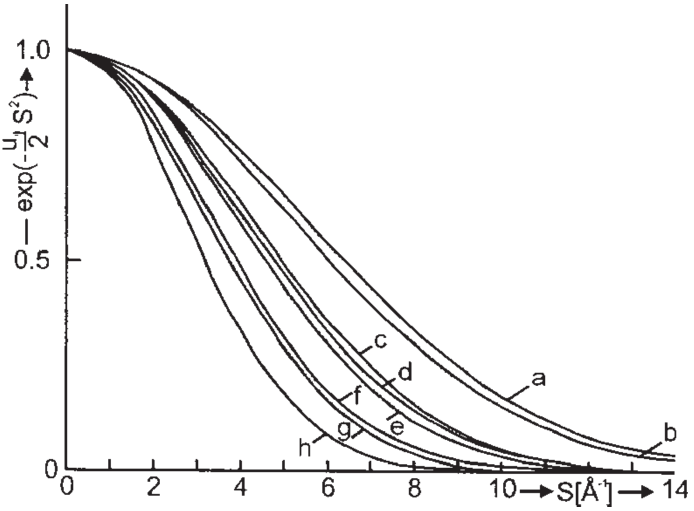

Figure 4. The temperature factors for the following atom pairs C–C and C···C in the molecule of 1,4-dimethylbenzene: *a* – 1.40 Å, *b* – 1.54 Å, *c* – 2.40 Å, *d* – 2.55 Å, *e* – 2.79 Å, *f* – 3.85 Å, *g* – 4.33 Å, *h* – 5.87 Å.

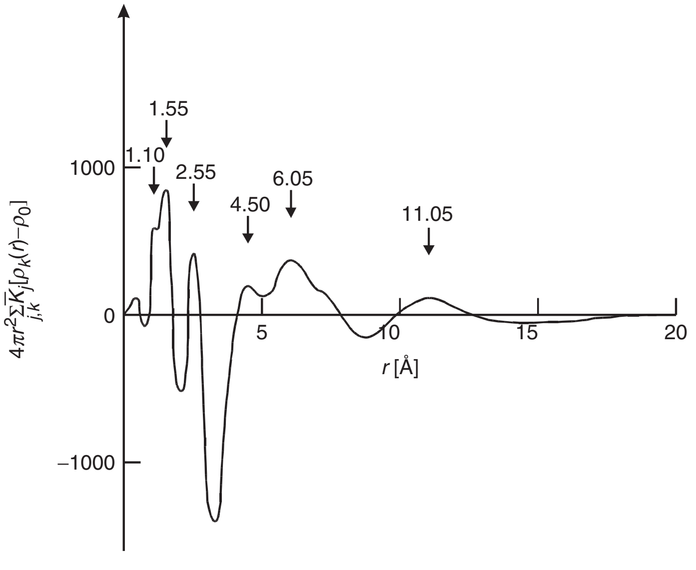

Figure 5. The electron-density radial-distribution function $4\pi r^2 \sum_{j,k} \bar{K}_j[\rho_k(r) - \rho_0]$ for liquid 1,4-dimethylbenzene.

coincide for $S \geq 5\,\text{Å}^{-1}$ (figure 1). This coincidence proves that the proposed model of the 1,4-dimethylbenzene molecule, and hence also the interatomic distances obtained, are correct.

The shape of the 1,4-dimethylbenzene molecule is described by the values of the three radii defined in the orthogonal projections of the molecule onto three mutually perpendicular planes (figure 2). Such models can be constructed on the basis of the bond lengths within the molecule and the van der Waals radii of C and H atoms.

The size of a 1,4-dimethylbenzene molecule is 4.1 Å (width) × 6.7 Å (length) × 9.7 Å (height). The methyl groups have the C_{3V} symmetry and lie along the $C_1 \cdots C_4$ axis (figure 2). On average it takes a volume of $V^{\max} = 203.6\,\text{Å}^3$, whereas an increment of the molecule volume [21] is $V^{\text{incr}} = 124.1\,\text{Å}^3$. The packing coefficient of molecules in liquid 1,4-dimethylbenzene is $\bar{k} = 0.60$. The value falls within the range determined for the liquid phase – from 0.51 to 0.68.

Because of short-range interatomic forces, the interactions of the first-order neighbours and then the second and further neighbours arranged in groups according to increasing distance, are taken into account. For the 1,4-dimethylbenzene molecule, the interactions with up to the fifth-order neighbours are taken into account (table 2).

The function $\bar{u}_{ij} = f(\bar{r}_{ij})$ in figure 3 illustrates the mean amplitude values of the vibrations of carbon atom pairs of the molecule studied used in the modified Debye formula (3). Figure 4 presents the temperature factor values taken into regard in analysis of the intermolecular interactions in carbon atom pairs of the molecule of the liquid studied. Thus obtained modified Debye function takes into regard the thermal motion of carbon atoms in the 1,4-dimethylbenzene molecule.

The assignment of intramolecular distances to the maxima (figure 5), has been performed assuming that the methyl group does not have a significant influence on the rigidity and interatomic distances in the benzene ring [22].

The radial distribution function for 1,4-dimethylbenzene (figure 5) reveals 6 maxima in the range up to 20 Å. In the range of the argument below 1 Å, the values of the radial distribution function making the interpretation difficult or even impossible (for example the negative ones) are not uncommon. They seem to be due to some approximations assumed in the method, e.g., to the extrapolation of small angle scattering results [8]. The maxima in the range of $3.50 \le \bar{r} < 6.00\,\text{Å}$, are interpreted as due to intra- and inter-molecular diffraction, whereas those for $\bar{r} \ge 6.00\,\text{Å}$ are due to intermolecular diffraction.

The four maxima of this function at 1.10, 1.55, 2.55, and 4.50 Å, are assigned to the distances between the following atom pairs: C–H, C_1–C_7, $C_2 \cdots C_7$, and $C_1 \cdots C_8$, in the molecule studied (table 2). The maximum at $\bar{r} = 11.05\,\text{Å}$ brings information about the difference between the observed and the average distribution of electron density.

Taking into regard the molecule size (figure 2), this result suggests that in liquid 1,4-dimethylbenzene the neighbouring molecules assume the conformation in which the planes of their benzene rings are parallel. The mean least intra- and inter-molecular distances were determined with the following accuracy: for $1 < \bar{r} \le 2\,\text{Å}$: $\Delta\bar{r} = \pm 0.05\,\text{Å}$, for $2 < \bar{r} \le 3\,\text{Å}$: $\Delta\bar{r} = \pm 0.10\,\text{Å}$, for $\bar{r} > 3\,\text{Å}$: $\Delta\bar{r} = 0.12\,\text{Å}$ [23]. The random error of the radial distribution function does not exceed 3%.

6. Conclusions

The method of reduction proposed by Mozzi–Warren with the modifications introduced by the author applied in analysis of the scattered radiation intensity permitted establishment of the correct model of the molecule 1,4-dimethylbenzene. In the analysis of intramolecular interactions between the pairs of atoms, the thermal factors have been taken into regard. The Debye function has been modified to take into account the thermal motions of the carbon atoms in the 1,4-dimethylbenzene.

The use of short-wave radiation from an X-ray tube with a molybdenum anode permitted determination of the mean structural parameters (the intra- and inter-molecular distances, the radii of coordination spheres, the packing coefficient of molecules) in the liquid 1,4-dimethylbenzene.

The appearance of clear maxima on the experimental structure functions and radial functions indicates the presence of short-range ordering in liquid 1,4-dimethylbenzene up to the distance of about 20 Å. The three maxima corresponding to the C–C distances appear at 1.55, 2.55, and 4.50 Å for the molecule studied. The maximum assigned to the C–H bond corresponds to the distance 1.10 Å within the ring. The values of $\bar{r} = 6.05$ Å and $\bar{r} = 11.05$ Å determined provide the information about intermolecular spatial configurations in the liquid studied. The mean intermolecular distances determined by the reduction method are in good agreement with the maxima on the electron-density radial-distribution function.

The packing coefficient of molecules in liquid 1,4-dimethylbenzene is equal to 0.60. This value falls within the range of $\bar{k}$ values acceptable for the liquid phase substances.

The structure of liquid 1,4-dimethylbenzene is determined by the presence of the benzene ring. We suggest that in liquid 1,4-dimethylbenzene at 293 K, the neighbouring molecules assume the configuration with their benzene ring planes in parallel to one another. The parallel conformation is probably assumed because it is more energetically favourable and enables a more favourable packing of the molecules. These results are also consistent with the values presumed in the conformational structure investigation of 1,4-dimethylbenzene performed by empirical and semi-empirical MO-LCAO calculations [24]. The results have also been confirmed by the conformation analysed based on minimization of the potential energy [25].

The approach proposed in this article gives a good description of intra- and intermolecular interactions in liquids and is a useful X-ray method for their analysis.

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