X-ray Diffraction Studies of Liquid Methylcyclohexane C_6H_{11}–CH_3 Structure at 293 K

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The structure of methylcyclohexane C_6H_{11}–CH_3 at 293 K was investigated using the X-ray diffraction method. An angular distribution of X-ray radiation scattered in liquid methylcyclohexane was measured. The observable range of scattering angles was $6° \leq 2\Theta \leq 120°$. Monochromatic radiation Mo K_α enabled determination of the scattered intensity between $S_{\min} = 0.92$ Å^{-1} and $S_{\max} = 15.313$ Å^{-1}. The differential radial distribution function of electron density was calculated. The mean structural parameters of liquid methylcyclohexane (inter- and intramolecular distances, radii of coordination spheres, and packing coefficient) were determined and discussed. The most probable binary radial correlation of molecules in liquid methylcyclohexane was proposed. The approach proposed in this paper gives a good description of intermolecular interactions in liquids and is a useful X-ray method for their analysis. The paper presents the structure and molecular correlations in liquid methylcyclohexane determined for the first time by the X-ray diffraction method. The study of methylcyclohexane is a continuation of our studies of cyclohexane derivatives cyclohexylamine and 2-methylcyclohexane. The aim of the study was to establish a relation between the *cis* and *trans* isomers and the conformation of the cyclohexane derivatives in the liquid phase.

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1. Introduction

The aim of the studies reported in this work was determination of intermolecular ordering in liquid methylcyclohexane C_6H_{11}–CH_3. The structural data obtainable by X-ray analysis for the liquid studied were discussed. Computer techniques were used to minimise the effects of experimental errors, uncertainties in the scattering factors, and termination errors. The most probable model of local molecular configurations in the first coordination sphere (for $\bar{r} \leq 10$ Å) was proposed. These results can be interpreted in terms of a simple model of local ar-

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rangement of molecules, which probably can be valid for a larger class of molecular liquids, i.e. monosubstituted derivatives of cyclohexane.

In methylcyclohexane a fast interconversion of conformations takes place between two chair conformations. In one conformation the methyl group occupies the equatorial position, while in the other it occupies the axial position. The occurrence of two conformation isomers is not equally probable as the equatorial conformation is by 1.8 kcal/mol more stable than the axial one [1]. At room temperature the equilibrium state is quickly reached with a prevalence of the favoured conformation with the methyl group at the equatorial position. X-ray diffraction is a very efficient method of studying the structure of matter in both solid and liquid phases [2]. Cyclohexane has been studied in the liquid [3, 4] and crystalline [5] phase. However, to the best of our knowledge, no reports have been published on the X-ray analysis of methylcyclohexane in the liquid state [6]. This work reports the first studies of liquid methylcyclohexane performed by the counter method for the range of the angular measurements intensity extended to the value of $\Theta = 60°$. Methylcyclohexane samples of 99% purity were purchased from Fluka (Switzerland).

Results of the study concerning molecular correlations in liquid phase may be important for explanation of mechanisms of certain physical and chemical processes taking place in such systems, e.g. diffusion or thermal conductivity [7].

2. Experimental

X-ray scattering in liquid methylcyclohexane (melting point 146.7 K, boiling point 374 K), at a temperature of (293 ± 0.1) K, was measured by applying Mo K_α radiation. The studies were performed using an X-ray apparatus TUR M-62. The scattered intensity distribution was measured for the angles $6° \leq \Theta \leq 120°$ at every 0.2°, with the accuracy $\Theta = 0.005°$. The diffracted X-ray pulses are counted in the time of 40 s. The radiation was monochromatised by reflection from the (002) planes of flat graphite with the angle of monochromatisation of $\Theta_\mathrm{m} = 6°00'$ ($\Theta_\mathrm{m} = 2.2'$). Deviations in intensity due to instability of the diffractometer work were about 1% in the whole range considered.

The X-ray diffraction patterns were recorded on a typical diffractometer equipped with a special cell for measurements of liquids, described by North and Wagner [8] and Drozdowski [9]. The studies were carried out with a special cuvette with exchangeable plates and closed 0.01 mm thick foil windows, constructed in our laboratory [10]. The material used and the thickness of the windows permitted us to neglect the absorption by the windows, which has been experimentally verified prior to measurements.

3. Calculations

The experimentally obtained function of the angular distribution of the scattered X-ray intensity was corrected to include the background (air scattering)

[11], polarisation [12], absorption [13], anomalous dispersion [14], and then normalised [15]. The experimental values of scattered radiation intensity were corrected by the Renninger and Kaplow computer program [16].

The Warren–Krutter–Morningstar method [17] was applied to obtain the differential radial distribution function of electron density (DRDF), $4\pi r^2 \sum_{j,k}^{n} \bar{K}_j[\rho_k(r) - \rho_0]$. The integral appearing in the expression for $\rho_k(r)$ was calculated numerically by the Simpson method for $0 \leq \bar{r} \leq 20$ Å, with a step of $\Delta\bar{r} = 0.05$ Å. The ranges of uncertainty for the structural parameters determined are as follows: for $1 \leq \bar{r} \leq 2$ Å: $\Delta\bar{r} = \pm 0.01$ Å, for $2 \leq \bar{r} \leq 3$ Å: $\Delta\bar{r} = \pm 0.05$ Å, for $\bar{r} > 3$ Å: $\Delta\bar{r} = \pm 0.10$ Å. The maximum experimental error in determination of the DRDF was estimated to be 3%.

4. Results

The normalised angular distribution of the scattered X-ray intensity in electron units, is shown in Fig. 1. The positions of the maxima on this function were found using the Lagrange polynomials method. In the range of 0.92 Å^{-1} $< S <$ 2.60 Å^{-1} the peak positions were determined with accuracy of $\Delta S = \pm 0.01$ Å^{-1}. In the range of 2.60 Å^{-1} $< S <$ 4.50 Å^{-1} the accuracy was $\Delta S \pm 0.02$ Å^{-1} and in the remaining range with $\Delta S \pm 0.03$ Å^{-1}. The curve was drawn taking into account corrections for polarisation and absorption of the scattered radiation. Small-angle scattering $(0° < \Theta < 3°)$ results were extrapolated to the origin of the coordinate system using a second-order function.
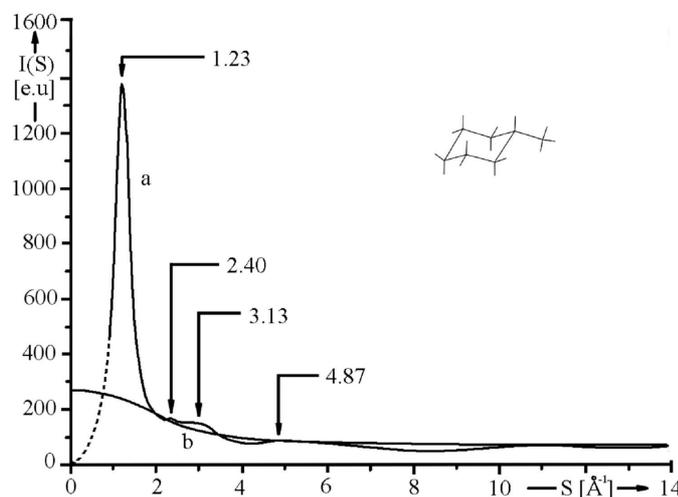

Fig. 1. (a) The normalized function $I(S)$ in electron units (where $S = 4\pi \sin \Theta / \lambda$) of angular distribution of intensity obtained for liquid methylcyclohexane. (b) Total independent scattering curve.
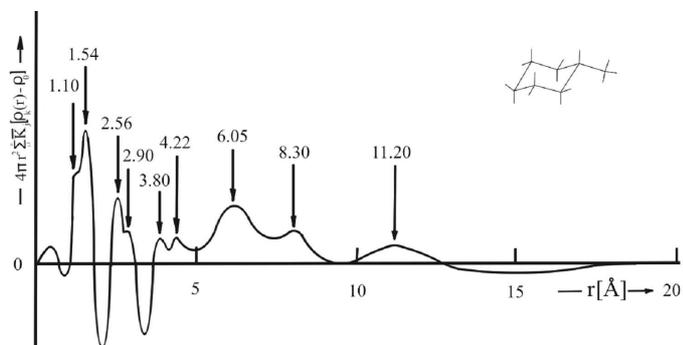
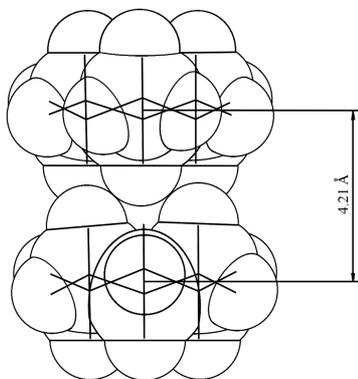Fig. 2. The differential radial distribution function for methylcyclohexane.

Fig. 3. Model of probable conformation of molecules in liquid methylcyclohexane $C_6H_{11}-CH_3$. The arrangement of molecules corresponding to the maxima in the DRDF.

TABLE

The range of coordination spheres for the studied methylcyclohexane.

Sphere	Range [Å]
1st	3.50–8.50
2nd	8.50–13.60
3rd	13.60–18.50

The differential function of the radial distribution of electron density is shown in Fig. 2. The appearance of distinct maxima in the angular distribution function of X-ray scattered radiation and the DRDF obtained for liquid methylcyclohexane indicates the presence of a short-range ordering in methylcyclohexane up to a distance of about 20 Å.

For the liquid studied, the presence of the coordination spheres of inter-molecular ordering was established. Subsequently, the ranges of the spheres of
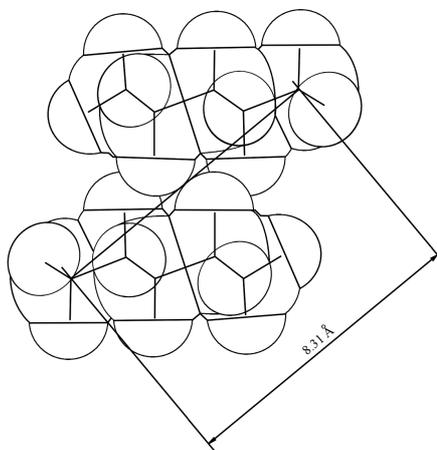
Fig. 4.   The antiparallel arrangement of molecules in liquid methylcyclohexane.

intermolecular ordering (Table) were determined. On the basis of the DRDF (Fig. 2), the three spheres of intermolecular ordering were distinguished. The positions of the maxima on the functions presented in Figs. 1 and 2 made the basis for the most probable models of molecular arrangements in liquid methylcyclohexane (Figs. 3 and 4). In the liquid methylcyclohexane the molecules are arranged with their cyclohexyl rings in parallel.

5. Discussion

From the position of the main maximum $I(S)$ (where $S = 4\pi \sin \Theta / \lambda$) of the least intermolecular distance, which is also the radius of the first coordination sphere, was determined [17] as $\bar{R} = 5.97 \pm 0.15$ Å. This distance corresponds to the position of the seventh maximum on the DRDF (Fig. 2).

The methylcyclohexane molecule has spatial structure. When a substituent greater than a hydrogen atom is at the axial position, it is in contact with two other axial substituents (hydrogen atoms or greater ones), whereas when it is at the equatorial position, the same substituent has much space available (is not squeezed). Therefore, the methylcyclohexane molecule tends to assume the chair conformation with the –CH$_3$ group at the equatorial position, characterised by greater stability and smaller (by 7.6 kJ/mol) energy than the conformation with the methyl group in the axial position. The two conformations are in a dynamic equilibrium, at which the isomer with the methyl group in the equatorial position occurs in 95%. Because of a small energy difference between the conformations, none of them can be isolated. Because of less spatial crowding of the equatorial positions, the cyclohexane derivatives tend to assume the equatorial conformation. The energy difference between the conformation isomers depends on the type of substituent. The size of a methylcyclohexane molecule is 7.9 Å(length) $\times$7.3 Å(width) $\times$5.0 Å(height). The methyl group –CH$_3$ shows the C_{3v} symmetry.

All the bonds between the atoms in the molecule are tetrahedral. A molecule of methylcyclohexane, on the average, takes a volume $V = 211.8$ Å^3, whereas an increment of the molecule volume $V^{\mathrm{incr}} = 119.5$ Å^3. The packing coefficient of molecules in liquid methylcyclohexane is approximately 56%. Regarding the size of the methylcyclohexane molecule, the first five maxima of DRDF can be assigned to intramolecular distances only.

The maxima on the DRDF have been ascribed to the following pairs of atoms: C(1)–H $=$ 1.10 Å, C(1)–C(2) $=$ 1.54 Å, C(1)$\cdots$CH$_3$ $=$ 2.56 Å, C(1)$\cdots$C(4) $= 2.90$ Å and C$_4\cdots$CH$_3$ $=$ 3.80 Å.

The distance between the centres of two neighbouring molecules is defined by van der Waals atomic radii. The mean distance calculated for two molecules of methylcyclohexane in the antiparallel arrangement between the carbon atoms of the functional groups $(\mathrm{CH}_3)_1\cdots(\mathrm{CH}_3)_2$ is 8.31 Å (Fig. 4).

6. Conclusions

The methods employed allowed a determination of the mean structural parameters and local ordering of molecules in liquid methylcyclohexane. The most probable intermolecular distances were found from the positions of the maxima of the DRDF. The use of short-wave radiation from an X-ray tube with a molybdenum anode permitted determination of the spheres of intermolecular ordering.

The most probable simple configurations of neighbouring molecules in the liquid in question can be examined by fitting the positions of the maxima of the DRDF to the distances between the centres of neighbouring, resulting from their van der Waals models.

In the liquid methylcyclohexane the neighbouring molecules assume the arrangement in which their dipole moments are antiparallel. The methyl group –CH$_3$ can occur only in the equatorial plane. The methyl group –CH$_3$ influences the orientation and packing of the molecules but does not deform the cyclohexyl ring. The cyclohexyl ring occurs mainly in the chair conformation and affects the positions of neighbouring molecules. These results are also consistent with the values presumed in the conformational structure investigation of methylcyclohexane performed by empirical and semi-empirical MO-LCAO calculations [18]. These results have also been confirmed by the conformation analysis based on minimisation of the potential energy [19]. Because of the supposed role of the cyclohexyl ring and the functional group –CH$_3$ attached to it at the *equatorial* position, for mutual configurations of molecules in liquid methylcyclohexane, it seems very probable that the proposed model of local arrangement can also hold for other derivatives of cyclohexane in the liquid phase.

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