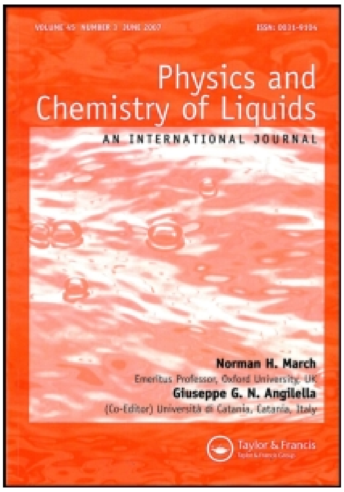

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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Zenon Bochyński[a]; Henryk Drozdowski[a]
[a] Non-crystalline Materials Division, Institute of Physics, Adam Mickiewicz University, Poznań 2, Poland

To cite this Article Bochyński, Zenon and Drozdowski, Henryk(2000) 'Short-Range Ordering in Liquid Bicyclohexyl by X-Ray Diffraction', Physics and Chemistry of Liquids, 38: 6, 713 — 722
To link to this Article: DOI: 10.1080/00319100008030318
URL: http://dx.doi.org/10.1080/00319100008030318

Phys. Chem. Liq., 2000, Vol. 38, pp. 713–722
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SHORT-RANGE ORDERING IN LIQUID BICYCLOHEXYL BY X-RAY DIFFRACTION

ZENON BOCHYŃSKI and HENRYK DROZDOWSKI*

Non-crystalline Materials Division, Institute of Physics, Adam Mickiewicz University, 60-780 Poznań 2, Grunwaldzka 6, Poland

(Received 1 December 1999)

The paper reports results of the X-ray diffraction structural studies of liquid bicyclohexyl, C_6H_{11}—C_6H_{11} at room temperature, using $CuK_{\bar{\alpha}}$ radiation. Angular distribution of X-ray scattered intensity was measured, and the electron-density radial-distribution function was calculated. Computer techniques were used to minimize the effects of experimental errors, uncertainties in the scattering factors, and termination errors. Good agreement between the theoretical and experimental functions was obtained on assuming the statistically most probable model of this molecule. The structural data obtainable by X-ray analysis for liquid bicyclohexyl were discussed. The mean distances between the neighbouring molecules and the radii of coordination spheres were found. The maxima in the differential radial distribution function were at: $\bar{r}_1 = 4.68$, $\bar{r}_2 = 5.57$, $\bar{r}_3 = 6.62$, $\bar{r}_4 = 8.05$ Å. X-ray structural analysis was applied to determine the packing coefficient of bicyclohexyl molecules. A simple model of short-range arrangement of the molecules in liquid bicyclohexyl was proposed.

Keywords: X-ray diffraction; liquid bicyclohexyl

1. INTRODUCTION

Bicyclohexyl (BCH) characterized by the melting point of 4.2°C and boiling point of 238.5°C, has been studied in the gas [1], liquid [2] and crystalline phase [2, 3]. BCH is the backbone of a group of compounds which form nematic and sometimes smectic liquid crystals [4]. BCH consists of two cyclohexyl rings joined so that each has the other as a rather bulky substituent which strongly prefers equatorial

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*Corresponding author. e-mail: riemann@main.amu.edu.pl position [5]. Force field calculations [6] have suggested that the preferred conformation of equatorial–equatorial anti (*ee anti*) BCH is the most stable.

X-ray diffraction is a very efficient method of studying the structure of matter in both solid and liquid phases [7]. However, to the best of our knowledge, no reports have been published on the X-ray analysis of BCH in the liquid state [2].

This work reports the first studies of liquid BCH performed by the counter method for the range of the angular measurements intensity extended to the value of $\vartheta = 60°$. The X-ray diffraction method permitted determination of mean structural parameters of liquid BCH (the inter- and intra-molecular distances, the radii of coordination spheres) and the packing coefficient at 293 K. The model of the most probable short-range ordering of BCH molecules in the liquid phase is also proposed.

BCH samples of 99% purity were purchased from Aldrich–Chemie (Germany).

2. EXPERIMENTAL

Structural studies were conducted using an X-ray diffractometer HZG-3 with a lamp working at the optimum voltage of 40 kV and anodic current of 35 mA [8]. The angular distribution of the X-ray scattered intensity was measured by applying $\mathrm{CuK}_{\bar{\alpha}}$ ($\lambda = 1.5418$ Å) radiation for the angles $3° \leq \vartheta \leq 60°$ at every 0.2°, where 2ϑ is the scattering angle. Monochromatization was obtained with a graphite crystal [9]. The measurements were performed using the transmission technique with the incident and diffracted beam symmetric upon the flat sample surface [8, 10]. The scattered X-ray intensities were measured by a VA-G-120 proportional counter (made by Otto Schön, Germany) and the results were registered by a digital printer.

The sample consisted of a layer of pure BCH 1 mm thick, between two windows of 0.01 mm styroflex foil. The material used and the thickness of the windows permitted us to neglect the absorption by the windows, which had been experimentally verified prior to measurements [11]. The cuvette was connected with a flow-through ultrathermostat U-10. The measurements were carried at (20.0 ± 0.1)°C, controlled by a differential copper-constantan thermocouple and a very sensitive mirror galvanometer, type GL-1. Inside the cuvette, temperature was measured by a temperature probe made by Testoterm GmbH & Co., Lenzkirch, Germany. Measurements were performed for different times of counting and a few times repeated so that a final result was an average.

3. CALCULATIONS

The experimental function of angular distribution of the scattered X-ray intensity was corrected to include the background [12], polarization [13], absorption [14], and anomalous dispersion [15]. Experimental data were normalized according to the Krogh-Moe [16] and Norman [17] method. The experimental values of scattered radiation intensity were corrected by the computer program [18] according to the scheme:

$$I = (I^{\exp} - I^{\mathrm{INC}} - I^{\mathrm{MULT}} - T)\,PA,$$

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 – polarising factor, and A – absorption factor. Small-angle scattering results ($0^\circ < \vartheta < 3^\circ$) were extrapolated to the origin of the coordinate system using the second-order function [18].

The Warren–Krutter–Morningstar method [19] was applied to obtain the electron-density radial-distribution functions (EDRDFs), $\sum_{j,k} \overline{K}_j 4\pi r^2 \rho_k(r)$. The integrals appearing in the expression for $\rho_k(r)$ were found numerically by the Simpson method for $0 \le \bar{r} \le 20\,\text{Å}$, at increments of 0.05 Å.

Coordination shells are delimited by minima of EDRDF [20]. The maximum experimental error in determination of radial distribution functions was estimated to be ±3%. The ranges of uncertainty for the structural parameters determined are as follows: $1 \le \bar{r} \le 4\,\text{Å}$, $\Delta\bar{r} = \pm 0.02\,\text{Å}$, for $\bar{r} > 4\,\text{Å}$: $\Delta\bar{r} = \pm 0.05\,\text{Å}$ [21]. In the calculations, the values of the structural and physical parameters of liquid BCH, collected in Table I, were used.

TABLE I Physical and structural parameters of liquid bicyclohexyl ($\Sigma_j Z_j$ denotes the sum of the atom numbers in one molecule)

Mean effective number of electrons per hydrogen atom $\bar{K}_H$	*Mean effective number of electrons per carbon atom* $\bar{K}_C$	$\sum_j \bar{K}_j$	$\sum_j Z_j$	*Macroscopic density* [*g/cm*^{3}]	*Molecular mass* [*g/mol*]	*Mean electron density* [*el/Å*^{3}]
0.670	6.628	94.000	94	0.8848	166.30	0.3013

4. RESULTS

The normalized angular-distribution function $I(S)$ [where $S = 4\pi \sin \vartheta / \lambda$] of BCH (Fig. 1) has one main and a few smaller diffuse maxima. The main maximum at $S_{\max} = 1.25\,\text{Å}^{-1}$ corresponds to the mean intermolecular distance in liquid BCH of $\bar{d} = 5.03\,\text{Å}$ as determined directly from the Bragg equation [22, 23]. The least mean intermolecular distance was found from the Voigtlaender-Tetzner formula [24] as 5.88 Å.

The most probable intermolecular distances were found from the positions of the maxima of the EDRDF (Fig. 2). The distribution

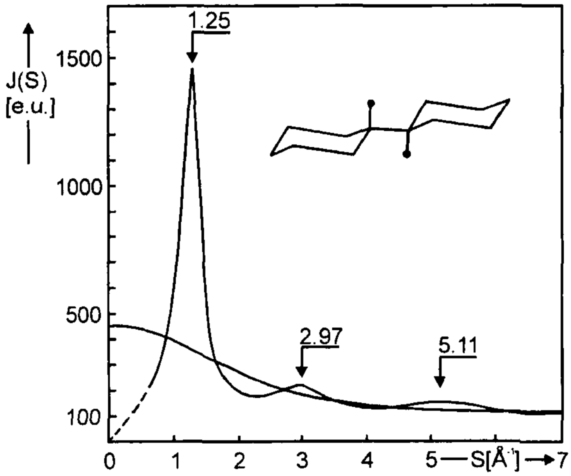

FIGURE 1 Normalized, experimental curve of angular distribution of X-ray scattered intensity (heavy line), and total independent scattering curve (light line) in liquid bicyclohexyl.

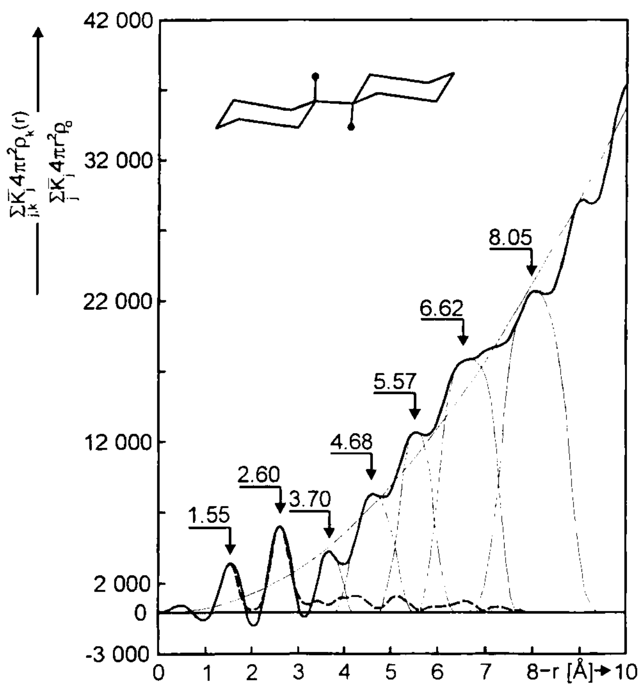

FIGURE 2 Electron-density radial-distribution function of liquid bicyclohexyl.

function shown in Figure 2 oscillates about the curve obtained for independent scattering theoretically calculated for $\rho_0 = 0.301$ el/Å^3. Broken line represents the molecular structure function calculated according to Debye [25].

The first two maxima were ascribed to the interferences within a bicyclohexyl molecule (Tab. II, Fig. 4). In the range of the argument below 1 Å, the values of the EDRDF 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 [18].

Numbering of atoms in BCH according to [1], see Figure 3.

Figure 4 shows the calculated radial distribution curve of BCH decomposed into the various atomic peaks [27].

In liquid BCH the presence of the coordination spheres of intermolecular ordering [28, 29] was established. Subsequently, the ranges of the spheres (Tab. III) were determined.

TABLE II Experimental Q_D and theoretical Q_T areas of the discrete maxima and corresponding intramolecular interactions

Maximum [*Å*]	*Intramolecular distances* [*Å*]	*Theoretical areas* $Q_T = 2 \cdot \bar{K}_j \cdot \bar{K}_k n[el^2]$	*Experimental areas* $Q_D[el^2]$
1.55	C1—H13 = 1.10	195.4	
	C1—C2 = 1.53	1142.2	
		1337.6	1358
2.60	C1—H15 = 2.16	390.8	
	C1—C4 = 2.50	1405.8	
	C2—H25 = 2.59	35.5	
	C1—H26 = 2.72	71.1	
	C1—H21 = 2.75	195.4	
	C1—H25 = 2.77	35.5	
	C2—C8 = 2.92	702.9	2857
		2837.0	

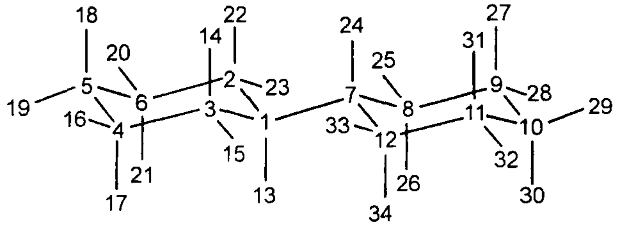

FIGURE 3 The most stable conformer (*ee anti*) of BCH.

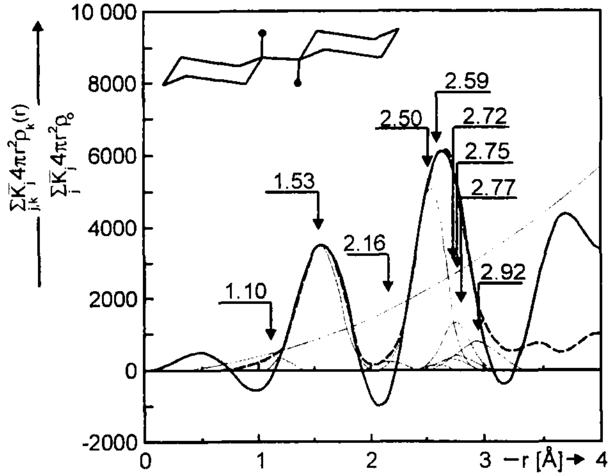

FIGURE 4 A part of electron-density radial-distribution curve with the partial maxima corresponding to intramolecular distances.

TABLE III The ranges of coordination spheres for the studied bicyclohexyl

Sphere	*Range* [*Å*]
1st	3.25 – 8.55
2nd	8.55 – 13.50
3rd	13.50 – 18.45

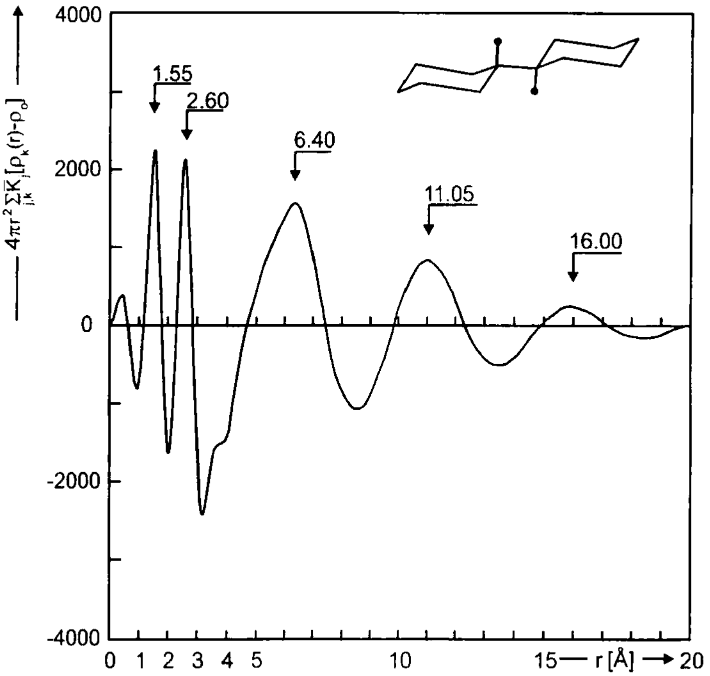

FIGURE 5 The differential radial distribution function for liquid BCH.

The differential function of electron-density radial distribution is shown in Figure 5.

5. DISCUSSION

A molecule of BCH, on the average, takes a volume $V = 312.2\,\text{Å}^3$, whereas an increment of the molecule volume [30] $V^{\text{incr}} = 187.1\,\text{Å}^3$. Due to the sizes of the BCH molecule, which can be evaluated from the van der Waals radii of carbon and hydrogen atoms, the first two maxima of the EDRDFs should be ascribed to the interferences inside a respective single molecule.

The first maximum of EDRDF, for $\bar{r}_1 = 1.55$ Å was ascribed to the interactions between the carbon and hydrogen atoms C1—H13 = 1.10 Å, and between the neighbouring carbon atoms C1—C2 = 1.53 Å in bicyclohexyl.

The second maximum on the EDRDF for $\bar{r}_2 = 2.60$ Å was assigned to the seven interatomic distances inside the BCH molecule: C1—H15 = 2.16 Å, C1—C4 = 2.50 Å, C2—H25 = 2.59 Å, C1—H26 = 2.72 Å, C1—H21 = 2.75 Å, C1—H25 = 2.77 Å, C2—C8 = 2.92 Å.

A good agreement between the theoretically calculated EDRDF (Fig. 4, dashed line), and the corresponding experimentally determined function (Fig. 4, solid line), in particular within intramolecular interaction range, indicates that the structural parameters of the molecule have been chosen correctly. The values of intramolecular distances are in agreement with the results of electron diffraction study of gaseous BCH [1] and those obtained by NMR method for liquid BCH [2].

The difference between the experimental Q_D and theoretical Q_T areas under the first two maxima of EDRDF is 20 el^2 (Tab. II). It can be explained as a result of the Compton scattering [31], whose influence on the EDRDF is more important for small than for greater r.

The subsequent maxima of the EDRDF correspond to the mean intermolecular distances in the BCH studied. 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 EDRDF to the distances between the centers of neighbours, resulting from their van der Waals models [32]. Such models can be constructed on the basis of the bond lengths within the molecule and of the van der Waals radii of C and H atoms.

The first maximum attributed to interactions of pairs of the nearest atoms in the neighbouring molecules occurs at 3.70 Å. The fourth maximum (for $\bar{r}_4 = 4.68$ Å) was assumed to correspond to the plane arrangement of molecules one over another. The fifth maximum (for $\bar{r}_5 = 5.57$ Å) was ascribed to the perpendicular or close to perpendicular arrangement of molecules. The sixth maximum (for $\bar{r}_6 = 6.62\,\text{Å}$) and the seventh one (for $\bar{r}_7 = 8.05\,\text{Å}$) – to the co-planar arrangement of bicyclohexyl molecules.

The results of the X-ray diffraction studies of liquid BCH prove the presence of local ordering of molecules of this compound within the distance r of about 16 Å (Fig. 5). The packing coefficient of molecules in liquid BCH is approximately constant in all coordination spheres and equal to 59%.

6. CONCLUSIONS

The methods employed allowed determination of the mean structural parameters (the inter- and intra-molecular distances, the radii of coordination spheres, and local ordering of molecules) in liquid bicyclohexyl. The appearance of distinct maxima in the angular distribution function of X-ray scattered radiation and radial distribution function of electron density obtained for liquid BCH indicates the presence of the short-range ordering in BCH up to a distance of about 16 Å.

The maxima in the range $1\,\text{Å} < \bar{r} \leq 3\,\text{Å}$ correspond to intramolecular interactions, whereas those appearing in the range from 3.00 Å to 7.50 Å are due to intermolecular diffraction. The values of $\bar{r}_4, \bar{r}_5$, $\bar{r}_6, \bar{r}_7$ determined provide the information about intermolecular spatial configurations in the liquid studied.

We suggest that in liquid BCH at room temperature, the neighbouring molecules assume the configuration with their cyclohexyl ring planes in parallel to one another for $\bar{r} \approx 4.80\,\text{Å}$ to $6.50\,\text{Å}$. These results are also consistent with the values presumed in the conformational structure investigation of BCH performed by empirical and semi-empirical MO-LCAO calculations [33]. The results have also been confirmed by the conformation analysis based on minimization of the potential energy [34].

Acknowledgements

The authors wish to thank K. Burdziak for assistance in measurements and determination of radial distribution functions. The work was performed within the research project No. 2 P 302 006 04 KBN financially supported by the State Committee for Scientific Research (Republic of Poland).

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