X-Ray Diffraction Study of Some Liquid Naphthalene Derivatives

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X-RAY DIFFRACTION STUDY OF SOME LIQUID NAPHTHALENE DERIVATIVES

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The structure of the liquids 1-Methylnaphthalene $C_{10}H_7$—CH_3 and 1-Chloronaphthalene $C_{10}H_7$—Cl was investigated using X-ray diffraction at 293 K. Monochromatic radiation MoK$_\alpha$ ($\lambda = 0.7107 \text{Å}$) enabled determination of the scattered radiation intensity between $S_0 = 4\pi \sin \vartheta_0/\lambda = 0.430 \text{ Å}^{-1}$ and $S_{max} = 14.311 \text{ Å}^{-1}$. Angular distributions of X-ray scattered intensity were measured, and differential radial distribution functions of electron density (DRDFs) were calculated. The mean distances between the neighbouring molecules and the ranges of the spheres of intermolecular ordering were found. X-ray structural analysis was applied for determination of the packing coefficient of molecules of the liquids studied. A simple model of short-range arrangement of the molecules was proposed, which seems to be valid for other weakly polar monosubstituted naphthalene derivatives in the liquid phase.

Keywords: X-ray diffraction; Differential radial distribution functions; Intermolecular ordering

1. INTRODUCTION

X-ray diffraction is a very efficient method of studying the structure of matter in both solid and liquid phase [1]. Recent papers [2, 3] have shown that the data provided by X-ray diffraction on liquid media allow not only a determination of interatomic distances in a molecule but also the kind of interaction among the molecules and degree of their ordering. Taking advantage of these reports, an attempt was

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made at determination of the structure of selected liquid derivatives of naphthalene. Results of the study concerning molecular correlations in the 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 [4].

Naphthalene, whose ring occurs in all these liquids, has been studied in three phases: gas [5], liquid [6] and solid [7, 8]. 1-Methylnaphthalene and 1-Chloronaphthalene have not been studied in the crystal and liquid phases by X-ray diffraction [9]. The structures of 1,2-Dichloronaphthalene [10], 1,2,3,4,6,7-Hexachloronaphthalene [11] have been studied in the crystal phase.

This paper reports results of X-ray diffraction study (MoK$_\alpha$ radiation of $\lambda = 0.7107$ Å) of the two naphthalene derivatives: 1-Methylnaphthalene and 1-Chloronaphthalene at 293 K. The aim of the study was to establish the role of the naphthalene ring and the functional groups (—CH$_3$, —Cl) attached to it at the α position in configurations of the molecules of the liquids studied. The method of X-ray scattering and Fourier analysis [12] enabled determination of the mean structural parameters (inter- and intramolecular distances, radii of coordination spheres and molecule packing coefficients) of the liquids studied.

These results can be interpreted in terms of a simple model of local arrangement of molecules, which probably can be valid for a larger class of molecular liquids, *i.e.*, weakly polar monosubstituted derivatives of naphthalene.

The values of the structural and physical parameters of liquids studied collected in Table I. The compounds to be studied (of 99% purity) were purchased from Aldrich-Chemie (Germany).

TABLE I Physical and structural parameters of liquid 1-Methylnaphthalene and 1-Chloronaphthalene ($\sum_j Z_j$ denotes the sum of the atom numbers in one molecule)

Liquids	Mean effective number of elecgtrons 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/cm³]	Molecular mass [g/cm³]	Mean electron density [el/Å³]
1-Methylnaphthalene C$_{10}$H$_7$—CH$_3$	0.650	6.318	76.000	76	1.001	142.20	0.3223
1-Chloronaphthalene C$_{10}$H$_7$—Cl	0.639	6.335	84.000	84	1.194	162.62	0.3842

2. EXPERIMENTAL

For each these samples, a cuvette with 0.01 mm thick windows of styroflex foil containing a 3 mm thick layer of the studied liquid was installed on an HZG-4 X-ray goniometer [13]. The angular distribution of the X-ray scattered intensity was measured by applying MoK_α ($\lambda = 0.7107$ Å) radiation for the angles $3° \leq \vartheta \leq 60°$ at every $0.2°$, where 2ϑ is the scattering angle. The radiation was monochromatized by reflection from the (002) planes of flat graphite with the angle of monochromatization of $\alpha = 6°00'$ [14]. The measurements were performed using the transmission technique with the incident and diffracted beam symmetric upon the flat sample surface [15]. The scattered X-ray intensities were measured by a proportional counter VA-G-120, coupled with the calculating unit, and the results were recorded by a computer. For each liquid measurements were performed for different times of counting and a few times repeated so that a final was an average.

3. CALCULATIONS

In each case, the experimental function of angular distribution of the scattered X-ray intensity was corrected to include the background [16], polarization [17], absorption [18], anomalous dispersion [19], and the Compton scattering [20]. Experimental data were normalized according to the Krogh-Moe [21] and Norman [22] method. Absorption in the cuvette windows was neglected [23].

The modified Warren–Krutter–Morningstar method [24] was applied to obtain the differential radial-distribution functions of electron density (DRDFs) $\sum_{j,k} \bar{K}_j 4\pi r^2 [\rho_k(r) - \rho_0]$. The integrals appearing in the expression for $\rho_k(r)$ were found numerically by the Simpson method for $0 \leq \bar{r} \leq 20$ Å, at increments of 0.05Å.

The maximum experimental error in determination of radial distribution functions was estimated to be $\pm 3\%$. The ranges of uncertainty for the structural parameters determined are as follows: $1 < \bar{r} \leq 2$ 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 [25]. Computer techniques were used to minimise the effects of experimental errors, uncertainties in the scattering factors, and termination errors. X-ray diffraction data of the studied

liquids were analyzed by Renninger–Kaplow program package [26]. The packing coefficient of the molecules was found by the method Kitaigorodsky [27].

4. RESULTS

The normalized functions $I(S)$ of scattered radiation intensity obtained for the liquids studied are presented in Figure 1. The positions of the maxima on these functions were found using the Lagrange polynomials method. Small-angle scattering results $(0° < \vartheta < 3°)$ were extrapolated to the origin of the coordinate system using a secondorder function.

Fourier analysis of the angular functions of intensity yielded the functions of radial distribution of electron density shown in Figure 2. Their positions correspond to the most probable interatomic and intermolecular distances in the studied liquids, which are considered in detail below. These functions bring information about the difference
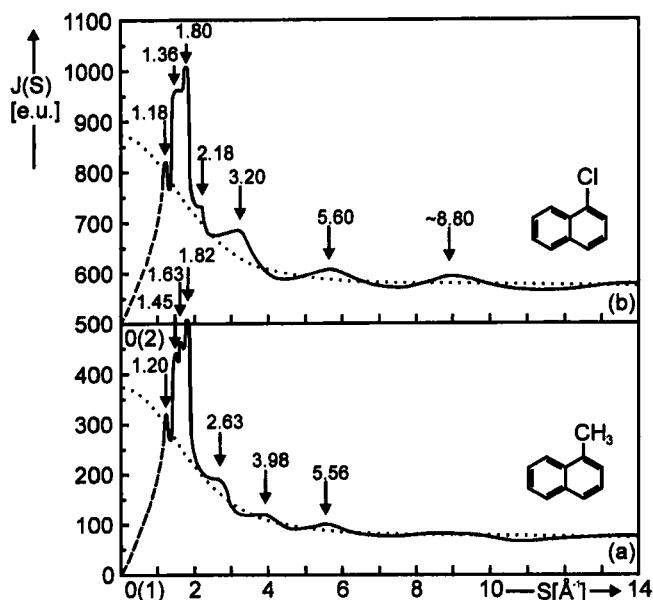
FIGURE 1 Normalized, experimental curves of angular distribution of X-ray scattered intensity (continuous lines), and total independent scattering curves (dotted lines) in liquid (a) 1-Methylnaphthalene $C_{10}H_7$—CH_3, (b) 1-Chloronaphthalene $C_{10}H_7$—Cl.
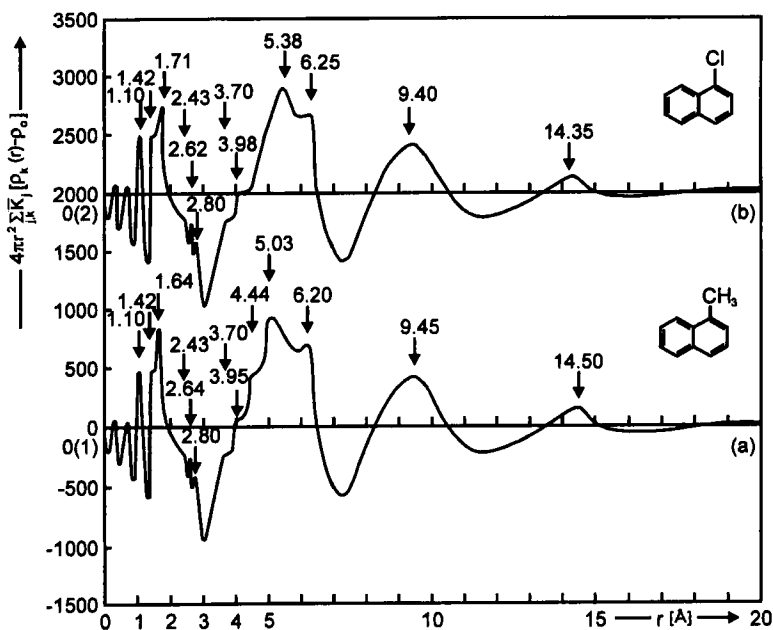
FIGURE 2 Differential functions of radial distribution of electron density of liquid (a) 1-Methylnaphthalene $C_{10}H_7$—CH_3, (b) 1-Chloronaphthalene $C_{10}H_7$—Cl.

TABLE II The range of coordination spheres for the studied liquids

Liquids	Range [Å]		
	Sphere I	Sphere II	Sphere III
1-Methylnaphthalene $C_{10}H_7$—CH_3	3.05–7.35	7.35–11.60	11.60–16.35
1-Chloronaphthalene $C_{10}H_7$—Cl	3.05–7.40	7.40–11.65	11.65–16.40

between the observed and the average distribution of electron density. Subsequently, the ranges of the spheres of intermolecular ordering (Tab. II) were determined. Coordination shells are delimited by the minima of DRDFs [28].

5. DISCUSSION

In the range of the argument below 1 Å, the values of the DRDFs (Fig. 2) making the interpretation difficult or even impossible 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 [26]. The maxima on the DRDFs have been ascribed to the following pairs of atoms: $C2 \text{—} H = 1.10 \text{Å}$, $C1 \text{—} C2 = 1.42 \text{Å}$, $C1 \text{—} CH_3 = 1.64 \text{Å}$, $C1 \text{—} C1 = 1.71 \text{Å}$, $C1 \cdots C3 = 2.43 \text{Å}$, $C2 \cdots C1 = 2.62 \text{Å}$, $C2 \cdots CH_3 = 2.64 \text{Å}$, $C1 \cdots C4 = 2.80 \text{Å}$, $C3 \cdots CH_3 = 3.95 \text{Å}$, and $C4 \cdots CH_3 = 4.44 \text{Å}$ (Fig. 2).

The subsequent maxima of the DRDFs correspond to the mean intermolecular distances in the liquids 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 DRDFs to the distances between the centres of neighbours, resulting from their van der Waals models (Fig. 3). Such models can be constructed on the basis of the bond lengths within the molecule and of the van der Waals radii of C, Cl and H atoms. The maxima on the DRDFs in the range $1 < \bar{r} < 4.5 \text{Å}$ are attributed to intramolecular interactions, whereas those for $\bar{r} > 4.5 \text{Å}$ are due to intermolecular diffraction. The conclusions that the broad maxima at $\bar{r} \geq 4.5 \text{Å}$ (Fig. 2) are intermolecular has been confirmed by the results of density calculations [29]. The packing coefficient of molecules in liquid 1-Methylnaphthalene and 1-Chloronaphthalene is approximately constant in all coordination spheres and equal to 0.64 and 0.62, respectively. This values falls within the range of k values acceptable for the liquid phase substances [27].

As indicated by the conformational analysis of the liquids studied, results of the potential energy minimization [30, 31] and the value of
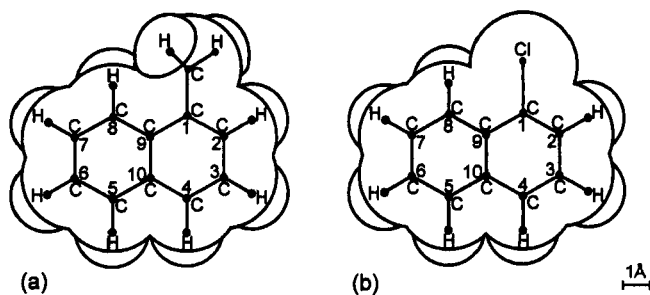

FIGURE 3   (a) A model of 1-Methylnaphthalene $C_{10}H_7 \text{—} CH_3$ molecule structure. (b) A model 1-Chloronaphthalene $C_{10}H_7 \text{—} Cl$.

the permanent dipolar moment $\mu = 0.38D$ [32] of the 1-Methyl-naphthalene molecule and $\mu = 1.35D$ [32] of the 1-Chloronaphthalene molecule, the optimum arrangement of these molecules is antiparallel planar, one on top of the other. Only in such an arrangement the distance between the centres of the two methyl groups of the neighbouring molecules is: $CH_3 \cdots CH_3' = 6.20 \pm 0.10$ Å, which leads to the mean distance between the pair of C3 atoms of the neighbouring molecules equal to $C3 \cdots C3' = 5.03$ Å.

In liquid 1-Chloronaphthalene only in the antiparallel conformation the distance between the centres of the chlorine groups is $Cl \cdots Cl' = 6.25 \pm 0.10$ Å, which leads to the mean distance $C4 \cdots C4' = 5.38$ Å between the corresponding C4 atoms.

In the range $\approx 4.5 \leq \bar{r} < 20$ Å the DRDFs can be divided into three regions corresponding to three spheres of intermolecular ordering [15].

6. CONCLUSIONS

The use of short-wave radiation MoK_α enabled determination of the shortest interatomic distances within the naphthalene ring. The three C—C atomic peaks occur at distances of 1.42, 2.43, and 2.80 Å corresponding to the distances between *ortho*, *meta*, and *para* carbon atoms and the C—H peak occurs at 1.10 Å in the studied liquids. It was also possible to determine the interactions between the carbon atom C1 in the naphthalene ring and the methyl group CH_3 in liquid 1-Methylnaphthalene $C1 - CH_3 = 1.64$ Å, and the chlorine group C1 in liquid 1-Chloronaphthalene $C1 - Cl = 1.71$ Å. As follows from the geometry of the naphthalene ring and the positions of the methyl and chlorine groups, the positions of particular peaks at the DRDFs can be assigned to the distances: $C2 \cdots Cl = 2.62$ Å, $C2 \cdots CH_3 = 2.64$ Å, $C3 \cdots CH_3 = 3.95$ Å, and $C4 \cdots CH_3 = 4.44$ Å.

The appearance of clear maxima on the function of the angular distribution of X-ray intensity and differential radial distribution function indicates the presence of short-range ordering in this liquids. The applied X-ray diffraction method combined with analytical calculations permits determination of the least mean interatomic and intermolecular distances up to about 15 Å. The maxima for 1 Å $< \bar{r} \leq 4.5$ Å are interpreted as a result of intramolecular diffraction.

The shape and the course of the DRDFs of the liquids studied are very similar. They are also similar to the DRDF of liquid naphthalene [6].

The attractive dipole interaction between neighbouring molecules can favour the plane arrangement of molecules one over another in antiparallel ($\rightleftharpoons$) arrangement, making such a configuration relatively more stable. The distance between the two methyl groups of neighbouring molecules in this arrangement in liquid 1-Methyl-naphthalene is of about 6.20 Å.

In liquid 1-Chloronaphthalene the distance between the centres of chlorine atoms of two neighbouring molecules in the antiparallel arrangement is approximately 6.25 Å. These results are also consistent with the values presumed in the conformational structure investigation of the liquids studied performed by empirical and semi-empirical MO-LCAO calculations [33]. The results have also been confirmed by the conformational analysis based on minimization of the potential energy.

Because of the supposed role of the naphthalene ring and the functional groups ($-CH_3, -Cl$) attached to it at the α position, for mutual configurations of molecules in liquid 1-Methylnaphthalene and 1-Chloronaphthalene, it seems very probable that the proposed model of local arrangement can also hold for other weakly polar derivatives of naphthalene in the liquid phase.

Acknowledgment

References

[1] Waseda, Y., *The Structure of Non-Crystalline Materials*, McGraw-Hill, New York, 1979.
[2] Bochyński, Z. and Drozdowski, H. (1999). *J. Mol. Liq.*, **80**, 53.
[3] Bochyński, Z. and Drozdowski, H. (1999). *Acta Phys. Slov.*, **49**, 409.
[4] Kohler, F., *The Liquid State*, Verlag Chemie, Weinheim/Bergstr., 1972.
[5] Ketkar, S. N. and Fink, M. (1981). *J. Mol. Struct.*, **77**, 139.

[6] Bochyński, Z., Dejneka, L. and Drozdowski, H. (2000) *J. Mol. Struct.*, **524**, 227.
[7] Brock, C. and Dunitz, J. (1982). *Acta Cryst.*, **B38**, 2218.
[8] Andrunikow, T. and Pawlikowski, M. (1998). *Acta Phys. Pol.*, **A93**, 707.
[9] CSD (Cambridge Structure Data Base), 1999; Allen, F. H., Kennard, O. and Taylor, R. (1999). *Acc. Chem. Res.*, **16**, 146.
[10] Trotter, J. (1964). *Acta Cryst.*, **17**, 63.
[11] Jakobsson, E., Eriksson, L. and Bergman, A. (1992). *Acta Chem. Scand.*, **46**, 527.
[12] Lighthill, M. J., *Introduction to Fourier Analysis and Generalized Functions*, University Press, Cambridge, 1969.
[13] North, D. M. and Wagner, C. N. J. (1969). *J. Appl. Cryst.*, **2**, 149.
[14] Schwarzenbach, D., *Crystallography*, John Wiley & Sons Chichester, New York, 1996.
[15] Hargittai, J. and Orville-Thomas, W. J., *Diffraction Studies on Non-Crystalline Substances*, Akadémiai Kiadó, Budapest, 1981.
[16] Schwager, P., Bartels, K. and Hubner, R. (1973). *Acta Cryst.*, **A29**, 291.
[17] Hope, H. (1971). *Acta Cryst.*, **A27**, 392.
[18] Warren, B. E. and Mozzi, R. L. (1970). *J. Appl. Cryst.*, **3**, 59.
[19] Waseda, Y. and Tamaki, S. (1976). *Z. Physik*, **B23**, 315.
[20] Strong, S. L. and Kaplow, R. (1966). *Rev. Sci. Instr.*, **37**, 1495.
[21] Krogh-Moe (1956). *Acta Cryst.*, **9**, 951.
[22] Norman, N. (1957). *Acta Cryst.*, **10**, 970.
[23] Milberg, M. E. (1958). *J. Appl. Phys.*, **29**, 64.
[24] Warren, B. E., *X-Ray Diffraction*, Reading, MA: Addison-Wesley, 1969.
[25] Konnert, J. H. and Karle, J. (1973). *Acta Cryst.*, **A29**, 702.
[26] Renninger, A. W. and Kaplow, R., *Computer Programs for Radial Distribution Analysis of X-Rays*, Cambridge, MA: Massachusetts Institute of Technology, 1987.
[27] Kitaigorodsky, A. I., *Molecular Crystals and Molecules*, Academic Press, New York-London, 1973.
[28] Cargill III, G. S. (1970). *J. Appl. Phys.*, **41**, 12.
[29] Skryshevskii, A. F., *Strukturnyy Analiz Zhidkostey i Amorfnykh Tel. Moskva*, Izd Vysshaya Shkola, 1980.
[30] Hoffmann, R. (1963). *J. Chem. Phys.*, **39**, 1397.
[31] Dewar, M. J. S. and Haselbach, E. (1970). *J. Amer. Chem. Soc.*, **92**, 590.
[32] Landolt-Börnstein, *Zahlenwerte und Funktionen, Atom- und Molekularphysik*, 3 Teil, Springer-Verlag, Berlin-Göttingen-Heidelberg, 1951.
[33] Haile, J. M., *Molecular Dynamics Simulations. Elementary Methods*, John Wiley & Sons, New York, 1992.