

# X-ray Analysis of Intermolecular Interactions in Liquid 2-chloronaphthalene at 353 K

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The aim of the study was to examine the structure of liquid 2-chloronaphthalene  $C_{10}H_7-Cl$  at 353 K by the X-ray diffraction method. Monochromatic radiation  $Mo K_{\alpha}$ ,  $\lambda = 0.71069 \text{ \AA}$  was used to determine the scattered radiation intensity between  $S_{\min} = 4\pi \sin \vartheta_{\min} / \lambda = 0.430 \text{ \AA}^{-1}$  and  $S_{\max} = 4\pi \sin \vartheta_{\max} / \lambda = 14.311 \text{ \AA}^{-1}$ . The curves of reduced intensity were analysed by the reduction method of Blum and Narten. Experimental distribution of X-ray scattered intensity was compared with theoretical results predicted for a proposed model of 2-chloronaphthalene molecule. The differential radial distribution function  $4\pi r^2 \sum_{j,k}^n \overline{K}_j [\rho_k(r) - \rho_0]$  was calculated and some intra- and intermolecular distances in liquid 2-chloronaphthalene were determined. X-ray structural analysis was applied to determine the packing coefficient of 2-chloronaphthalene molecules at 353 K. The intermolecular distance  $Cl \cdots Cl'$  was also determined as  $7.90 \pm 0.15 \text{ \AA}$ . 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.

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## 1. Introduction

The knowledge of atomic and molecular structure of liquids and the mechanism of the structural processes taking place in them is of fundamental importance in comprehensive explanation of their physical and chemical properties. The physical properties of liquids are not only related to the type of molecular distribution but also to the character of motion and mutual interactions of atoms and molecules.

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These parameters can be determined by a method based on the phenomenon of X-ray diffraction.

The method applied for analysis of the experimental data is based on the use of equations describing the diffraction. As a result of subjecting them to the Fourier transform we obtained the differential radial distribution function (DRDF). The method of determination of intra- and intermolecular interactions applied in this work is based on the use of the radial distribution function (RDF) and DRDF. The method has been used for the first time for liquid 2-chloronaphthalene. It was possible to fit the theoretical predictions to the experimental data and propose the most probable model of intermolecular interactions and thus the most probable structural model of liquid 2-chloronaphthalene.

The results of the study of molecular correlations in liquid phase may be important for explanation of mechanisms of certain physical and chemical processes taking place in similar systems, e.g. thermal conductivity or diffusion.

The structures of 1,2-dichloronaphthalene [1], 1,2,3,4,6,7-hexachloronaphthalene [2], 2-phenylnaphthalene [3], 1,2,3,4-tetraphenylnaphthalene [4], 1- and 2-methylnaphthalene [5] and octaphenylnaphthalene [6] have been studied in the crystal phase. On the basis of the known liquid structures of 1-methylnaphthalene [7], 1-chloronaphthalene [8], 1-phenylnaphthalene [9, 10] and 1- and 2-methylnaphthalene [11, 12] we can predict the structures of their weakly polar derivatives. However, 2-chloronaphthalene has not been studied in the liquid phase by diffraction methods [13].

The subject of the studies reported in this work is 2-chloronaphthalene. For the sake of comparison similar studies were performed for naphthalene. A compar-

TABLE I

Physical and structural parameters of liquid naphthalene and 2-chloronaphthalene.

Parameters/liquids	Naphthalene	2-chloronaphthalene
Mean effective number of electrons per hydrogen atom $\bar{K}_H$	0.331	0.639
Mean effective number of electrons per carbon atom $\bar{K}_C$	6.556	6.335
Mean effective number of electrons per chlorine atom $\bar{K}_{Cl}$	–	19.623
Total effective number of electrons in one molecule $\sum_j \bar{K}_j$	68.000	84.000
Total of atom numbers in one molecule $\sum_j Z_j$	68	84
Macroscopic density [g/cm <sup>3</sup> ]	0.963	1.138
Molecular mass [g/mol]	128.16	162.62
Mean electron density [el/Å <sup>3</sup> ]	0.3080	0.3540

ison of the radial distribution functions for these two liquids was made. Naphthalene  $C_{10}H_8$  (melting point — 353 K, boiling point — 491 K) has been studied in gas [14], liquid [15], and crystalline form [16].

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

In the present paper new results obtained by X-ray diffraction studies in liquid 2-chloronaphthalene at 353 K are reported.

## 2. Experimental and treatment

X-ray scattering in liquid 2-chloronaphthalene  $C_{10}H_7-Cl$  (melting point — 333 K, boiling point — 536 K), at a temperature of 353 K, was measured by applying  $MoK_\alpha$  radiation,  $\lambda = 0.71069 \text{ \AA}$ , monochromatized by a graphite crystal. The scattered intensity distribution was measured for the angles  $3^\circ \leq \vartheta \leq 60^\circ$  at every  $0.2^\circ$ , where  $2\vartheta$  is the scattering angle. The X-ray diffraction patterns were recorded on an X-ray diffractometer equipped with a special cell for measurements of liquids, described by North et al. [17] and Drozdowski [11].

The intensity of radiation scattered by a layer of the studied liquid was determined by the transmission method, Fig. 1. Absorption in the cuvette windows was neglected [18].

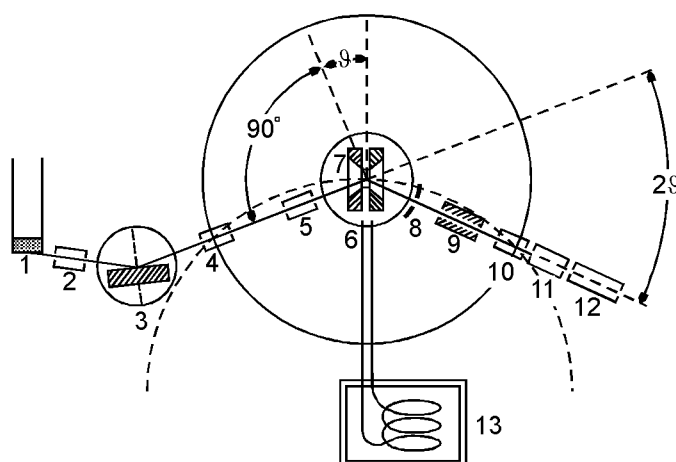


Fig. 1. A scheme of a measuring system of a goniometer in the transmission method; 1 — X-ray lamp anode, 2 — a system of output slits of the lamp, 3 — monochromator, 4 — a system of input slits of the goniometer, 5 — slits controlling the width and divergence of the beam, 6 — the goniometer table, 7 — cell with the liquid studied, 8 — a shield against the scattered parasite radiation, 9 — Soller slits, 10 — a system of output slits, 11 — radiation counter, 12 — electronic amplifier, 13 — ultrathermostat.

The experimental function of angular distribution of the scattered X-ray intensity was corrected for the background (air scattering) and noise counter [19], polarization [20], absorption by the sample [21], multiple scattering [22], anomalous dispersion [23], and then normalized [24]. In processing the data the computer procedure developed by Renninger and Kaplow [25] was used.

The differential radial distribution function for liquid 2-chloronaphthalene was determined from the modified Warren–Krutter–Morningstar equation [26] in the following form:

$$4\pi r^2 \sum_{j,k}^n \bar{K}_j [\rho_k(r) - \rho_0] = \frac{2r}{\pi} \int_0^\infty Si(S) \exp(-\alpha^2 S^2) \sin(Sr) dS, \quad (1)$$

where  $r$  is the distance from an atom or molecule selected as a scattering centre,  $\rho_k(r)$  — the function of radial electron density,  $K_j = f_j/f_e$  is the effective number of electrons in the atom  $j$ , and

$$f_e(S) = \frac{\sum_{uc} f_j(S)}{\sum_{uc} Z_j} \quad (2)$$

is the mean value of the atomic scattering factor for a molecule per electron,  $f_j$  — the atomic scattering factor of the  $j$ -th atom,  $Z_j$  — the atomic number (Table I), and  $\exp(-\alpha^2 S^2)$  is a convergence factor.

The mean effective number of scattering electrons was found from the integral average

$$\bar{K}_j = \frac{1}{S_2 - S_1} \int_{S_1}^{S_2} K_j dS, \quad (3)$$

where  $S = (4\pi/\lambda) \sin \vartheta$ ,  $\lambda$  — the X-ray scattering wavelength and  $\vartheta$  — the Bragg angle. The calculations were performed for a finite range of  $S$  values from  $S_1 = 0.430 \text{ \AA}^{-1}$  to  $S_2 = 14.311 \text{ \AA}^{-1}$ . In Eq. (1) the function  $i(S)$  is defined as:

$$i(S) = \frac{\bar{I}_{eu}(S)/N - \sum_{uc} f_i^2(S)}{f_e^2(S)}, \quad (4)$$

where  $\bar{I}_{eu}(S)/N$  is the experimentally observed total coherent intensity of scattered radiation per one structural unit,  $\sum_{uc} f_i^2(S)$  denotes the theoretical independent scattering on atoms of one structural unit.

The mean electron density was found from the formula [27]

$$\rho_0 = \frac{10^{-24} N_A d}{M} \sum_j Z_j, \quad (5)$$

where  $d$  is the macroscopic density of the liquid,  $N_A$  — the *Avogadro constant*,  $Z_j$  is the number of electrons in the  $j$ -th atom and  $M$  — *molar mass* (see Table I).

X-ray diffraction study of liquids is based on the Fourier analysis of the reduced intensity  $i(S)$  function, defined [28] as:

$$i(S) = i_m(S) + i_d(S), \quad (6)$$

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 about intermolecular correlations from the experimental data. In order to determine  $i(S)$  from the experimental data,  $\bar{I}_{eu}(S)/N$  and  $\sum_{uc} f_i^2(S)$  must be given in the same units.

### 3. Calculations

The literature values of the length of interatomic bonds often differ from the corresponding values obtained in experiment for liquid substances. Because variations in the interatomic distances really do occur, and the admissible deviation from the mean values usually is  $\pm 0.01 \text{ \AA}$  to  $\pm 0.03 \text{ \AA}$  [29], in this paper were considered different bond lengths and different values of the angles in 2-chloronaphthalene.

#### 3.1. Fit of the interference molecular function to the experimental function.

##### *Adjustment of the molecule model*

An important step in investigation of a liquid structure is to assume a model of the molecule and to select trial values for the internuclear distances  $r_{ij}$ . On the basis of the modified Debye equation:

$$i_m(S) = \left[ \sum_{uc} \sum_{i \neq j}^N f_i f_j A_{ij} \frac{\sin(Sr_{ij})}{Sr_{ij}} \right] \left[ \sum_i^N f_i(S) \right]^{-2}, \quad (7)$$

we can calculate various scattering curves to compare them with the experimental curve. In this equation  $r_{ij}$  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  $\exp\left[-\frac{\langle u_{ij} \rangle}{2} S^2\right]$ , where  $\langle u_{ij} \rangle$  is the mean-square variation in the distance  $r_{ij}$  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. (7)  $f_i$  and  $f_j$  are the atomic scattering factors for the  $i$ -th and  $j$ -th atoms. For calculation of mean amplitudes of vibrations  $\langle u_{ij} \rangle$  of different pairs of atoms of a liquid studied, the empirical formula of Mastryukov and Cyvin was applied [30]

$$\langle u_{ij} \rangle = a + br + cr^2, \quad (8)$$

where  $r$  is the internuclear distance in the molecule, and  $a$ ,  $b$ ,  $c$  are constants equal  $a = 0.0013837$ ;  $b = 0.023398$ ;  $c = -0.000147$ . This formula was proposed by Mastryukov and Cyvin on the basis of a large body of data from electron diffraction studies. The molecular function of structure  $i_m(S)$  was calculated by the formula (7) for the Bragg angle  $\vartheta$  varying from  $0^\circ$  to  $60^\circ$ . In order to choose

correct molecular parameters  $r_{ij}$  and damping factor value  $A_{ij}$  the function  $i_m(S)$  was fitted to the experimental function  $i(S)$  for  $S \geq 5 \text{ \AA}^{-1}$ .

The calculated curve that gives the best fit to the experimental curve is assumed to be the correct one, and the values of  $r_{ij}$  which were used to obtain this curve are taken as characteristic of the molecule studied.

### 3.2. Fit of the model RDF to the experimental function

The RDF may be represented as a sum of the Gaussian functions [31]

$$4\pi r^2 \sum_{i=1}^n \sum_{j=1}^n \overline{K}_i \rho_j(r) = \sum_{i,j}^n 2\overline{K}_i \overline{K}_j (\pi\sigma_i\sigma_j)^{-1/2} \exp [-(r - r_{ij})^2(\sigma_i\sigma_j)^{-1}], \quad (9)$$

where  $r_{ij}$  is the interatomic distance inside a molecule,  $\sigma_i$  and  $\sigma_j$  are the standard deviations of position atoms, which can be expressed as a function of the covalent radii of  $i$  and  $j$  atoms. By changing the internuclear distances  $r_{ij}$  we can get the best fit of the model function (9) to the experimental function. Accurate determination of the interatomic distances and covalent radii from such a fit was made using a home-made computer program for model RDF calculations (unpublished).

### 3.3. Conformational analysis of molecules of 2-chloronaphthalene by the minimisation of the potential energy

The main problem in the computer experiment was to assume the correct model of forces acting between atoms in the 2-chloronaphthalene molecule. Considering this molecule, we should definitely take into regard: (1) the potential of the interactions between the nearest neighbours determining the central force between them and (2) the potential dependent on the angle between the chemical bonds of the nearest neighbours and the length of these bonds. The problem was to select such a potential function which would correctly describe the molecule geometry. The potential energy of the molecule —  $U$  can be expressed as a function of bond-lengths, valency angles and the interactions between the atoms not being in a direct contact,  $U_{\text{nb}}$ :

$$U = \frac{1}{2} \sum_d K_d (d - d_0)^2 + \frac{1}{2} \sum_\alpha K_\alpha (\alpha - \alpha_0)^2 + U_{\text{nb}}, \quad (10)$$

where  $K_\alpha$  with appropriate indices stands for the force constants of bond deformation ( $d$ ) and deformation angle ( $\alpha$ ),  $d_0$  is the ideal distance, while  $\alpha_0$  is the ideal value of the valency angle. The carbon atoms in the naphthalene ring are trigonal ( $sp^2$  hybridization) and for them  $\alpha_0 = 120^\circ$ . It was assumed that the energy of non-covalent interactions is described by the additive function of interaction of all atom pairs:

$$U_{\text{nb}} = \sum_{i>j} \sum f_{ij}(r), \quad (11)$$

where  $f_{ij}$  is the atom–atom potential,  $r_{ij}$  is the distance between the  $i$ -th and  $j$ -th atoms.

In the calculations of the conformation of 2-chloronaphthalene the two-parameter Lennard–Jones “6–12” potential of the form [32] was used:

$$U_{ij} = \frac{d_{ij}}{r_{ij}^{12}} - \frac{e_{ij}}{r_{ij}^6}, \quad (12)$$

where

$$e_{ij} = \frac{\frac{3}{2}e(\hbar/m^{1/2})\alpha_i\alpha_j}{(\alpha_i/N_i)^{1/2} + (\alpha_j/N_j)^{1/2}}, \quad d_{ij} = e_{ij}r_{\text{min}}^6/2, \quad (13)$$

where  $\alpha_i$  and  $\alpha_j$  are the polarizabilities of the  $i$ -th and  $j$ -th atoms [33],  $N_i$  and  $N_j$  are the numbers of electrons in the external electron shell,  $\hbar$ ,  $e$ ,  $m$  are the *Planck constant*, charge and mass of the electron, respectively. The energy of the system of many molecules in general can be written as a series:

$$U = \sum_i f_i + \frac{1}{2!} \sum_i \sum_j f_{ij} + \frac{1}{3!} \sum_i \sum_j \sum_k f_{ijk} + \dots, \quad (14)$$

where  $f_i$  is the one-molecular function of energy of each molecule,  $f_{ij}$  are the corresponding functions of interaction of molecular pairs,  $f_{ijk}$  are the potential functions for three molecules, etc. The energy described by the third order terms does not exceed 10–15% of the energy of interaction of molecular pairs [34] and in the calculations of the conformation it was assumed that the total energy of interaction of a group of molecules is equal to a sum of energies of interactions of pairs of molecules.

#### 4. Results

The elementary condition for obtaining the correct structural information for liquid is to know the experimental function  $i(S)$  for a wide range of  $S$  values (Fig. 2). The experimental curve  $i(S)$ , marked in Fig. 2 by the solid line, is a structurally sensitive part of the total experimental coherent intensity  $\bar{I}_{\text{eu}}(S)/N$  per molecule, and represents the so-called total function of structure, because it involves both intra- and intermolecular scattering effects. A comparison of the measured diffraction pattern with the model calculations of the interference function gives a full agreement in the range of wave vector values from  $S \geq 5 \text{ \AA}^{-1}$  to the end of the range studied. The agreement proves that the assumed interatomic distances in the molecule are correct. The values of  $i_m(S)$  from Fig. 2 have been calculated using formula (7) for the proposed model of 2-chloronaphthalene, which is shown in Fig. 3. The calculated mean amplitudes of vibration  $\langle u_{ij} \rangle$  for 2-chloronaphthalene are shown in Table II. The numbering of atoms follows common notation in organic

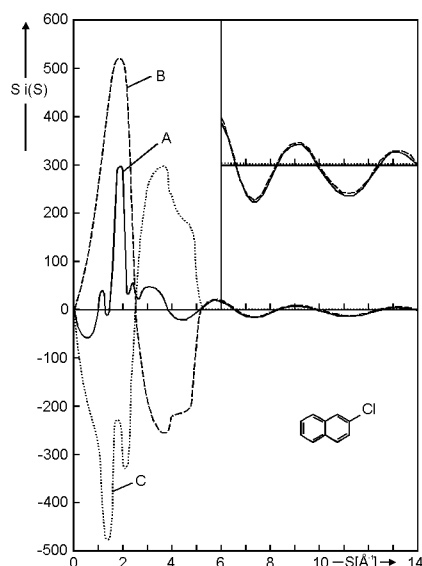


Fig. 2. Curve *A* (continuous line), the experimental structure function  $S_i(S) \exp(-\alpha^2 S^2)$ . Curve *B* (dashed line), the molecular structure function  $S_{i_m}(S)$  calculated according to Debye. Curve *C* (dotted line), subtraction of the calculated curve *B* from the curve *A*,  $S[i(S) \exp(-\alpha^2 S^2) - i_m(S)]$ .

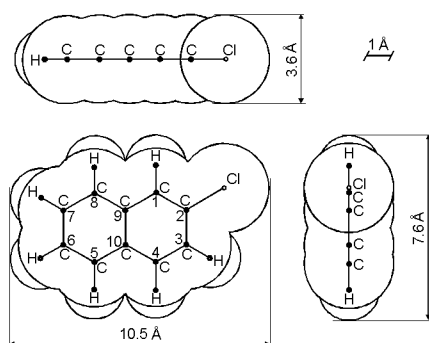


Fig. 3. A model of 2-chloronaphthalene  $C_{10}H_7-Cl$  molecule structure.

chemistry. Molecular parameters  $r_{ij}$  and the coefficients  $\langle u_{ij} \rangle$  (the mean-square variation of the distance  $r_{ij}$  between the pair of atoms (Table II) have been fitted by a testing method [35] assuming that  $i(S) \approx i_m(S)$  for values of  $S$  ( $S \geq 5 \text{ \AA}^{-1}$ ). Figure 2 also includes the so-called distinct structure function  $i_d(S) = i(S) - i_m(S)$  — the dotted line *C*, which provides the information about intermolecular correlations and does not affect the high-angle scattering. Figure 4a presents the RDF calculated for liquid naphthalene with separated maxima corresponding to different atomic positions [31]. We assume that the shape of a maximum corre-



TABLE II

The values of parameters of 2-chloronaphthalene molecule model applied in Debye formula Eq. (6). Atom notation the same as in Fig. 3,  $\langle u_{ij} \rangle$  denotes the root-mean-square variation at the distance  $r_{ij}$  between pairs of atoms [30].

Type of intramolecular interactions	Intramolecular distances $r_{ij}$ [Å]	Mean amplitude $\langle u_{ij} \rangle$ [Å]
C-H	1.09	0.077
C <sub>1</sub> -C <sub>2</sub>	1.36	0.046
C <sub>2</sub> -C <sub>3</sub>	1.41	0.061
C <sub>1</sub> -C <sub>9</sub>	1.42	0.047
C <sub>2</sub> -Cl	1.71	0.056
C <sub>1</sub> ...C <sub>3</sub>	2.43	0.062
C <sub>3</sub> ...Cl	2.73	0.077
C <sub>1</sub> ...C <sub>4</sub>	2.80	0.056
C <sub>1</sub> ...C <sub>5</sub>	3.70	0.068
C <sub>4</sub> ...Cl	4.16	0.109
C <sub>1</sub> ...C <sub>6</sub>	4.22	0.067
C <sub>2</sub> ...C <sub>7</sub>	4.85	0.057
C <sub>2</sub> ...C <sub>6</sub>	5.05	0.068
C <sub>8</sub> ...Cl	5.17	0.122
C <sub>5</sub> ...Cl	6.03	0.149
C <sub>6</sub> ...Cl	6.81	0.163

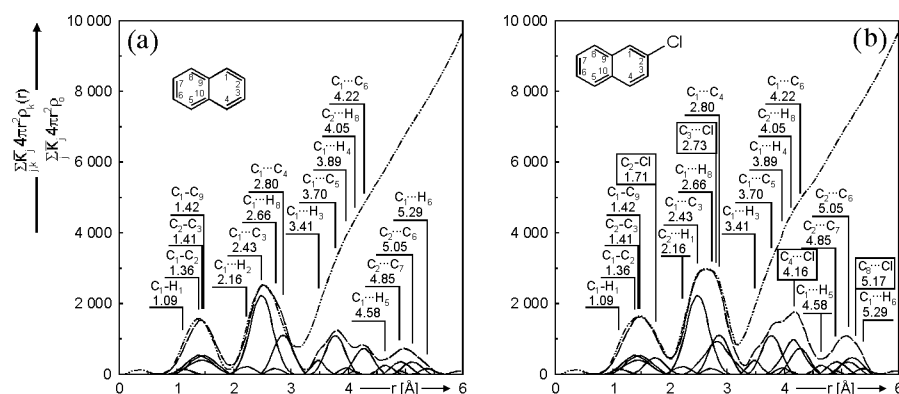


Fig. 4. The experimental RDF (dot-dot-dashed line) of naphthalene (a) decomposed into its atomic peaks (continuous line) and of 2-chloronaphthalene C<sub>10</sub>H<sub>7</sub>-Cl (b) decomposed into its atomic peaks (continuous line). Dashed line represents the sum of intramolecular contributions to RDF.

sponding to an atomic position is described by Eq. (9). The decomposition into Gaussian maxima was performed by subsequent iterations on self-consistent decomposition, so by a repeated fit of the first peak after elimination of the fitted second peak, then the repeated fit of the first and second after elimination of the third and so on, until getting a self-consistent system. The partial distributions of the first and second maximum of the radial function  $\sum_{i,j} \bar{K}_j 4\pi r^2 \rho_k(r)$  (Fig. 4a), have confirmed the co-planar arrangement of the carbon and hydrogen atoms in the molecule of naphthalene, at an average distance C–C = 1.40 Å (shared  $\pi$ -electrons) to the accuracy of  $\pm 0.01$  Å. The first maximum of this function for  $r = 1.40$  Å has been assigned to the interactions between carbon and hydrogen atoms C–H = 1.09 Å and between the neighbouring carbon atoms in the naphthalene ring: C<sub>1</sub>–C<sub>2</sub> = 1.36 Å, C<sub>2</sub>–C<sub>3</sub> = 1.41 Å, C<sub>1</sub>–C<sub>9</sub> = 1.42 Å. Knowing the scattering powers of carbon atoms  $\bar{K}_C = 6.556$  el and hydrogen atoms  $\bar{K}_H = 0.331$  el, we could calculate the areas corresponding to particular interatomic distances in the molecule and compare them with the areas determined from the RDFs. The best fit of the model function to the experimental total radial distribution function was obtained for the interatomic distances given in Table IIIa. The areas under the maxima determined theoretically and experimentally agree with accuracy of 1%.

TABLE IIIa

Experimental  $Q_D$  and theoretical  $Q_T$  areas of the discrete maxima and corresponding intramolecular interactions for liquid naphthalene C<sub>10</sub>H<sub>8</sub>.

Maximum [Å]	Intramolecular distances [Å]	Theoretical areas $Q_T = 2 \cdot n \cdot \bar{K}_j \cdot \bar{K}_k$ [el <sup>2</sup> ]	Experimental areas $Q_D$ [el <sup>2</sup> ]
1.40	C <sub>1</sub> –H <sub>1</sub> = 1.09	$2 \cdot 8 \cdot \bar{K}_C \cdot \bar{K}_H = 34.72$	967.81
	C <sub>1</sub> –C <sub>2</sub> = 1.36	$2 \cdot 4 \cdot \bar{K}_C \cdot \bar{K}_C = 343.85$	
	C <sub>2</sub> –C <sub>3</sub> = 1.41	$2 \cdot 4 \cdot \bar{K}_C \cdot \bar{K}_C = 343.85$	
	C <sub>1</sub> –C <sub>9</sub> = 1.42	$2 \cdot 3 \cdot \bar{K}_C \cdot \bar{K}_C = 257.89$	
		$\sum = 980.31$	
2.50	C <sub>1</sub> ...H <sub>2</sub> = 2.16	$2 \cdot 16 \cdot \bar{K}_C \cdot \bar{K}_H = 69.44$	1791.50
	C <sub>1</sub> ...C <sub>3</sub> = 2.43	$2 \cdot 14 \cdot \bar{K}_C \cdot \bar{K}_C = 1203.47$	
	C <sub>1</sub> ...H <sub>8</sub> = 2.66	$2 \cdot 4 \cdot \bar{K}_C \cdot \bar{K}_H = 17.36$	
	C <sub>1</sub> ...C <sub>4</sub> = 2.80	$2 \cdot 6 \cdot \bar{K}_C \cdot \bar{K}_C = 515.77$	
		$\sum = 1806.04$	

The second maximum of this function for  $r = 2.50$  Å, is assigned to subsequent interatomic distances inside the naphthalene ring: C<sub>1</sub>...H<sub>2</sub> = 2.16 Å, C<sub>1</sub>...C<sub>3</sub> = 2.43 Å, C<sub>1</sub>...H<sub>8</sub> = 2.66 Å, C<sub>1</sub>...C<sub>4</sub> = 2.80 Å. The partial maxima sum up to give the theoretical radial distribution function following closely the experimental function in the range up to  $r = 3.25$  Å. On the basis of the agreement we assumed the above distances are accurate approximations of the real

interatomic distances. The distances are in agreement with the data obtained by other authors [36].

The proposed model of the liquid 2-chloronaphthalene molecule was constructed assuming rigidity of the naphthalene ring and no deforming effect of the chlorine atom on this ring (Fig. 4b, Table IIIb).

TABLE IIIb

Experimental  $Q_D$  and theoretical  $Q_T$  areas of the discrete maxima and corresponding intramolecular interactions for liquid 2-chloronaphthalene  $C_{10}H_7-Cl$ .

Maximum [ $\text{\AA}$ ]	Intramolecular distances [ $\text{\AA}$ ]	Theoretical areas $Q_T = 2 \cdot n \cdot \bar{K}_j \cdot \bar{K}_k$ [ $\text{el}^2$ ]	Experimental areas $Q_D$ [ $\text{el}^2$ ]
1.48	$C_1-H_1 = 1.09$	$2 \cdot 7 \cdot \bar{K}_C \cdot \bar{K}_H = 30.38$	1245.56
	$C_1-C_2 = 1.36$	$2 \cdot 4 \cdot \bar{K}_C \cdot \bar{K}_C = 343.85$	
	$C_2-C_3 = 1.41$	$2 \cdot 4 \cdot \bar{K}_C \cdot \bar{K}_C = 343.85$	
	$C_1-C_9 = 1.42$	$2 \cdot 3 \cdot \bar{K}_C \cdot \bar{K}_C = 257.89$	
	$C_2-Cl = 1.71$	$2 \cdot 1 \cdot \bar{K}_C \cdot \bar{K}_{Cl} = 257.30$	
		$\sum = 1233.27$	
2.63	$C_2 \dots H_1 = 2.16$	$2 \cdot 14 \cdot \bar{K}_C \cdot \bar{K}_H = 60.76$	2294.27
	$C_1 \dots C_3 = 2.43$	$2 \cdot 14 \cdot \bar{K}_C \cdot \bar{K}_C = 1203.47$	
	$C_1 \dots H_8 = 2.66$	$2 \cdot 4 \cdot \bar{K}_C \cdot \bar{K}_H = 17.36$	
	$C_3 \dots Cl = 2.73$	$2 \cdot 2 \cdot \bar{K}_C \cdot \bar{K}_{Cl} = 514.60$	
	$C_1 \dots C_4 = 2.80$	$2 \cdot 6 \cdot \bar{K}_C \cdot \bar{K}_C = 515.77$	
	$\sum = 2311.96$		

The application of Fourier transform to the curve  $i(S)$  gave the DRDF displayed in Fig. 5. The differential radial distribution function  $4\pi r^2 \sum_{j,k}^n \bar{K}_j [\rho_k(r) - \rho_0]$  determined by the integral,  $\frac{2r}{\pi} \int_{S_0}^{S_{\max}} Si(S) \exp(-\alpha^2 S^2) \sin(Sr) dS$  was calculated by the numerical Simpson method for  $0 \leq r \leq 20 \text{ \AA}$  at a step of  $\Delta r = 0.05 \text{ \AA}$ . The distribution of random uncertainty  $\sigma(r)$  on DRDF, caused by standard deviations  $\sigma[Si(S)]$  of the experimental function  $i(S)$  was calculated on the basis of the data of Konnert and Karle [37] from the following formula:

$$\sigma(r) = \sum_S \sigma[Si(S)] \sin(Sr) \exp(-\alpha^2 S^2), \quad (15)$$

where  $\sigma[Si(S)] = [S/g^2(S)]\sigma_E(S)$  and  $\sigma_E(S)$  is the standard deviation of the experimental function of intensity distribution. The maximum experimental uncertainty of the paired functions was estimated as  $\pm 3\%$ . The margins of errors of the mean distances determined are given in Table IV. The random error of the radial distribution function does not exceed 3%.

The DRDF of liquid 2-chloronaphthalene has 13 maxima in the range of  $1 \leq r \leq 20 \text{ \AA}$ . Their positions correspond to the most probable interatomic and

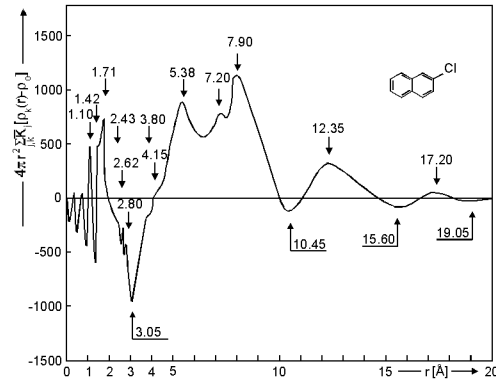


Fig. 5. The differential radial distribution function  $4\pi r^2 \sum_{j,k} \bar{K}_j [\rho_k(r) - \rho_0]$  for liquid 2-chloronaphthalene.

TABLE IV  
Accuracy intervals of the structural parameters determined.

Accuracy intervals of the structural parameters $r$ [Å]	Accuracy of measurement $\pm \Delta r$ [Å]
$1 < r \leq 2$	$\pm 0.01$
$2 < r \leq 3$	$\pm 0.02$
$3 < r \leq 4$	$\pm 0.05$
$4 < r \leq 5$	$\pm 0.10$
$r > 5$	$\pm 0.15$

TABLE V  
The range of coordination spheres for the studied 2-chloronaphthalene.

Sphere	Range [Å]
1 st	3.05–10.45
2 nd	10.45–15.60
3 rd	15.60–19.05

intermolecular distances in the liquid studied, which are considered in detail below. On the basis of the DRDF (Fig. 5), the spheres of intermolecular ordering [38] were distinguished. Subsequently, the ranges of the spheres (Table V) were determined. Coordination shells are delimited by the DRDF minima. The DRDF is charged with a certain error following from the application of the integral Fourier formula derived for infinite limits of integration to an experimental situation in which measurements are conducted in a finite range of argument values.

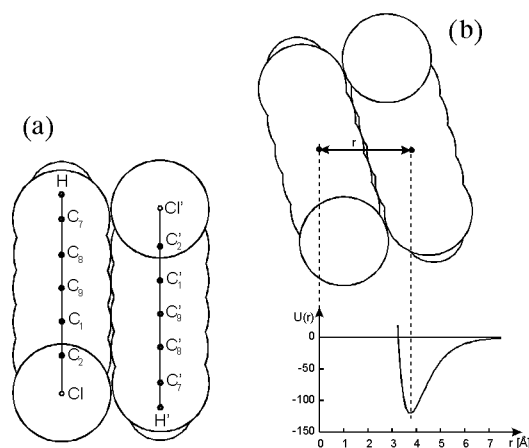


Fig. 6. The model of probable conformation of molecules in liquid 2-chloronaphthalene  $C_{10}H_7-Cl$ . The arrangement of molecules corresponding to the maxima in the DRDF (a); the potential energy curve describing the interaction of two molecules of 2-chloronaphthalene (b).

A simple model of short-range arrangement of the molecules in liquid 2-chloronaphthalene was proposed as shown in Fig. 6. The same parameters  $r_{ij}$  were determined by the fit of the theoretical curve  $B$  (Fig. 2) to the experimental curve  $A$  in high  $S$  region. In the calculations we optimised seven parameters of the 2-chloronaphthalene molecule: the length of the bonds C-C, C-H, C-Cl, and the angle C-C-C. The following initial values were assumed for the above parameters [39]:  $C_1-C_2 = 1.36 \text{ \AA}$ ,  $C_2-C_3 = 1.41 \text{ \AA}$ ,  $C_1-C_9 = 1.42 \text{ \AA}$ ,  $C_2-Cl = 1.71 \text{ \AA}$ ,  $C_1-H_1 = 1.09 \text{ \AA}$ , angles  $C_1-C_2-C_3 = 119.90^\circ$ ,  $C_2-C_3-C_4 = 121.02^\circ$ . The mean distances between pairs of different atoms belonging to neighbouring molecules of 2-chloronaphthalene are given in Table VI. The numbering of the atoms is consistent with the notation assumed in Fig. 6a.

TABLE VI

The mean distances  $r_{ij}$  and mean amplitude  $\langle u_{ij} \rangle$  between pairs of atoms in liquid 2-chloronaphthalene.

Distances between pairs of atoms	Distances determined from the DRDF [ $\text{\AA}$ ]	Mean amplitude $\langle u_{ij} \rangle$ [ $\text{\AA}$ ]
$C_9 \dots C'_9$	3.80	0.126
$C_1 \dots C'_1$	4.15	0.167
$C_2 \dots C'_2$	5.38	0.267
$C_7 \dots C'_7$	7.20	0.167
$Cl \dots Cl'$	7.90	0.183

## 5. Discussion

The experimental  $i(S)$  data  $Si(S)\exp(-\alpha^2S^2)$  (Fig. 2, curve *A*) were fitted for  $S > 5 \text{ \AA}^{-1}$  with the theoretical data for the curve  $i_m(S)$  (Fig. 2, curve *B*) to  $S_{\max}$  value equal to  $14 \text{ \AA}^{-1}$ . The obtained coincidence of the high  $S$  region of these two curves proves that the proposed model of 2-chloronaphthalene molecule, Fig. 3 and in particular the interatomic distances in the molecule, are correct. A detailed analysis of the results obtained proved that a fit between the theoretical and experimental curves is possible for  $\alpha = 0.03$  and for  $S$  values ranging from  $5 \text{ \AA}^{-1}$  to  $14 \text{ \AA}^{-1}$ . The integral of  $i_m(S)S^2$  from zero to infinity is zero, and for high values of  $S$  (taking into regard the temperature factor) subsequent oscillations bring decreasing contribution to this integral. This procedure is the basis of the method of normalisation presented in the work of Krogh-Moe and Norman [24]. The assignment of intramolecular distances to the maxima (Figs. 4a, b, and 5), has been performed assuming that the chlorine atom does not have a significant influence on the rigidity and interatomic distances in the naphthalene ring. This assumption follows from the results of the theoretical study on the ring deformations under the effect of monosubstitutions. The quantum-chemical calculations performed by Scharfenberg [40] for 22 monosubstituted benzene derivatives have shown that the greatest changes between the carbon atoms in the ring are of an order of  $0.01 \text{ \AA}$ .

In the range of the argument below  $1 \text{ \AA}$ , 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 [27]. The maxima on the DRDF in the range of  $1 < r \leq 3 \text{ \AA}$  are attributed to intramolecular interactions. The three maxima corresponding to the C–C distances appear at  $1.42 \text{ \AA}$ ,  $2.43 \text{ \AA}$ , and  $2.80 \text{ \AA}$  for the molecule studied. These distances correspond to those between the carbon atoms in the *ortho*, *meta*, and *para* positions in the naphthalene ring. The maximum assigned to the C–H bond corresponds to the distance of  $1.10 \text{ \AA}$  within the ring. The maxima on the DRDF (Fig. 5) in the range of  $1 < r \leq 3 \text{ \AA}$  have been ascribed to the following pairs of atoms: C<sub>1</sub>–H =  $1.10 \text{ \AA}$ , C<sub>1</sub>–C<sub>9</sub> =  $1.42 \text{ \AA}$ , C<sub>2</sub>–Cl =  $1.71 \text{ \AA}$ , C<sub>1</sub>...C<sub>3</sub> =  $2.43 \text{ \AA}$ , C<sub>1</sub>...Cl =  $2.62 \text{ \AA}$ , C<sub>1</sub>...C<sub>4</sub> =  $2.80 \text{ \AA}$ , C<sub>9</sub>...C'<sub>9</sub> =  $3.80 \text{ \AA}$ . The maxima in the range of  $3 \leq r < 6 \text{ \AA}$ , are interpreted as due to intra- and intermolecular diffraction, whereas those for  $r \geq 6 \text{ \AA}$  are due to intermolecular diffraction.

The packing coefficient, defined by Kitaigorodsky [41] as the ratio of the specific volume of the molecule to the volume per a molecule in a given liquid, takes a value of 0.57. This value falls within the range determined for the liquid phase — from 0.51 to 0.68. A molecule of 2-chloronaphthalene occupies the average volume  $\bar{V} = 237.3 \text{ \AA}^3$ , whereas an increment of the molecule volume [41] is  $\bar{V}^{\text{incr}} = 135.2 \text{ \AA}^3$ .

The experimental function RDF was determined by the X-ray scattering from a liquid sample and compared with the corresponding theoretical function calcu-

lated for the most probable assumed model of the structure of 2-chloronaphthalene. The model was defined as an average structural unit which coherently scatters X-rays. 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 the neighbours, resulting from their van der Waals models. Such models can be constructed on the basis of the bond lengths within the molecule and the van der Waals radii of C, Cl, and H atoms. The shape, positions and amplitude of the maxima appearing in the range of  $r \in (3.05 \div 10.45) \text{ \AA}$  (Fig. 5) allow us to conclude about the occurrence of interactions among particular atoms belonging to neighbouring molecules. The calculations performed by the method of minimisation of the potential energy [39] of the structure of 2-chloronaphthalene, suggested the binary arrangement of molecules (Fig. 6a), which can be explained by the presence of the Lennard–Jones potential minimum “6–12”, Fig. 6b. Because of the permanent dipole moment of the 2-chloronaphthalene molecule  $\mu = 1.62 \text{ D}$  [42], the neighbouring molecules are arranged so that their dipolar moments are antiparallel. This orientation is confirmed by the peaks on the DRDF appearing at:  $C_9 \dots C'_9 = 3.80 \pm 0.05 \text{ \AA}$ ,  $C_1 \dots C'_1 = 4.15 \pm 0.10 \text{ \AA}$ ,  $C_2 \dots C'_2 = 5.38 \pm 0.15 \text{ \AA}$ ,  $C_7 \dots C'_7 = 7.20 \pm 0.15 \text{ \AA}$ , and  $Cl \dots Cl' = 7.90 \pm 0.15 \text{ \AA}$ . Figure 6a, b presents the two molecules of 2-chloronaphthalene in the most energetically favourable mutual arrangement. The interactions between two molecules of 2-chloronaphthalene lead to the formation of complexes. The values of the most probable energies of interactions and distances between the two molecules are characteristic of a given intermolecular complex. The maxima of this function at  $\bar{r} = 12.35 \text{ \AA}$  and  $\bar{r} = 17.20 \text{ \AA}$  bring information about the difference between the observed and the average distribution of electron density.

## 6. Conclusions

The use of short-wave radiation from an X-ray tube with a molybdenum anode allowed determination of the mean structural parameters (the inter- and intramolecular distances, the radii of coordination spheres) and local ordering of the molecules in the liquid 2-chloronaphthalene. The appearance of clear maxima on the functions of angular-distribution of X-ray radiation and DRDF indicates the presence of short-range ordering in liquid 2-chloronaphthalene up to the distance of about  $20 \text{ \AA}$ .

The most probable model of the short-range order structure was obtained using the method of exact analysis of the distribution curve in terms of DRDF. From the shape of the radial distribution functions and in particular from the positions of their maxima, we can conclude about the most probable mutual configurations of molecules of a given liquid. The structure of liquid 2-chloronaphthalene is determined by the presence of the naphthalene ring. The presence of clear maxima in the range of  $1 < r \leq 3 \text{ \AA}$  of the RDF (Fig. 4a, b) and DRDF (Fig. 5) functions confirm that the chlorine atom does not have deforming influence on the

structure of naphthalene ring. A realistic estimation of the uncertainties of interatomic distances ( $\Delta r = 0.01 \div 0.02$ ) Å determined in the range of  $1 < r \leq 3$  Å justifies putting forward a hypothesis that the method of X-ray diffraction in liquids does not allow determination of possible deformations in the naphthalene ring ( $0.0003 \div 0.01$ ) Å. The values of  $r = 3.80, 4.15, 5.38, 7.20,$  and  $7.90$  Å determined provide the information about intermolecular spatial configurations in the liquid studied. The proposed approximate binary model of interactions is related to the mutual antiparallel orientation of chlorine atoms from the neighbouring molecules. The analysis of the angular and radial functions has confirmed the antiparallel orientation of the dipole moments and the fact that the naphthalene rings are stacked one over the other.

The packing coefficient of molecules in liquid 2-chloronaphthalene is approximately constant in all coordination spheres and equals to 0.57. This value falls within the range of  $\bar{k}$  values acceptable for the liquid phase substances. These results are also consistent with the values presumed in the conformational structure investigation of 2-chloronaphthalene performed by empirical and semi-empirical MO-LCAO calculations [43].

As the molecules of 2-chloronaphthalene have permanent electric moment in liquid they should assume such an orientation that their dipolar moments would be antiparallel. Such an orientation is confirmed by the occurrence of intermolecular interactions suggested in the model of the molecule. The results can be interpreted on the basis of simple models of local ordering of molecules.

As indicated by the conformational analysis of the liquid studied, results of the potential energy minimization and the value of the permanent dipole moment of the 2-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 chlorine atoms of the neighbouring molecules is:  $\text{Cl} \dots \text{Cl}' = 7.90 \pm 0.15$  Å, which leads to the mean distance between the pair of  $\text{C}_7$  atoms of the neighbouring molecules equal to  $\text{C}_7 \dots \text{C}'_7 = 7.20 \pm 0.15$  Å.

The results of this paper permit the following conclusions to be drawn:

1. A satisfactory fit can be obtained between the theoretically calculated radial distribution function for the chosen simplified model of intermolecular interactions and the experimentally obtained radial distribution function.
2. The DRDF maxima at 3.80, 4.15, 5.38, 7.20, and 7.90 Å correspond to the intermolecular  $\text{C}_9 \dots \text{C}'_9, \text{C}_1 \dots \text{C}'_1, \text{C}_2 \dots \text{C}'_2, \text{C}_7 \dots \text{C}'_7,$  and  $\text{Cl} \dots \text{Cl}'$ , interactions. The attractive dipole interaction between neighbouring molecules can favour the plane arrangement of molecules one over another (i.e. the antiparallel one), making such a configuration relatively more stable.
3. The approach proposed in this paper gives a good description of intermolecular interactions in liquid 2-chloronaphthalene and is a useful X-ray method for their analysis.



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