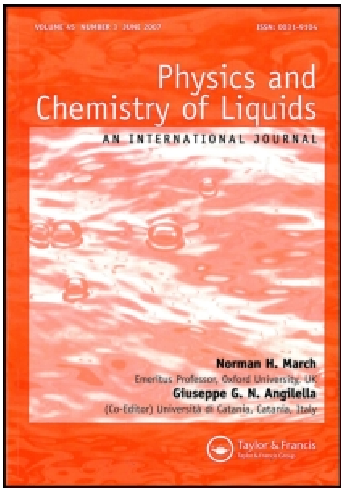

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X-ray study of the structure and of the internal ordering degree in liquid α- and β-naphthalene derivatives

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X-ray study of the structure and of the internal ordering degree in liquid α- and β-naphthalene derivatives

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Structure and molecular correlations in liquid selected derivatives of naphthalene $C_{10}H_7$–R have been studied by X-ray diffraction and Fourier analysis. The compounds are obtained as a result of substitution of hydrogen atoms in the naphthalene molecule by a functional group R (in position α or β): $R = Cl$ and CH_3 in chloronaphthalene and methylnaphthalene. The measurements of scattered radiation intensity were performed in a wide range of wave vector ($S_{min} = 4.30\,nm^{-1}$ to $S_{max} = 153.10\,nm^{-1}$), with the use of X-ray radiation MoK_α ($\lambda = 0.071069\,nm$). The mean parameters of the liquid structure (intra- and intermolecular distances, radii of spheres, coordination numbers) were found. A comparative analysis of these compounds has been made and the influence of particular functional groups (–Cl, $–CH_3$) and their position α or β in the ring on the molecular arrangement and packing coefficient has been discussed. The results of the study of molecular correlations in liquid α- and β-naphthalene derivatives may be important for explanation of mechanisms of certain physical and chemical processes taking place in similar systems, e.g., diffusion or thermal conductivity. The proposed experimental procedure and methods of data processing and interpretation can be used in investigation of other molecular liquids.

Keywords: X-ray diffraction in liquids; Molecular ordering; Differential radial distribution functions

1. Introduction

The structure and interactions of naphthalene $C_{10}H_8$ have been a subject of a number of studies [1–3]. The structures of 1,2,3,4-tetraphenylnaphthalene [4], octaphenylnaphthalene [5], 1,2-dichloronaphthalene [6], and 1,2,3,4,6,7-hexachloronaphthalene [7] have been studied in the crystal phase. On the basis of the known liquid structures of α-chloronaphthalene [8], α-methylnaphthalene [9], β-chloro- and β-methylnaphthalene [10] we can predict the structures of their polar derivatives. No comparative analysis of ordering in these liquids has been made.

This article reports results of structural X-ray diffraction study of the four naphthalene derivatives: α- and β-chloronaphthalene $C_{10}H_7$–Cl and α- and

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Table 1. Melting point (mp), boiling point (bp), and temperature of measurements (tm) of the liquids studied under normal pressure.

Liquids	mp (K)	bp (K)	tm (K)
α-chloronaphthalene	253	386	293
β-chloronaphthalene	333	536	353
α-methylnaphthalene	251	516	293
β-methylnaphthalene	313	388	333

Table 2. Physical and structural parameters of liquid α- and β-naphthalene derivatives.

Parameters/liquids	Chloronaphthalene	Methylnaphthalene
Mean effective number of electrons per hydrogen atom $\bar{K}_H$ (el)	0.639	0.650
Mean effective number of electrons per carbon $\bar{K}_C$ (el)	6.335	6.318
Total of atom numbers in one molecule $\sum_j \bar{K}_j$	84	76
Molecular mass (g/mol)	162.62	142.20

β-methylnaphthalene $C_{10}H_7$–CH_3. The aim of the study is to establish the role of the naphthalene ring and the functional groups (–Cl, –CH_3) attached to it at the α and β positions in determining configurations of the molecules of the liquids studied. On the basis of the courses of the radial functions it is possible to determine the mutual orientations of the functional groups of the molecules with respect to the naphthalene ring of the other molecules. 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. polar monosubstituted derivatives of naphthalene.

The temperatures at which measurements were performed for particular liquids are given in table 1. The X-ray measurements of the liquid β-derivatives of naphthalene were carried out at temperatures by 20 K higher than their melting points (table 1).

In the calculations, the values of the structural and physical parameters of liquids studied, collected in table 2, were used.

The compounds to be studied (of 99% purity) were purchased from Aldrich-Chemie (Germany) and Janssen Chimica (Belgium).

2. Experimental

The structure of α- and β-naphthalene derivatives was studied by diffraction of strictly monochromatic X-ray radiation. For each of 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 a X-ray goniometer. The angular distributions of the X-ray scattered intensity were measured by applying MoK_α ($\lambda = 0.071069$ nm) radiation for the angles $3 \leq \Theta \leq 60^\circ$, at every 0.2°, where 2Θ is the scattering angle. The radiation was monochromatised by reflection from the (002) planes of flat graphite with the angle of monochromatisation of $\alpha_m = 6^\circ 00'$. The measurements were performed using the transmission technique with the incident and diffracted beam symmetric upon the flat sample surface. The method is described in details in [3, 10].

The scattered X-ray intensities were measured by a proportional counter and the results were registered by a computer. For each liquid measurements were performed for different times of counting and repeated a few times so that the final result 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 polarisation and absorption factors [11], and then normalised [12]. Absorption in the cuvette was neglected.

The Warren–Krutter–Morningstar method [13] was applied to obtain the differential radial distribution functions (DRDFs) $4\pi r^2 \sum_{j,k}^{n} \bar{K}_j[\rho_k(r) - \rho_0]$. The integrals appearing in the expression for $\rho_k(r)$ were found numerically by the Simpson method for $0 < \bar{r} \leq 2.0$ nm, at every 0.005 nm. The radial distribution functions were calculated with the use of the computer program written by Drozdowski [9].

4. Results

The normalised functions $\bar{I}(S)$ 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. The positions of the maxima of the function $\bar{I}(S)$ in the range $9.00\,\mathrm{nm}^{-1} < S < 22.00\,\mathrm{nm}^{-1}$ were determined to an accuracy of $\Delta S = \pm 0.10\,\mathrm{nm}^{-1}$. The positions of the peaks in the range $9.00 < S < 45.00\,\mathrm{nm}^{-1}$ were read out to an accuracy $\Delta S = \pm 0.20\,\mathrm{nm}^{-1}$, while the further ones with the measuring uncertainty of $\Delta \mathrm{S} = \pm 0.30\,\mathrm{nm}^{-1}$. Small-angle scattering results $(0 < \Theta < 3^\circ)$ were extrapolated to the origin of the coordinate system using a second-order function.

From the positions of the peaks in the angular distributions (figure 1a and b) in the range of $9.00\,\mathrm{nm}^{-1} < S < 22.00\,\mathrm{nm}^{-1}$ we can conclude about not only mean intermolecular distances but also the distances between chlorine atoms and methyl groups in two neighbouring molecules of liquids studied.

The application of Fourier transforms [14] to the experimental curves $I(S)$ gave the functions of electron density distribution presented in figure 2. The distribution functions were interpreted by the Warren [13] method and were determined by the structure integral $2r/\pi \int_{S_{\min}}^{S_{\max}} Si(S)\sin(S\bar{r})\mathrm{d}s$, calculated by the numerical Simpson method for $0 < \bar{r} \leq 2.0$ nm, at a step of $\Delta\bar{r} = 0.005$ nm. These functions bring the information about the difference between the observed and the average distribution of electron density [15]. The maximum experimental errors $\Delta(\bar{r})$ of the radial distribution curves were estimated to be 3% [2]. The DRDFs are 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 [2]. In the experimental conditions applied $S_{\min} = 4\pi \sin \Theta_{\min}/\lambda = 4.30\,\mathrm{nm}^{-1}$, and $S_{\max} = 4\pi \sin \Theta_{\max}/\lambda = 153.10\,\mathrm{nm}^{-1}$ for the characteristic radiation of MoK_α.

The maxima for $0.110\,\mathrm{nm} \leq \bar{r} \leq 0.450$ nm on the DRDFs (figure 2a and b) have been assigned to the following pairs of atoms: $\mathrm{C{-}H} = 0.110$ nm, $\mathrm{C_1{-}C_2} = 0.142$ nm, $\mathrm{C_1{-}CH_3} = 0.164$ nm, $\mathrm{C_1{-}Cl} = 0.171$ nm, $\mathrm{C_1 \cdots C_3} = 0.243$ nm, $\mathrm{C_2 \cdots Cl} = 0.262$ nm,

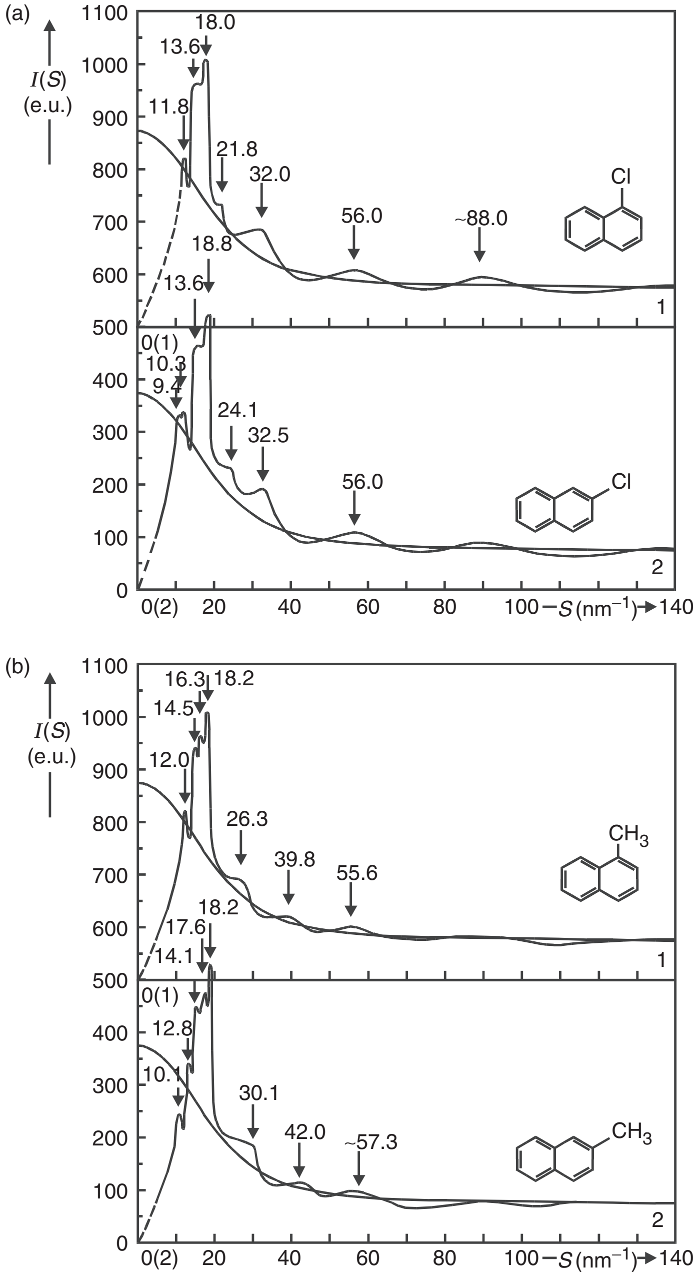

Figure 1. Normalised, experimental curves of angular distribution of X-ray scattered intensity in liquid α and β-chloronaphthalene (a), and α- and β-methylnaphthalene (b).

$C_2\cdots CH_3 = 0.264$ nm, $C_1\cdots C_4 = 0.280$ nm, $C_1\cdots C_5 = 0.370$ nm, $C_3\cdots CH_3 = 0.395$ nm, and $C_4\cdots CH_3 = 0.444$ nm.

In the range of distances $\bar{r} \rightarrow < 0.450–2.0 >$ nm, we can talk about the spheres of intermolecular ordering in the liquids studied. The conclusions that the broad maxima

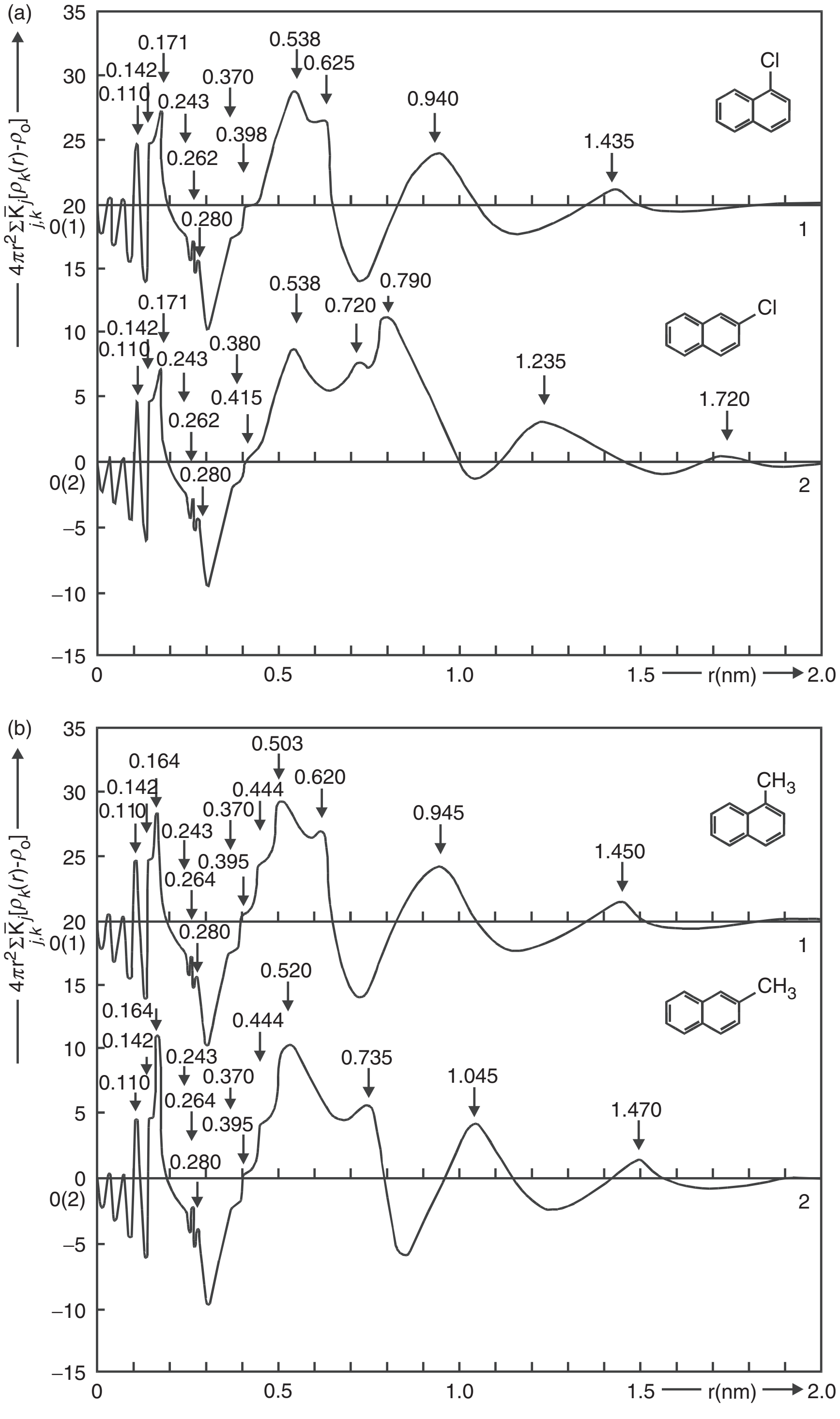

Figure 2. Differential radial distribution functions of electron density of liquid α- and β-chloronaphthalene (a), and α- and β-methylnaphthalene (b).

Table 3. The range of the coordination spheres (nm) and the number of molecules in each sphere (in parentheses) for the liquid studied.

Liquids	Sphere 1	Sphere 2	Sphere 3
α-chloronaphthalene	0.305–0.740 (8.5)	0.740–1.165 (28.3)	1.165–1.640 (56.4)
β-chloronaphthalene	0.305–1.045 (10.1)	1.045–1.560 (29.7)	1.560–1.905 (55.8)
α-methylnaphthalene	0.305–0.735 (8.4)	0.735–1.160 (29.1)	1.160–1.635 (57.6)
β-methylnaphthalene	0.305–0.845 (8.3)	0.845–1.240 (28.8)	1.240–1.655 (57.4)

Table 4. The van der Waals volume of the molecules $\bar{V}_0$, the volumes per molecule in the liquid $\bar{V}$, the packing coefficients $\bar{k}$, the mean diameter $\bar{D}$, and the macroscopic density d of the molecules studied.

Liquids/parameters	$\bar{V}_0$ (nm^3)	$\bar{V}$ (nm^3)	$\bar{k}$ (%)	$\bar{D}$ (nm)	d (g/cm^3)
α-chloronaphthalene	0.1352	0.2186	61	0.670	1.194
β-chloronaphthalene	0.1352	0.2373	57	0.659	1.138
α-methylnaphthalene	0.1508	0.2359	63	0.700	1.001
β-methylnaphthalene	0.1508	0.2519	60	0.689	0.994

at $\bar{r} \geq 0.450$ nm (figure 2a and b) are intermolecular have been confirmed by the results of density calculations. Coordination shells were delimited by the minima of DRDFs [15]. Subsequently, the ranges of the spheres and coordination numbers (table 3) were determined.

The mean diameter of the molecules studied $\bar{D}$ (table 4) was calculated assuming the Stuart–Briegleb model [16] describing the spatial distribution of atoms in the molecule. The specific volume of the molecule $\bar{V}_0$ (table 4) was determined on the basis of the volume increments corresponding to the contribution of particular kinds of atoms in the total volume. The mean volume per one molecule $\bar{V}$ of the liquid was calculated from the known macroscopic density, molecular mass, and the Avogadro number [17]. The packing coefficient $\bar{k}$ defined by Kitaigorodsky [18] as a ratio of the volume of the molecule to the volume per molecule in the liquid for α- and β-naphthalene derivatives takes values from 57% to 63% (table 4).

The simple models of short-range arrangement of the molecules in compounds studied were proposed (figure 3a and b).

The mean distances between pairs of different atoms belonging to neighbouring molecules of liquids studied are given in table 5. The numbering of the atoms is consistent with the notation assumed in figure 3a and b. The arrangement of molecules corresponds to the maxima in the DRDFs.

5. Discussion

Comparative analysis of the scattered radiation distribution function (figure 1a and b) indicates that the function is sensitive to the shape of the molecules studied, that is the positions of the maxima on the angular distribution functions change with the functional groups attached to the naphthalene ring.

The positions of the radial distribution function maxima (figure 2a and b) corresponding to the mean least intermolecular distances and distances between the

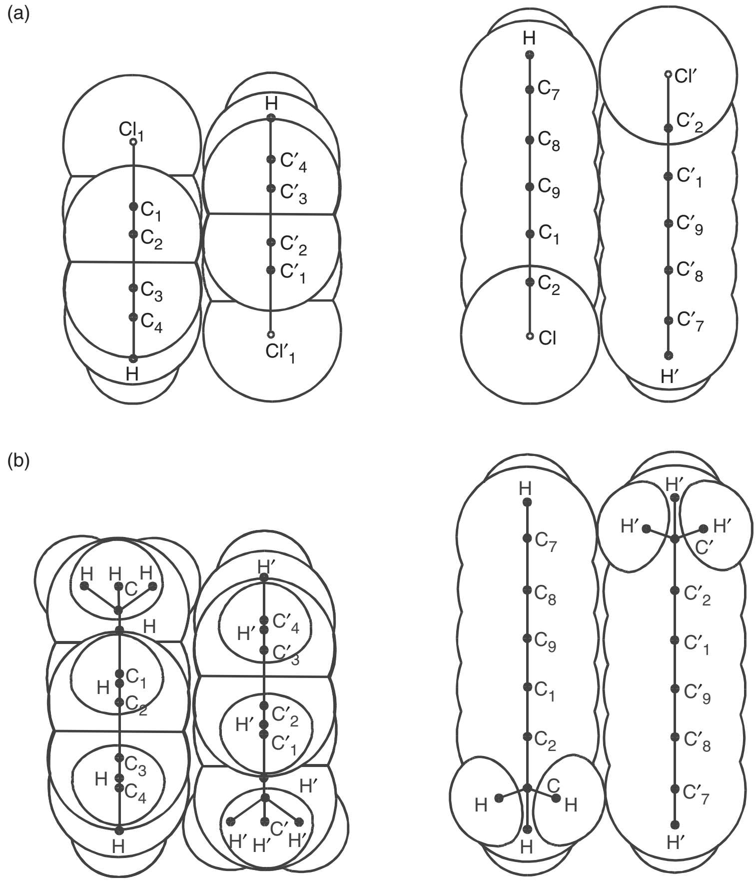

Figure 3. Models of probable conformation of molecules in liquid α- and β-chloronaphthalene $C_{10}H_7$–Cl (a) and α- and β-methylnaphthalene $C_{10}H_7$–CH_3 (b). The arrangement of molecules corresponds to the maxima in the DRDFs.

Table 5. The mean distances $\bar{r}$ between pairs of different atoms in liquid studied.

Liquid	Distances between pairs of atoms (nm)
α-chloronaphthalene	$C_1 \cdots C_1' = 0.398$
	$C_4 \cdots C_4' = 0.538$
	$Cl \cdots Cl' = 0.625$
β-chloronaphthalene	$C_9 \cdots C_9' = 0.380$
	$C_1 \cdots C_1' = 0.415$
	$C_2 \cdots C_2' = 0.538$
	$C_7 \cdots C_7' = 0.720$
	$Cl \cdots Cl' = 0.790$
α-methylnaphthalene	$C_3 \cdots C_3' = 0.503$
	$CH_3 \cdots CH_3' = 0.620$
β-methylnaphthalene	$C_9 \cdots C_9' = 0.444$
	$C_2 \cdots C_2' = 0.520$
	$CH_3 \cdots CH_3' = 0.735$

centres of the functional groups $\mathrm{Cl}\cdots\mathrm{Cl}'$ and $\mathrm{CH}\cdots\mathrm{CH}_3'$ of neighbouring molecules are directly related to the maxima of the intensity distribution in the range $9.00\,\mathrm{nm}^{-1} < S < 22.00\,\mathrm{nm}^{-1}$.

Observation of the distinct maxima in the angular and radial distribution functions is possible, thanks to the use of the short-wave radiation from the anode of a molybdenum lamp. The maxima on the DRDFs in the range for $0.110\,\mathrm{nm} \le \bar{r} \le 0.450\,\mathrm{nm}$ are attributed to intramolecular interactions, whereas those for $\bar{r} \ge 0.450\,\mathrm{nm}$ are due to intermolecular diffraction.

As indicated by the conformational analysis of the liquids studied, results of the potential energy minimisation [19] and the value of the permanent dipolar moment $\mu = 1.35\,\mathrm{D}$ of the α-chloronaphthalene and $\mu = 1.62\,\mathrm{D}$ of the β-chloronaphthalene molecule, the optimum arrangement of these molecules is antiparallel planar, one on top of the other (figure 3a). Only in such an arrangement the distance between the centres of the two chlorine atoms of the neighbouring molecules is: $\mathrm{Cl}\cdots\mathrm{Cl}' = (0.625 \pm 0.010)\,\mathrm{nm}$ for α-chloronaphthalene and $\mathrm{Cl}\cdots\mathrm{Cl}' = (0.790 \pm 0.015)\,\mathrm{nm}$ for β-chloronaphthalene.

In liquid α- and β-methylnaphthalene only in the antiparallel conformations (figure 3b) the distance between the centres of the methyl groups is $\mathrm{CH}_3\cdots\mathrm{CH}_3' = (0.620 \pm 0.010)\,\mathrm{nm}$ for α-methylnaphthalene, and $\mathrm{CH}_3\cdots\mathrm{CH}_3' = (0.735 \pm 0.015)\,\mathrm{nm}$ for β-methylnaphthalene.

The assignment of intramolecular distances to the maxima (figure 2a and b), has been performed assuming that the chlorine atoms and methyl groups do 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 [20] for 22 monosubstituted benzene derivatives have shown that the greatest changes between the carbon atoms in the ring are of an order of 0.001 nm.

A comparison of the mean values of the packing coefficients of the α- and β-naphthalene derivatives molecules leads to the relation:

$$\bar{k}_\alpha > \bar{k}_\beta, \tag{1}$$

where $\bar{k}_\alpha$ and $\bar{k}_\beta$ are the mean packing coefficients of α- and β-naphthalene derivatives.

The inequality (1) holds because the following relations are valid

$$\begin{gathered} \bar{D}_\alpha > \bar{D}_\beta \text{ and } d_\alpha > d_\beta \\ \Downarrow \\ Mp_\alpha < Mp_\beta, \end{gathered} \tag{2}$$

where D_α and D_β are the mean diameters of the molecules, Mp_α and Mp_β are the melting points, while d_α and d_β are the macroscopic densities of α- and β-naphthalene derivatives.

The distance between the centres of the substituents of the two neighbouring molecules at position β is greater than that between the centres of the same groups in position α. This increase is a result of the antiparallel orientation of the dipole moments of the neighbouring molecules and the fact that the substituent at one molecule approaches the naphthalene ring of the second molecule (figure 3a and b). As a result, the functional groups tend to occupy the free space close to the naphthalene rings of the neighbouring molecules, which leads to denser packing.

6. Conclusions

The use of short-wave radiation MoK_α enabled determination of the shortest interatomic distances within the naphthalene ring. The maxima for $0.110\,\mathrm{nm} \le \bar{r} \le 0.450\,\mathrm{nm}$ on the DRDFs were interpreted as a result of intramolecular diffraction. The three C–C atomic peaks occur at distances of 0.142, 0.243, and 0.280 nm corresponding to the distances between ortho, meta, and para carbon atoms, and the C–H peak occurs at 0.110 nm in the studied liquids. It was also possible to determine the interactions between the carbon atom C_1 in the naphthalene ring and the methyl group CH_3 in liquid α- and β-methylnaphthalene C_1–$CH_3 = 0.164\,\mathrm{nm}$, and the chlorine atom Cl in liquid α- and β-chloronaphthalene C_1–$Cl = 0.171\,\mathrm{nm}$ As follows from the geometry of the naphthalene ring and the positions of the methyl groups and chlorine atoms, the positions of particular peaks at the DRDFs can be assigned to the distances: $C_2 \cdots Cl = 0.262\,\mathrm{nm}$ $C_2 \cdots CH_3 = 0.264\,\mathrm{nm}$ $C_3 \cdots CH_3 = 0.395\,\mathrm{nm}$ and $C_4 \cdots CH_3 = 0.444\,\mathrm{nm}$.

The positions of peaks on the angular distribution functions in the range $9.00\,\mathrm{nm}^{-1} < S < 22.00\,\mathrm{nm}^{-1}$ provide information on the mean intermolecular distances and mean distances between the centres of the functional groups $Cl \cdots Cl'$ and $CH \cdots CH_3'$ in the neighbouring antiparallel molecules in α- and β-derivatives of naphthalene.

The molecules of the α- and β-derivatives of naphthalene should assume such an orientation in which their dipolar moments were antiparallel [21]. The results of the simulation study [22] with the potential energy minimisation and computer modelling [23] have confirmed the stability of such configurations.

On the basis of the differential radial distribution functions it is possible to conclude about the mutual orientations of the functional groups (–Cl, –CH_3) of molecules with respect to the naphthalene rings of the neighbouring molecules. The antiparallel arrangement of the molecules dipole moments is indicated by the positions of the maxima on the functions and the size of the molecules. The orientations can be concluded about from the positions of the intermolecular scattering and the distances between the pairs of neighbouring molecules: in α-chloronaphthalene $Cl \cdots Cl' = (0.625 \pm 0.010)\,\mathrm{nm}$ and in β-chloronaphthalene $Cl \cdots Cl' = (0.790 \pm 0.015)\,\mathrm{nm}$ in α-methylnaphthalene $CH_3 \cdots CH_3' = (0.620 \pm 0.010)\,\mathrm{nm}$ and in β-methylnaphthalene $CH_3 \cdots CH_3' = (0.735 \pm 0.015)\,\mathrm{nm}$.

The structure of liquid α- and β-derivatives of naphthalene is determined by the presence of the naphthalene ring. The models of the intermolecular interactions proposed take into regard the mutual orientations of the chlorine atoms and methyl groups in neighbouring molecules.

The most important results of this study are listed below.

- New experimental data on the structure of α- and β-chloro-and methylnaphthalene in liquid phase.
- New information on mutual arrangement, orientation, and packing of the molecules studied.

- Proposition of models of intermolecular binary radial correlations in the antiparallel orientation of dipole moments in the liquids from the homologue series $C_{10}H_7$-R (R a substituent).
- Analysis of the functions of angular distribution of intensity and differential radial distribution functions of electron density allows a determination of mean distances, radii of coordination spheres, coordination numbers, packing coefficients, arrangement of molecules, and degree of ordering. The functions are sensitive to the shape of molecules of the liquid studied, so they bring information on molecular structures in them and thus also on intra- and intermolecular interactions.
- The presence of short-range ordering reaching about 2 nm in the molecular liquids studied has been proved.
- The melting point of α- and β-chloro- and methylnaphthalene increases with decreasing mean diameter of their molecules.

Because of the supposed role of the naphthalene ring and functional groups (–Cl, –CH_3) attached to it at the α- and β-positions, for mutual configurations of molecules in liquids studied, it seems very probable that the proposed models of local arrangements can also hold for other derivatives of naphthalene in the liquid phase.

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