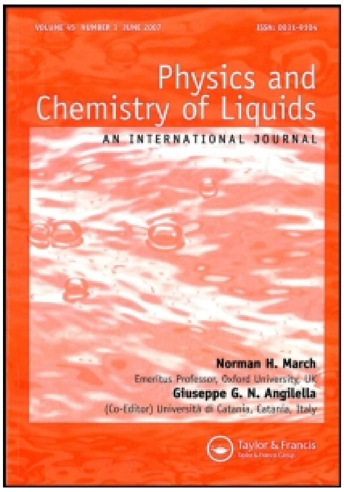

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X−ray analysis of intermolecular interactions in solution of ortho−nitroanisole $C_7H_7NO_3$ in 1,4−dimethylbenzene

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Structural analysis of a 10% solution of *ortho*−nitroanisole $C_7H_7NO_3$ in 1,4−dimethylbenzene by X-ray monochromatic radiation scattering method has been made at room temperature for the scattering angle range Θ varying from 3° to 60°. Diffraction patterns of the solution were obtained on an X-ray diffractometer with an X-ray lamp with a molybdenum anode. The first lower maximum corresponds to the intermolecular distance of $R_1 = 7.51$ Å, and the higher one to the intermolecular distance of $R_2 = 5.69$ Å. The angular distribution of the intensity of X-rays scattered by 10% solution of *o*−nitroanisole in 1,4−dimethylbenzene is compared to that for liquid *o*−nitroanisole. The mean least distance obtained for the solution studied is $\bar{R} = 7.51$ Å. This value is almost the same as the mean distances calculated for two molecules in pure *o*−nitroanisole in the antiparallel arrangement between the oxygen atoms and the nitrogen atoms of the functional groups $(O\text{–}CH_3)_1 \ldots (O\text{–}CH_3)_1$ and $(NO_2)_1 \ldots (NO_2)_1$, equal to 7.57 Å. The results have shown that in the liquid *ortho*−nitroanisole, similarly as in 1,4−dimethylbenzene, the molecules are arranged with their benzene rings in parallel. The results concern a wide class of molecular liquids, in particular, polar compounds being benzene nitroderivatives.

Keywords: X-ray scattering in liquid solutions; Angular-distribution function; Molecular ordering

1. Introduction

X-ray diffraction is a very efficient method of studying the structure of matter in both solid and liquid phase [1]. *Ortho*−nitroanisole has been studied in the solid [2], liquid [3, 4] and gas phase [5]. Investigation of *o*−nitroanisole was initiated by Donle [3] and Cowley [4], who determined the dipole moment of this liquid molecule in benzene solution. Cowley and Partington [4] determined the dipole moments of *o*−, *m*− and *p*−nitroanisoles in benzene to find out the relation with the moments of corresponding nitrophenols. Then Eda and Ito [6] determined the dipole moment of *o*−nitroanisole molecule at 298 K to be $\mu = 4.83$D. This value of the dipole moment corresponds to the coplanar arrangement of the nitric group relative to the benzene ring (figure 1).

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The $-OCH_3$ group can perform rotations about the C(1)–O(3) bond [7]. However, because of the $N0_2$ group in the *ortho* position and the coupling effect with the benzene ring it is a hindered rotation, reduced to vibrations about the energetically favoured configurations.

Ortho−nitroanisole in the crystalline phase has a $P2_1/c$ symmetry and its elementary cell contains four molecules [2]. Biswas [8] reported the elementary cell parameters of the 1,4−dimethylbenzene crystal $a = 7.56$ Å, $b = 8.45$ Å, $c = 11.11$ Å, $\beta = 98°57'$. The compound crystallizes in the monoclinic system in the space group $C^2_{2h}(P2_1/m)$, and contains four molecules in the elementary cell.

The structure of liquid 1,4−dimethylbenzene has been determined [9–11]. The values of the physical parameters of liquid *o*−nitroanisole are collected in table 1. Nitroanisole samples of 99% purity were purchased from Fluka (Switzerland).

2. Experimental methods

X-ray scattering in a 10% solution of *o*−nitroanisole in 1,4−dimethylbenzene was measured by applying $MoK_{\bar{\alpha}}$ radiation generated by a 1400 W tube (U = 45 KV, $I_A = 25$ mA). The windows of the lamp, of 1 cm in diameter and 1 mm in thickness were

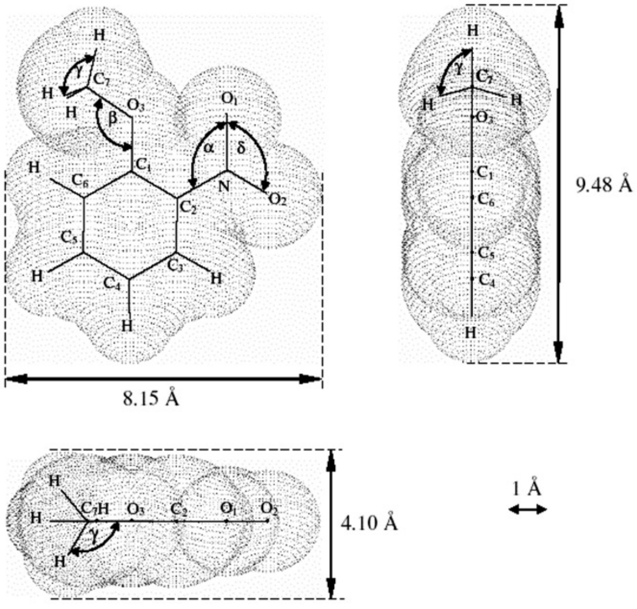

Figure 1. Model of *ortho*−nitroanisole molecule; $\mu = 4.93$D. Numbers $1-7$ label carbon atoms; $\alpha = 118°92'$, $\beta = 126°47'$, $\gamma = 109°28'$, $\delta = 115°80'$ ($R_C = 1.80$ Å, $R_N = 1.50$ Å, $R_O = 1.40$ Å, $R_H = 1.17$ Å) [7].

Table 1. Physical parameters of liquid *ortho*−nitroanisole.

Macroscopic density d [$g\,cm^{-3}$]	1.248
Molecular mass M [$g\,mol^{-1}$]	153.14
Melting point [K]	283
Boiling point [K]	546

made of beryllium. The characteristic radiation of the lamp was monochromatised by reflection from the (002) planes of flat graphite with the angle of monochromatization of $\Theta_m = 6^\circ 00'$ ($\Delta\Theta_m = 2.2'$)[12]. The angular distributions of the X-ray scattered intensity were measured for the angles $3^\circ \leq \Theta \leq 60^\circ$, at every 0.2°, where 2Θ is the scattering angle.

The samples were placed in thermostated cells and measurements were made at 293 K. 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 solution were installed on a X-ray goniometer.

The X-ray diffraction patterns were recorded on a X-ray diffractometer equipped with a special cell for measurements of liquids, described by North *et al.* [13] and Drozdowski [14].

Intensity of radiation scattered by a layer of the solution studied was determined by the transmission method. The method is described in detail in [13].

The scattered X-ray intensities were measured by a proportional counter coupled with a pulse counter at the counting rate up to 3.10^5 per second. The results were recorded by a computer. For liquid *o*−nitroanisole and the solution studied, the measurements were performed for different times of counting and a few times repeated, so that a final result was an average of a few measurements.

The intensity measured was corrected for: the background (air scattering) and noise of the counter [15], polarization [16], absorption by a sample [17], multiple scattering [18] and anomalous dispersion [19].

3. Calculations

The most probable parameters of *ortho*−nitroanisole molecule and the solution studied were determined from a detailed analysis of the distributions of scattered X-radiation intensity.

The value of the mean least intermolecular distance $\bar{R}$ can be obtained directly from the experimental curve of the scattered radiation intensity [20]. The intensity of the scattered radiation can be expressed by the following formula taking into account both inter− and intramolecular effects:

$$I^{\text{theor.}} = F_i^2 + F_a^2 \bar{N}\left(\frac{\sin S\bar{R}}{S\bar{R}}\right), \tag{1}$$

where F_i and F_a are the intra− and intermolecular scattering factors, respectively, while $\bar{N}$ is the coordination number, $S = 4\pi \sin\Theta/\lambda$, λ is the wave−length, and 2Θ is the scattering angle. As follows from equation (1), the angular distribution of the scattered radiation intensity I^{theor} is determined by the function $\sin S\bar{R}/S\bar{R}$. The first maximum of this function corresponds to the first maximum in the experimental curve of the scattered intensity $I(S)$

Since this maximum appears for $S\bar{R} = 7.73$, we can write the following formula allowing us to find approximately the mean value of the least intermolecular distance as:

$$\bar{R} = \frac{7.73}{S_{\max}} - 0.3. \tag{2}$$

The correction factor that must be taken into account for molecular liquids is determined by the external factor of molecular scattering F_a, which causes a slight shift of the maximum of the $\sin S\bar{R}/S\bar{R}$ dependence on the scattered radiation intensity. The correcting factor 0.3 for molecular liquids has been found empirically [21].

4. Results

From the angular distributions of the scattered radiation intensity in figures 2 and 3, we obtained the mean least intermolecular distance for pure *ortho*–nitroanisole and for 10% solution of *ortho*–nitroanisole $C_7H_7NO_3$ in 1,4–dimethylbenzene, table 2. 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 intermolecular interactions.

The positions of the maxima on these functions were found using the Lagrange polynomials method. The small-angle scattering results ($0° < \Theta \leq 3°$) were extrapolated to the origin of the coordinate system using a second-order function [22].

At $\Theta = 3.20°$(figure 3) the intermolecular distance reaches a minimum of 7.51 Å, within the error of $\Delta\bar{R} = \pm 0.04$ Å.

The mean diameter of the *o*–nitroanisole molecule (figure 1) was calculated assuming the Stuart–Briegleb model [23] describing the spatial distribution of atoms in the molecule. The size of *ortho*–nitroanisole molecule is 8.15 Å (length) X 4.10 Å (width) X 9.48 Å (height).

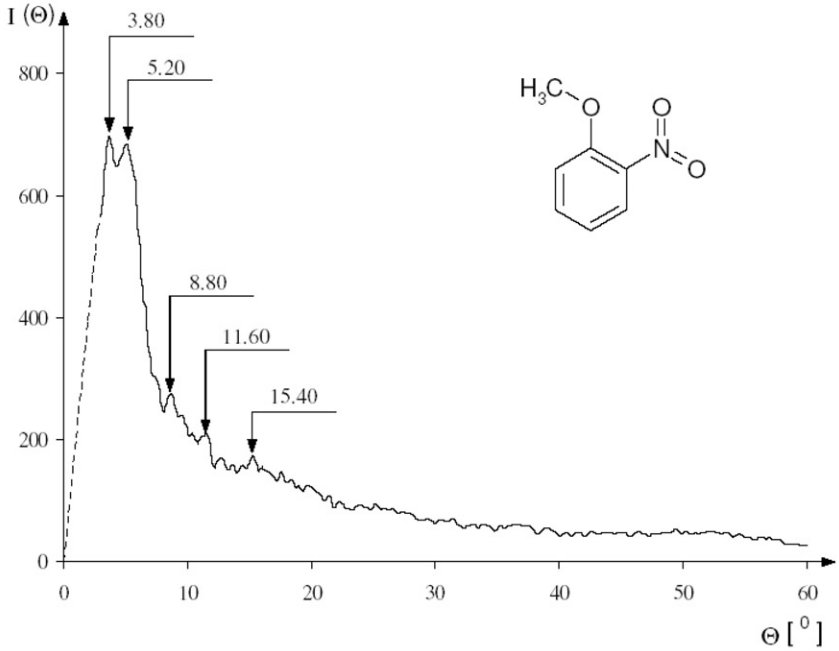

Figure 2. Mean angular distribution of the scattered radiation intensity for pure *ortho*–nitroanisole $C_7H_7NO_3$.

The specific volume of the molecule was determined on the basis of the volume increments corresponding to the contribution of particular kinds of atoms in the total volume of the molecule [24]. On average, it takes a volume of $\bar{V}_0^{\max} = 203.76\,\text{Å}^3$, whereas an increment of the molecule volume is $\bar{V}^{\text{incr}} = 140.97\,\text{Å}^3$.

5. Discussion

The method of X-ray scattering enabled determination of the mean inter–and intramolecular distances of the liquid *ortho*–nitroanisole and the solution studied. Table 3 presents the distances between the pairs of atoms in the *ortho*–nitroanisole molecule [7,19].

From the position of the main maximum in the scattered radiation intensity distribution the mean of the least intermolecular distance $\bar{R}$ was calculated. The benzene rings of two molecules are situated in parallel planes, which results in the antiparallel arrangement of the dipole moments of the *ortho*–nitroanisole molecules. The attractive dipole interaction between neighbouring molecules can favour the planar arrangement of molecules one over another in antiparallel arrangement, making such a configuration relatively more stable.

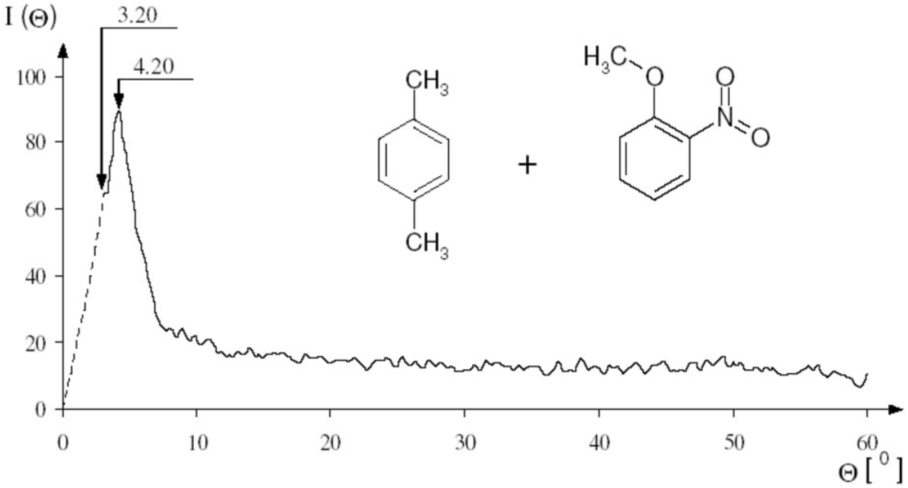

Figure 3. Mean angular distribution of the scattered radiation intensity for 10% solution of *ortho*–nitroanisole $C_7H_7NO_3$ in 1,4–dimethylbenzene.

Table 2. The position of the main maxima in the experimental curve (Θ[°]) and the mean value of the least intermolecular distances ($\bar{R}$[Å]).

Substances	Θ_1 [°]	Θ_2 [°]	$\bar{R}_1$[Å]	$\bar{R}_2$[Å]
o–Nitroanisole	3.80	5.20	6.31	4.53
Solution studied	3.20	4.20	7.51	5.69

Table 3. Intramolecular distances for the $o-$nitroanisole molecule model shown in figure 1. Labelling of atoms in accordance with the notations given in figure 1 without taking into account the hydrogen atoms.

No.	Type of intramolecular interactions	Intramolecular distances $\bar{r}_{ij}$ (Å)
1	$C_1{-}C_2$, $C_2{-}C_3, \ldots$	1.39
2	$C_1{-}O_3$, $O_3{-}C_7$	1.40
3	$C_2{-}N$	1.40
4	$N{-}O_1$, $N{-}O_2$	1.21
5	$O_1 \ldots O_2$	2.05
6	$C_2 \ldots O_1$, $C_2 \ldots O_2$	2.25
7	$C_1 \ldots C_3$, $C_2 \ldots C_4, \ldots$	2.40
8	$C_1 \ldots N$, $C_3 \ldots N$	2.45
9	$C_2 \ldots O_3$, $C_6 \ldots O_3$	2.45
10	$O_1 \ldots O_3$	2.45
11	$C_1 \ldots C_7$	2.50
12	$C_1 \ldots O_1$, $C_3 \ldots O_2$	2.70
13	$C_1 \ldots C_4$, $C_2 \ldots C_5$, $C_3 \ldots$	2.80
14	C_6	2.80
15	$N \ldots O_3$	2.90
16	$C_6 \ldots C_7$	3.50
17	$C_1 \ldots O_2$, $C_3 \ldots O_1$	3.70
18	$C_4 \ldots N$, $C_6 \ldots N$	3.70
19	$C_3 \ldots O_3$, $C_5 \ldots O_3$	3.70
20	$C_2 \ldots C_7$	3.75
21	$C_7 \ldots O_1$	4.00
22	$O_2 \ldots O_3$	4.10
23	$C_4 \ldots O_2$, $C_6 \ldots O_1$	4.20
24	$C_5 \ldots N$	4.20
25	$O_4 \ldots O_3$	4.20
26	$C_7 \ldots N$	4.30
27	$C_7 \ldots C_5$	4.70
28	$C_4 \ldots O_1$, $C_2 \ldots O_2$	4.90
29	$C_5 \ldots O_1$, $C_5 \ldots O_2$	4.90
30	$C_3 \ldots C_7$	5.10
31	$C_4 \ldots C_7$ $C_7 \ldots O_2$	5.40

Assumption of the planar model of the $o-$nitroanisole molecule corresponds to the energetically most stable position of the $-OCH_3$ group as then the π–electron cloud of the oxygen atom is maximally overlapped with the π–electron cloud of the double bonds of the benzene ring.

We suggest that in a 10% solution of nitroanisole in 1,4−dimethylbenzene at 293 K, the neighbouring molecules assume the configuration with their benzene ring planes in parallel to one another. The distance between the two functional groups: $-OCH_3$ and $-NO_2$ of neighbouring molecules in this arrangement in the solution studied is of about 7.51 Å. The mean distances calculated for two molecules of $o-$nitroanisole in the antiparallel arrangement between the oxygen atoms and the nitrogen atoms of the functional groups $(O{-}CH_3)_1 \cdots (O{-}CH_3)_2$ and $(NO_2)_1 \cdots (NO_2)_2$ are 7.57 Å.

6. Conclusions

The appearance of clear maxima on the function of the angular distribution of X-ray intensity indicates the presence of short-range ordering in the 10% solution of nitroanisole in 1,4−dimethylbenzene studied. The maxima for $3.20^\circ \leq \Theta \leq 4.20^\circ$ are interpreted as a result of intermolecular diffraction. Observation of the distinct maxima in the angular distribution functions is possible thanks to the use of the short-wave radiation from the anode of the molybdenum lamp.

The positions of peaks on the angular distribution function in the range $3.20^\circ \leq \Theta \leq 4.20^\circ$ provide information on the mean intermolecular distances and mean distances between the centres of the functional groups $(O–CH_3)_1 \ldots (O–CH_3)_2$ and $(NO_2)_1 \ldots (NO_2)_2$ in the neighbouring antiparallel molecules in the 10% solution of *ortho*−nitroanisole in 1,4−dimethylbenzene.

Because of the permanent dipole moment of the molecule *o*−nitroanisole, $\mu = 4.83D$ [6], the neighbouring molecules are arranged so that their dipolar moments are antiparallel. Only in such an arrangement the distance between the oxygen atoms and the nitrogen atoms of the functional groups $(O–CH_3)_1 \ldots (O–CH_3)_2$ and $(NO_2)_1 \ldots (NO_2)_2$ is 7.57 Å. This orientation is probably assumed because it is more energetically favourable and enables a more favourable packing of the molecules. The results have also been confirmed by the conformational analysis based on the minimisation of the potential energy [25].

In the liquid *ortho*−nitroanisole, similarly as in 1,4−dimethylbenzene, the molecules are arranged with their benzene rings in parallel. These results are also consistent with the values presumed in the conformational structure investigation of the liquid studied performed by empirical and semi-empirical MO−LCAO calculations [26].

The structure of liquid *ortho*−nitroanisole and solution of *ortho*−nitroanisole in 1,4−dimethylbenzene is determined by the presence of the benzene ring. The models of the intermolecular interactions proposed take into regard the mutual orientations of the functional groups ($–OCH$,$–NO_2$) in neighbouring molecules.

Because of the supposed role of the benzene ring and the functional groups ($–OCH_3$, $–NO_2$) attached to it, in mutual configurations of molecules in liquid *ortho*−nitroanisole, it seems very probable that the proposed model of local arrangement can also hold for other polar nitroderivatives of benzene in the liquid phase.

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