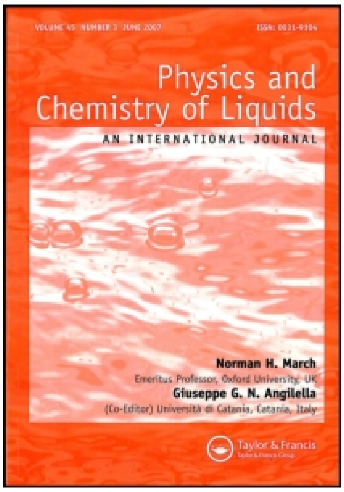

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Liquid structure of benzene and its derivatives as studied by means of X-ray scattering

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The liquid structures of benzene, toluene, aniline, benzaldehyde and nitrobenzene were investigated by the X-ray scattering method. The X-ray scattering data were analysed by a method without constructing any structure models. The obtained liquid structure of benzene is different from the previous X-ray scattering results which were derived from the quasi-lattice structure for the liquid based on the crystal structure of benzene. This is because a molecular arrangement which is not found in the crystal structure is left out of consideration. In liquid toluene, benzaldehyde and nitrobenzene, two molecules are associated with the dipole–dipole interaction in the antiparallel fashion. Two aniline molecules are hydrogen-bonded in liquid aniline. The third molecule weakly interacts with the other two in liquid toluene, aniline and benzaldehyde. In liquid nitrobenzene, the parallel dipole–dipole interaction of the third molecule with another one is present in the coplanar form. The substituent effect on the liquid structures is discussed.

Keywords: liquid structure; benzene and its derivatives; substituent effect; X-ray scattering

1. Introduction

Benzene is useful as a solvent and also as a reagent for deriving aromatic compounds. Much attention has been paid for its hexagonal molecular structure by many chemists and a lot of investigations have been done. The structural studies for liquid benzene have also been performed by the X-ray [1–8] and neutron scattering methods [6,9–11], and computer simulation [10–12]. Narten [5] reported that the liquid structure of benzene at 25°C is similar to that found in the crystalline state. Three molecular orientations were pointed out: (1) L configuration, where two molecules fit together like six-toothed bevel gear wheels whose axes are almost at right angles, (2) stacked configuration, in which one molecule lies on top of the other and the axes of the two molecules are inclined at 41° and (3) T configuration, where the planes of two molecules are inclined at 64° and the extension of the plane of one molecule passes close to the centre of the other. By using the reference interaction site model, he proposed that the L configuration is the predominant configuration in liquid benzene and a small number of molecular pairs have the stacked and T configurations.

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A similar conclusion was drawn by Bartsch *et al.* [6] using neutron scattering data measured at 25°C. Bochynski *et al.* [7,8] qualitatively assigned the peaks at 410, 515 and 615 pm in the X-ray radial distribution function at 20°C to the stacked, perpendicular T and L arrangements, respectively. On the other hand, the result by a pulsed neutron total scattering experiment at room temperature supported the T configuration in which two molecules are inclined at about 73° [9]. On the contrary to the above observations, analyses of neutron scattering data from the liquid to the supercritical states with the aid of the molecular dynamics simulation revealed that there is no preferential orientational ordering of the neighbouring molecules on average at ambient conditions although the parallel and perpendicular configurations are slightly favoured [10,11]. Thus, much different results on the structure of liquid benzene have been reported so far. We recently proposed a simple approach for determining a liquid structure using X-ray scattering data, in which a liquid structure is evaluated without constructing any structural models [13]. Here, the method has been applied to liquid benzene at room temperature.

The melting point of toluene (−95.0°C) is much lower than that of benzene (5.5°C) [14], which shows that the benzene crystal is much more stable than the toluene crystal due to the high symmetry of benzene molecule. On the other hand, the boiling point of toluene (110.6°C) is higher than that of benzene (80.1°C) [14]. This fact suggests that the intermolecular interactions among toluene molecules in a liquid phase are not so weakened on the methyl substitution of benzene, despite the fact that the density and viscosity of toluene are smaller than those of the benzene. The viscosity of aniline (3.770 cP) is larger than that of benzene (0.603 cP), toluene (0.553 cP), benzaldehyde (1.321 cP) and nitrobenzene (1.619 cP) [14]. This is because aniline is a hydrogen-bonding liquid. In fact, the viscosity is larger than that of hydrogen-bonding liquids such as water (0.892 cP), methanol (0.551 cP), ethanol (1.083 cP) and formamide (3.302 cP) [14]. However, the dielectric constant of aniline (6.71) is surprisingly smaller than that of water (78.30), methanol (32.66), ethanol (24.55) and formamide (111.0) [14]. Moreover, the dielectric constant of aniline is smaller than that of benzaldehyde (17.8) and nitrobenzene (34.8) [14]. Thus, it must be interesting to determine the liquid structures of toluene, aniline, benzaldehyde and nitrobenzene. The information on molecular orientations in liquid is most useful for understanding the liquid properties. However, as far as we know, a limited number of studies on liquid structures for these aromatic liquids by the X-ray or neutron scattering method have been reported so far [15–17], as compared with benzene. For liquid toluene, Lipinski [16] explained the X-ray scattering data by supposing that the influence of the methyl group on the local arrangements of molecules is small. However, detailed local molecular arrangements have never been described. In liquid nitrobenzene, the plane-antiparallel arrangement was proposed by Bochynski [17]. A quasi-lattice structure for the liquid was considered similar to that of benzene. In this study, the liquid structures of toluene, aniline, benzaldehyde and nitrobenzene were obtained by the same procedure as that of benzene and the substituent effect on the liquid structures is discussed.

2. Experimental

2.1. *Reagents*

Benzene, toluene, aniline, benzaldehyde and nitrobenzene of reagent grade (Wako, Japan) were used. Benzene was treated with molecular sieve 4A and distilled under atmospheric pressure. Toluene, aniline, benzaldehyde and nitrobenzene were purified by distillation under a reduced pressure. The distilled reagents were stored in a dark place by adding molecular sieve 4A.

2.2. *X-ray scattering measurements*

All X-ray scattering measurements for benzene, toluene, aniline, benzaldehyde and nitrobenzene were made at room temperature on the X-ray diffractometer (Rigaku, Japan) combined with a charge-coupled device (CCD) (Quantum 1, ADSC) detector [18]. The diffractometer of the transmission geometry was used and a Mo rotating anode was operated at 50 kV and 220 mA. The emitted radiation was reflected by a graphite (0 0 2) surface to extract the Mo-Kα line ($\lambda = 71.07$ pm). A liquid sample was sealed in a glass capillary with a diameter of 2.0 mm. The CCD detector was moved stepwise at 0°, 40°, 80° and 120° to cover the scattering angle range of about 140°. Measured intensities were recorded on the CCD detector as 2-D data. They were corrected for absorption by the sample and air and then integrated into 1-D data by a method reported previously [18]. After the correction of background, the observed intensities were extrapolated to zero angle and then corrected for polarisation [19] and multiple scattering [20] in a usual manner.

The obtained intensities $I_{\mathrm{corr}}(\theta)$ were converted to the structure function, $i(s)$, the variable s being defined as $4\pi \sin\theta/\lambda$,

$$i(s) = KI_{\mathrm{corr}}(s) - \sum_i n_i I_i^{\mathrm{inc}}(s) - \sum_i n_i \left[\left\{ f_i(s) + \Delta f_i' \right\}^2 + \left(\Delta f_i'' \right)^2 \right], \tag{1}$$

where K denotes the normalisation factor, which can be obtained at the high-angle region or Krogh-Moe–Norman method [21,22], n_i is the number of atom i in a unit volume and $I_i^{\mathrm{inc}}(s)$ is the incoherent scattering intensity of atom i. In this study, the value of $148.5 \times 10^6\,\mathrm{pm}^3$ for the unit volume was used as the one occupied by a benzene molecule. $f_i(s)$ represents the atomic scattering factor of atom i, and $\Delta f'$ and $\Delta f''$ are the real and imaginary parts of anomalous dispersion, respectively [23].

The radial distribution function, $D(r)$, was derived by the Fourier transformation of the structural function $i(s)$,

$$D(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^{s_{\max}} s i(s) M(s) \sin(rs) \mathrm{d}s, \tag{2}$$

where ρ_0 denotes the average electron density in the unit volume. $M(s)$ is a modification function having the form $[\sum n_i f^2(0)/\sum n_i f^2(s)]\exp(-\kappa s^2)$ and $\kappa = 100\,\mathrm{pm}^2$ was used in this study. The structure and the radial distribution functions were calculated by using the programme KURVLR [24].

A comparison between the experimental structure function and theoretical one, $i_{\mathrm{calc}}(s)$, was made by a least-squares method to minimise the following u:

$$u = \sum_{s_{\min}}^{s_{\max}} s^2 \left\{ i_{\mathrm{calc}}(s) - i(s) \right\}^2. \tag{3}$$

The theoretical function is related to the pair interatomic interactions characterised by the distance between atoms i and j, r_{ij}, the temperature factor of the *i–j* atom pair, b_{ij}, and the number of the pair, n_{ij},

$$i_{\text{calc}}(s)=\sum_i\sum_j n_{ij}\Big[\{f_i(s)+\Delta f_i'\}\{f_j(s)+\Delta f_j'\}+\Delta f_i''\Delta f_j''\Big]\times\frac{\sin(sr_{ij})}{sr_{ij}}\exp(-b_{ij}s^2). \tag{4}$$

In the analysis of the intermolecular interactions, each molecule was assumed to take a rigid molecular structure. A molecule is situated at the origin, which was selected as the centre of gravity for electrons. The atoms in the central molecule at the origin were set to have no atomic scattering power and then n molecules with X-ray scattering power are randomly distributed around it. The orientations and positions of n molecules relative to the central one are defined by the polar coordinates, R,Θ, Φ and the Euler's angle, ψ, θ, ϕ,

$$\begin{bmatrix}x_i\\y_i\\z_i\end{bmatrix}=\begin{bmatrix}\cos\phi\cos\theta\cos\psi-\sin\phi\sin\psi & -\sin\phi\cos\theta\cos\psi-\cos\phi\sin\psi & \sin\theta\cos\psi\\ \cos\phi\cos\theta\sin\psi+\sin\phi\cos\psi & -\sin\phi\cos\theta\sin\psi+\cos\phi\cos\psi & \sin\theta\sin\psi\\ -\cos\phi\sin\theta & \sin\phi\sin\theta & \cos\theta\end{bmatrix}\cdot\begin{bmatrix}x_o\\y_o\\z_o\end{bmatrix}+\begin{bmatrix}R\cos\Phi\cos\Theta\\R\cos\Phi\sin\Theta\\R\sin\Phi\end{bmatrix}, \tag{5}$$

where x_o, y_o and z_o are the Cartesian coordinates of an atom o within the molecule located at the origin, and x_i, y_i and z_i are those of an atom i within one of the other molecules. The x_o, y_o and z_o values were fixed at the values initially given. By the use of the Cartesian coordinates, x_i, y_i and z_i, of an atom i within one surrounding molecule with those, x_j, y_j and z_j, of an atom j within another surrounding molecule, the intermolecular interatomic distances between ${}_nC_2$ pairs of all surrounding molecules were calculated according to the following equation:

$$r_{ij}=\sqrt{(x_i-x_j)^2+(y_i-y_j)^2+(z_i-z_j)^2}. \tag{6}$$

Then, by inserting these distances to Equation (4), error-square sum was obtained in Equation (3). Because Equation (6) includes the intermolecular structural parameters R, Θ, Φ, ψ, θ and ϕ, the partial derivatives of $i(s)$ with respect to R, Θ, Φ, ψ, θ and ϕ were obtained. Then, the intermolecular structural parameters relative to the central molecule were refined by a non-linear least-squares procedure. The intermolecular temperature factor B, which is related with the temperature factor in Equation (4) in the form of $b_{ij}=(r_{ij}\times B)^2/2$, was fixed at 0.1 in this study. The details of the analysis for the intermolecular interactions were described previously [13].

3. Results and discussion

3.1. *Intramolecular interactions*

The $si(s)$ and $(D(r)-4\pi r^2\rho_0)$ curves of benzene, toluene, aniline, benzaldehyde and nitrobenzene are shown in Figures 1 and 2, respectively. In the radial distribution functions for all liquids, the first peak at about 140 pm is due to the C–H and C–C

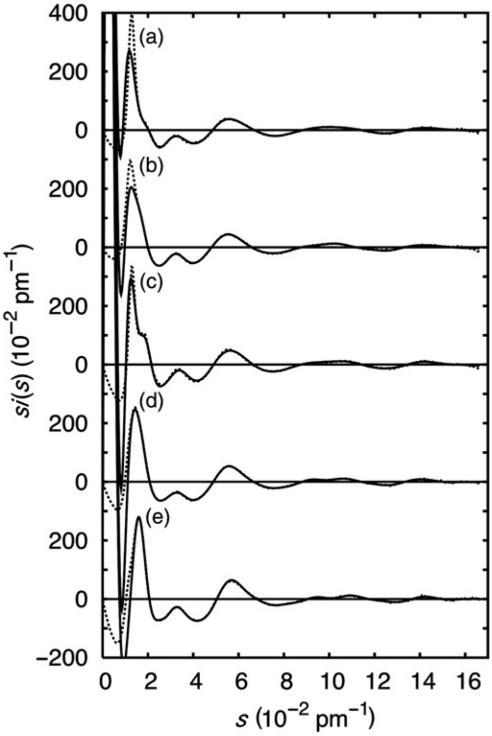

Figure 1. Structure functions, $si(s)$, for (a) benzene, (b) toluene, (c) aniline, (d) benzaldehyde and (e) nitrobenzene. The solid lines show the calculated curves for both intramolecular and intermolecular interactions, and the dotted lines are the experimentally obtained ones.

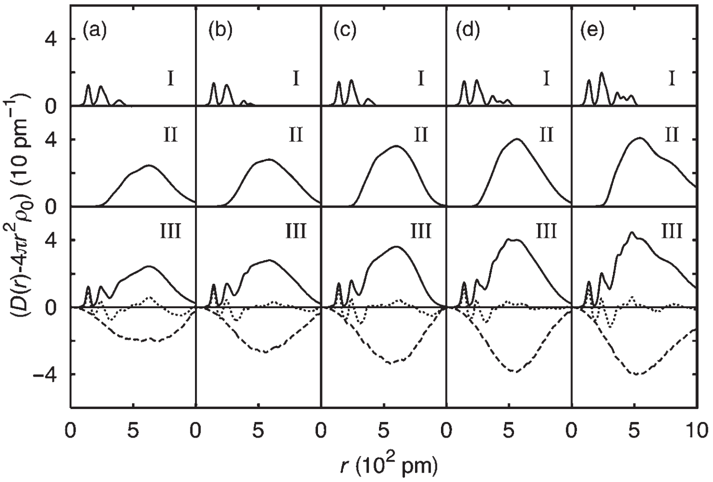

Figure 2. Differential radial distribution curves, $D(r)-4\pi r^2\rho_0$, for (a) benzene, (b) toluene, (c) aniline, (d) benzaldehyde and (e) nitrobenzene. The calculated peak shapes for the intramolecular and intermolecular interactions are shown in I and II, respectively. The dashed line in III stands for the residual curve after the subtraction of the sum of the calculated curves (solid lines) in I and II from the experimental curve (dotted line).

bonds and the second peak at about 240 pm mainly corresponds to the intramolecular C···H and C···C pairs in the benzene ring. In the analyses of the intramolecular interactions, the C–C(CH$_3$) and C···C(CH$_3$) interactions for toluene, the N–H, C–N and C···N interactions for aniline, the C=O, O···H, C···C(CO) and C···O interactions for benzaldehyde and the O–N, C–N, O···O, C···O and C···N interactions for nitrobenzene were taken into account. The structure parameters of these interactions were optimised by a least-squares procedure applied to the $si(s)$ curve in the region of $4 \times 10^{-2}\,\mathrm{pm}^{-1} < s < 16 \times 10^{-2}\,\mathrm{pm}^{-1}$ for toluene and aniline. The range of $5 \times 10^{-2}\,\mathrm{pm}^{-1} < s < 16 \times 10^{-2}\,\mathrm{pm}^{-1}$ was used for benzene, benzaldehyde and nitrobenzene. The intramolecular bond distances were quoted from the electron diffraction results of benzene [25], toluene [26], aniline [27], benzaldehyde [28] and nitrobenzene [29] and these values were fixed in the course of the refinements. The obtained intramolecular structural parameters are shown in Table 1.

3.2. *Intermolecular interactions*

For the analyses of the intermolecular interactions, two molecules were at first randomly distributed in a space without consideration of any structure models and a least-squares calculation was performed. If the fit between the measured and calculated structure functions is not well, one molecule was additionally distributed in a space and a least-squares calculation was again carried out. This procedure was repeated until the obtained intermolecular interaction parameters reproduced well the experimental X-ray scattering data and a further introduction of a molecule did not improve the result. The fitted range of s for the determination of the intermolecular structure parameters was from 1.0×10^{-2} to $5.0 \times 10^{-2}\,\mathrm{pm}^{-1}$ for all liquids since the contribution from the intermolecular interactions is negligibly small in a higher s range than $5.0 \times 10^{-2}\,\mathrm{pm}^{-1}$. It turned out that three molecules are enough to best reproduce the X-ray scattering data for all systems. Some initial distributions of molecules were checked by randomly changing both sites and orientations of molecules, but the obtained results were not affected by the initial configurations. The determined intermolecular structural parameters are summarised in Tables 2 and 3. The solid lines in Figure 1, which are the $si(s)$ curves calculated using the intramolecular and intermolecular structure parameters, coincide well with the observed value (dotted lines in Figure 1) in the wide region of $1 \times 10^{-2}\,\mathrm{pm}^{-1} < s < 16 \times 10^{-2}\,\mathrm{pm}^{-1}$. After subtracting the peaks due to the intramolecular and intermolecular interactions (solid lines shown in I and II, respectively, of Figure 2), the residual curves of the $(D(r) - 4\pi r^2 \rho_0)$ functions (dashed lines in III of Figure 2) are smooth, with no distinct peak over the range $r < 1000$ pm. These facts clearly suggest that our structural analysis is quite reliable. The molecular orientations calculated from the intermolecular structural parameters are shown in Figure 3.

3.3. *Structure of liquid benzene*

In the radial distribution function of benzene (Figure 2(a)), the large peak at 635 pm is ascribed to the intermolecular interactions between the nearest neighbour molecules. The peak is well explained in terms of the molecular arrangement

Table 1. Intramolecular structural parameters for benzene and its derivatives.

Interaction	r (pm)	b ($10\,\mathrm{pm}^2$)	n
Benzene			
C–H	110^a	1^a	6^a
C–C	140^a	1^a	6^a
C···H	217^b	2^a	12^a
C···C	240(1)	7(1)	6^a
C···C	278(1)	5(1)	3^a
C···H	382(7)	2^a	12^a
C···H	391(15)	2^a	6^a
Toluene			
C–H	112^a	1^a	8^a
C–C	140^a	1^a	6^a
C–C	151^a	1^a	1^a
C···H	218^b	2^a	13^a
C···C	239(1)	4^a	6^a
C···C	258(1)	3^a	2^a
C···C	276(1)	3^a	3^a
C···C	381(2)	3^a	2^a
C···C	436(4)	6^a	1^a
Aniline			
N–H	103^a	1^a	2^a
C–H	110^a	1^a	5^a
C–C	140^a	1^a	6^a
C–N	141^a	1^a	1^a
C···H	215^b	2^a	10^a
C···C	237(1)	4^a	6^a
C···N	247(1)	4^a	2^a
C···C	275(1)	3^a	3^a
C···N	370(1)	5^a	2^a
C···N	406(3)	4^a	1^a
Benzaldehyde			
C–H	112^a	1^a	6^a
C–O	121^a	1^a	1^a
C–C	140^a	1^a	6^a
C–C	148^a	1^a	1^a
O···H	203^c	2^a	1^a
C···H	216^b	2^a	11^a
C···O	238(23)	2^a	1^a
C···C	239(7)	4^a	6^a
C···C	249(5)	7^a	2^a
C···C	277(2)	2^a	3^a
C···O	282(8)	8^a	1^a
C···O	359(2)	3^a	1^a
C···C	373(1)	4^a	2^a
C···C	414(4)	5^a	1^a
C···O	433(3)	5^a	1^a
C···O	480(3)	4^a	1^a
C···O	495(4)	9^a	1^a

(*Continued*)

Table 1. Continued.

Interaction	r (pm)	b (10 pm^2)	n
Nitrobenzene			
C–H	111^a	1^a	5^a
O–N	122^a	1^a	2^a
C–C	139^a	1^a	6^a
C–N	148^a	1^a	1^a
C···H	217^b	2^a	10^a
O···O	223(2)	2^a	1^a
C···O	236(14)	2^a	2^a
C···C	237(7)	3^a	6^a
C···N	251(2)	4^a	2^a
C···C	274(14)	3^a	3^a
C···O	274(15)	2^a	2^a
C···O	358(2)	3^a	2^a
C···N	367(2)	3^a	2^a
C···N	408(12)	6^a	1^a
C···O	413(5)	6^a	2^a
C···O	462(3)	7^a	2^a
C···O	485(2)	7^a	2^a

Notes: SDs are given in parentheses.
[a] The values are kept constant during the calculations.
[b] Assumed that the H–C–C bond angle is 120°.
[c] Assumed that the H–C–O bond angle is 120°.

Table 2. Intermolecular structure parameters for benzene and its derivatives.

Molecule	ψ (°)	θ (°)	ϕ (°)	r (pm)	Θ (°)	Φ (°)	B
Benzene							
A	42(6)	1(3)	5(6)	240(14)	165(3)	−12(3)	0.1
B	−27(2)	−49(3)	−7(3)	377(13)	64(5)	61(2)	0.1
C	178(3)	47(2)	111(2)	388(15)	−56(2)	−46(3)	0.1
Toluene							
A	12(6)	3(1)	−8(5)	349(7)	187(2)	23(2)	0.1
B	13(2)	113(1)	68(2)	358(9)	39(2)	20(2)	0.1
C	−85(2)	0(2)	271(3)	246(10)	−58(2)	−70(2)	0.1
Aniline							
A	25(1)	−17(1)	−107(1)	458(5)	129(2)	74(1)	0.1
B	78(1)	−45(1)	−100(1)	300(8)	86(1)	−40(1)	0.1
C	−8(2)	−10(1)	7(2)	211(7)	233(1)	26(1)	0.1
Benzaldehyde							
A	35(1)	−52(1)	129(1)	286(8)	267(1)	61(1)	0.1
B	32(1)	−62(1)	−63(1)	271(6)	71(1)	21(1)	0.1
C	16(1)	−11(1)	−15(1)	351(8)	240(1)	−73(1)	0.1
Nitrobenzene							
A	158(1)	23(1)	60(1)	295(5)	47(1)	35(1)	0.1
B	165(1)	37(1)	−143(1)	293(5)	197(1)	−80(1)	0.1
C	176(1)	32(1)	45(1)	514(5)	217(1)	−2(1)	0.1

Notes: The values in parentheses are SDs. See Table 3 for Cartesian coordinates of atoms.

Table 3. Cartesian coordinates of atoms with no atomic scattering power in molecules located at the origin.

Atom	x (10^2 pm)	y (10^2 pm)	z (10^2 pm)
Benzene			
C	1.399	0	0
C	0.700	1.212	0
C	−0.700	1.212	0
C	−1.399	0	0
C	−0.700	−1.212	0
C	−0.700	−1.212	0
Toluene			
C	0.905	0	0
C	0.205	1.212	0
C	−1.195	1.212	0
C	−1.895	0	0
C	−1.195	−1.212	0
C	0.205	−1.212	
C(CH_3)	2.412	0	0
Aniline			
C	0.917	0	0.014
C	0.221	1.206	0.014
C	−1.171	1.206	0.014
C	−1.867	0	0.014
C	−1.171	−1.206	0.014
C	0.221	−1.206	0.014
N	2.348	0	0.014
Benzaldehyde			
C	−0.117	1.075	0
C	−1.515	1.075	0
C	−2.213	−0.135	0
C	−1.515	−0.134	0
C	−0.117	−1.345	0
C	2.060	−0.135	0
C(CO)	0.581	−0.135	0
O	2.630	0.937	0
Nitrobenzene			
C	0.254	0	0
C	−0.441	1.205	0
C	−1.833	1.205	0
C	−2.528	0	0
C	−1.833	−1.205	0
C	−0.441	−1.205	0
N	1.732	0	0
O	2.309	1.072	0
O	2.309	−1.072	0

depicted in Figure 3(a). The A and B molecules are in the closest contact with the centre–centre distance of 498 pm and the angle between the two molecular planes is 49°. The molecular plane of the B molecule almost directs towards the centre of the A molecule. Thus, the A–B interaction is concluded to be through the T configuration. The centre separation between the A and C molecules is 525 pm and slightly larger

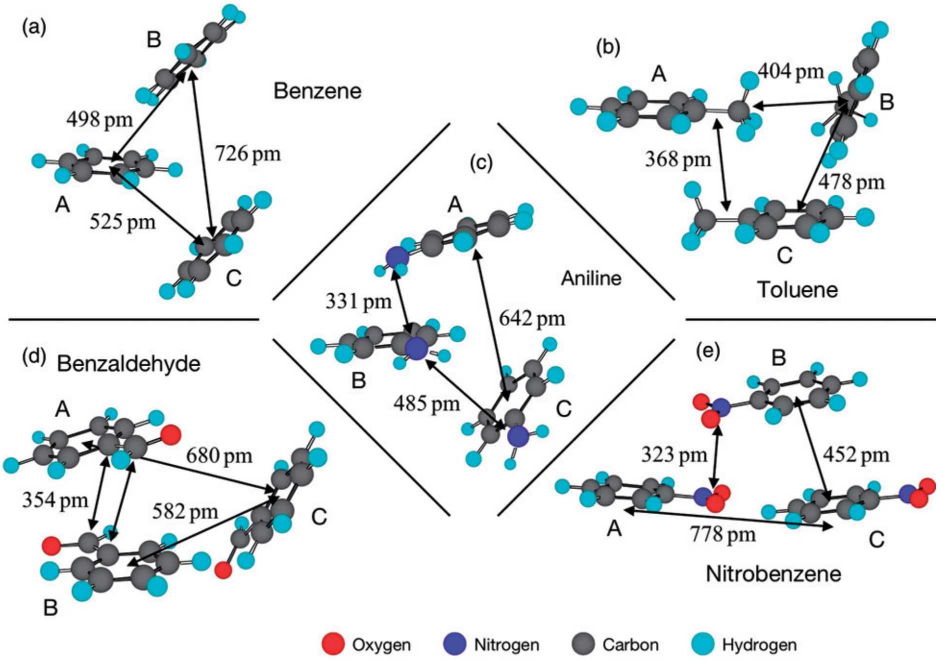

Figure 3. Liquid structure of (a) benzene, (b) toluene, (c) aniline, (d) benzaldehyde and (e) nitrobenzene.

than that of the A–B pair. The two ring planes intersect at an angle of 48°, which is virtually the same as that of the A–B interaction, but neither of the molecular planes of the A and C molecules point to the centre of another molecule. Hence, the configuration formed by the A and C molecules is a distorted L shape. In the liquid structure model of benzene proposed by Narten [5], there predominantly exists the L configuration, while this study suggests that both the T and distorted L configurations are comparably present in liquid benzene. Two planes of the B and C molecules are inclined at 18° and hence the two molecules are interacting with an almost parallel fashion. However, the two rings are not stacked and the centre–centre distance is 726 pm, which is much larger than the values (350 [5] and 410 pm [7,8]) proposed previously. These different results may arise from the fact that the previous X-ray scattering studies accepted the quasi-lattice structure for the liquid based on the crystal structure of benzene. A slightly favourable presence of the parallel and perpendicular configurations was indicated by the molecular dynamics simulation [10,11]. However, our result suggests that the parallel (stacked) configuration is not the major one and the perpendicular configuration exists predominantly. In the previous simulation, the Williams [30] potential was used, which provides a good reproduction of a crystal structure. A molecular arrangement which is not found in the crystal structure is left out of consideration. In our analytical method for the X-ray scattering data, there is no need to make any initial configurations of benzene molecules with consideration. Thus, this method for the determination of a liquid structure without constructing any structure models is useful.

3.4. *Structure of liquid toluene*

The radial distribution curve of toluene shows that the peak assigned to the intermolecular interactions of toluene is broader than that of benzene (Figure 2(b)); the peak position of 600 pm of toluene agrees well with that of benzene, while the amplitude of toluene is much less than that of benzene. As seen in Figure 3(b), the A and C molecules are arrayed to form the antiparallel dipole–dipole orientation with a distance of 368 pm although the dipole moment (1.03×10^{-30} C m [14]) caused by the introduction of the methyl group to the benzene ring is small. The mean intermolecular C(methyl)···C(phenyl) distance is 368 pm. For the B–C interaction, the angle between the rings is 67° and the centre–centre distance between the two benzene rings is 478 pm, which is smaller than that found in benzene. Thus, the nearest neighbour interactions in toluene are rather strong compared to those in benzene. This fact leads to higher boiling point of toluene than that of benzene, although the higher molecular weight of toluene also contributes to the higher boiling point. The molecular orientation by the dipole–dipole interaction between the A and C molecules is truncated by the presence of the methyl group in the C molecule in toluene, while the nearest neighbour molecular arrangement of benzene can extend to some extent in liquid benzene because of the absence of a methyl group. This leads to the lower viscosity of toluene than that of benzene.

3.5. *Structure of liquid aniline*

The shapes of the radial distribution functions of aniline and benzene are similar in a range larger than 500 pm (Figure 2), where the intermolecular interactions contribute predominantly. In fact, the molecular arrangement of aniline is very similar to that of benzene as shown in Figure 3(c). The closest intermolecular distance between nitrogen atoms in a pair of aniline molecules (the A–B interaction) is 331 pm. This value is similar to the distances of 318 and 337 pm found in the aniline crystal [31]. The orientation of the A and B molecules in Figure 3(c) shows the existence of the hydrogen bond. The separations of the A–C and B–C interactions are 642 and 485 pm, respectively. Hence, the interaction between the hydrogen-bonded A and B molecules is much stronger than that of the A–C and B–C pairs. The cause of the large viscosity of aniline is explained by the fact that the two hydrogen-bonded molecules simultaneously migrate and an apparent molecular weight is large in liquid aniline.

3.6. *Structure of liquid benzaldehyde*

For liquid benzaldehyde, the peak observed at 400–600 pm in the radial distribution curve in Figure 2(d) is attributed to the intermolecular interactions. There is no peak over the region $r > 700$ pm. This implies that the molecular arrangements of benzaldehyde are disordered beyond the nearest neighbour molecules. Two benzaldehyde molecules A and B interact through the dipole–dipole interaction with a mean distance of 354 pm by the large dipole moment of benzaldehyde (10.1×10^{-30} C m in benzene [14]). The distances of the A–C and B–C interactions are 680 and 582 pm, respectively. Hence, the interactions between the A and C molecules as well as the B and C molecules are much weaker than that of the A–B pair. This is consistent with the observation from the radial distribution curve, the disordered molecular arrangement beyond the nearest neighbour molecules.

3.7. *Structure of liquid nitrobenzene*

Figure 2 reveals quite a different pattern of the radial distribution curve of nitrobenzene from those of benzene, toluene, aniline and benzaldehyde. Two peaks due to the intermolecular interactions are clearly observable at 500 and 800 pm in Figure 2(e). Actually, the peak at 500 pm is a result of the dipole–dipole interaction in an antiparallel way between the A and B molecules and the stacked interaction between the B and C molecules, as depicted in Figure 3(e). The value of dipole moment (13.3×10^{-30} C m in benzene [14]) of nitrobenzene is large, so the ordered liquid structure is expected. In fact, the peak at 800 pm is arising from the parallel dipole–dipole interaction in the coplanar form between the A and C molecules. This configuration contributes to the large dielectric constant of liquid nitrobenzene.

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