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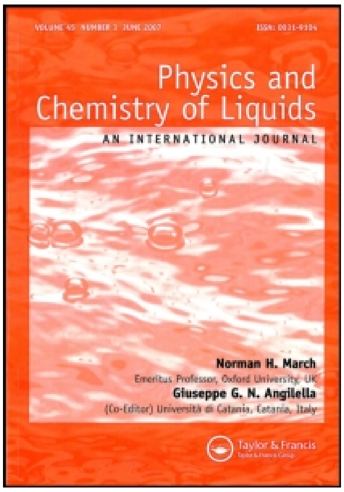

Physics and Chemistry of Liquids

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Molecular ordering in some liquid aromatic hydrocarbons

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To cite this Article Drozdowski, Henryk and Taberski, Bartosz(2005) 'Molecular ordering in some liquid aromatic hydrocarbons', Physics and Chemistry of Liquids, 43: 5, 449 — 457
To link to this Article: DOI: 10.1080/00319100500196302
URL: http://dx.doi.org/10.1080/00319100500196302

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Physics and Chemistry of Liquids
Vol. 43, No. 5, October 2005, 449–457

Molecular ordering in some liquid aromatic hydrocarbons

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(*Received 1 March 2005; in final form 27 March 2005*)

This study presents a comparison of the structures and molecular correlations for the linear aromatic hydrocarbons: benzene, naphthalene, and anthracene in the liquid phase, performed for the first time by the method of X-ray diffraction. Also for the first time the X-ray diffraction results obtained for anthracene at 513 K have been reported. Monochromatic radiation CuK_α was used to determine the scattered radiation intensity between $S_{\min} = 4\pi \sin \Theta_{\min}/\lambda = 0.417\,\text{Å}^{-1}$ and $S_{\max} = 4\pi \sin \Theta_{\max}/\lambda = 7.06\,\text{Å}^{-1}$. The mean angular distributions of X-ray scattered intensity were measured and the differential radial distribution functions of electron density (DRDFs) were calculated. The mean distances between the neighbouring molecules and the mean coordination numbers were found. The most probable models of local ordering of these molecules were suggested. Correlations have been found between the number of benzene rings in the molecules studied and their physical properties.

Keywords: X-ray diffraction; Molecular ordering; Aromatic hydrocarbons

1. Introduction

Benzene (C_6H_6, melting point 278 K, boiling point 353 K) has been studied in the gas [1], liquid [2], and crystalline [3] phases. Numerous X-ray studies confirmed its planar hexagonal structure [3,4]. The results reported in this work are in good agreement with the literature data. An elementary cell of a crystalline benzene belonging to the rhombic system (space group Pbca) contains 4 molecules.

Naphthalene ($C_{10}H_8$, melting point 353 K, boiling point 491 K) has been studied by X-ray diffraction methods [5,6], electron scattering [7], and spectroscopic methods [8,9]. An elementary cell of a crystalline naphthalene (monoclinic system, group $P2_1/c$) contains 2 molecules. Liquid naphthalene has been investigated by X-ray methods [5,6,10], and in the form of gas it has been studied by IR and Raman spectroscopies [11], UV spectroscopy [12], and electron diffraction [13]. The structure of crystalline naphthalene

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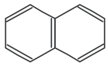
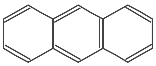
Physics and Chemistry of Liquids
ISSN 0031-9104 print: ISSN 1029-0451 online © 2005 Taylor & Francis
DOI: 10.1080/00319100500196302

Table 1. Comparison of the structural data for the crystals of benzene, naphthalene, and anthracene [18].

Compounds	 Benzene	 Naphthalene	 Anthracene
Crystal system	Rhombic	Monoclinic	Monoclinic
a (Å)	7.44	8.24	8.56
b (Å)	9.65	6.00	6.04
c (Å)	6.81	8.66	11.16
α (°)	–	90.00	90.00
β (°)	–	122.90	124.70
γ (°)	–	90.00	90.00

has also been analysed by the method of optimization of the potential of carbon–carbon interactions [14].

Anthracene ($C_{14}H_{10}$, melting point 491 K, boiling point 615 K) crystallizes in the monoclinic system, it belongs to the space group $P2_1/a$ and contains 2 molecules in an elementary cell [15]. The crystalline anthracene has been studied by the X-ray diffraction method at: 94, 140, 181, 220, 259, and 295 K [16]. The changes in the elementary cell parameters of anthracene have been found to lead to the volume changes from $V = 456.5\,\text{Å}^3$ (94 K) to $473.2\,\text{Å}^3$ (295 K). Anthracene in the gas phase has been studied by electron diffraction methods [11]. Hitherto, no X-ray diffraction data for liquid anthracene have been published [17].

Table 1 gives a comparison of the structural data for the crystals of benzene, naphthalene, and anthracene [18].

For naphthalene and anthracene, the mean angular distributions of intensity were expressed as a function of the wave vector S and compared with structural data for benzene. Moreover, a comparison of the DRDFs for these three liquids was made.

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

2. Experimental

The structures of the molecular liquids: benzene, naphthalene, and anthracene were studied by X-ray diffraction of strictly monochromatic CuK_α radiation, $\lambda = (1.5418 \pm 0.0012)$ Å. The X-ray studies of liquids have been described in detail in [19,20].

The measurements were performed using the transmission method with the preparation mounted symmetrically with respect to the incident and reflected beams [19]. The liquids studied were placed in a plane-parallel cell of adjustable thickness and with windows of thin mica layer.

Studies of anthracene in the liquid phase have been very difficult because of its sublimation properties. To be able to proceed at 513 K, a specially constructed measuring cell, heated by a system of four electric heaters of power $P = 800$ W each, was used. The construction of the cell is described in detail in [20]. The cell was tightly sealed by a teflon foil of 1 mm in thickness.

The values of the physical and chemical parameters of liquids studied are collected in table 2.

Table 2. Physical and chemical parameters of liquid benzene, naphthalene, and anthracene.

Physical and chemical parameters	Benzene	Naphthalene	Anthracene
Mean effective number of electrons per hydrogen atom $\overline{K}_H$	0.652	0.647	0.645
Mean effective number of electrons per carbon atom $\overline{K}_C$	6.369	6.556	6.274
Total of atomic number in one molecule $\sum_j Z_j$	42	68	94
Macroscopic density ($\mathrm{g\,cm^{-3}}$)	0.879	0.963	0.957
Molecular mass ($\mathrm{g\,mol^{-1}}$)	78.12	128.16	178.23
Mean electron density ($\mathrm{e\,Å^{-3}}$)	0.285	0.308	0.304
Temperature of measurements (K)	293	368	513

In each case, the shapes of the scattered intensity were analysed subsequent to correction for polarization of the monochromatic radiation [21] and absorption in plane samples [22] and after normalization to electron units [23].

3. Calculations

The modified Warren–Krutter–Morningstar method [24] was applied to obtain the DRDFs $\sum_{j,k}\overline{K}_j 4\pi r^2[\rho_k(r)-\rho_0]$. The integrals appearing in the function $\rho_k(r)$ were calculated numerically by Simpson's method for values of parameters from $r=0$ to 20 Å in steps of 0.05 Å. The radial distribution functions were calculated with the use of the computer program written by Drozdowski [25].

The most probable intermolecular distances were found from the positions of the maxima of the DRDFs, whereas the corresponding numbers were obtained from the area delimited by these maxima [26]. In the range of experimentally accessible values of the ϑ angle ($3^\circ \le \vartheta \le 60^\circ$) the total $\Delta\vartheta$ maximum error does not exceed $\pm 0.2^\circ$. Taking into account the applied method, causing both systematic and random errors in the experimental data, the accuracy of the DRDF obtained is estimated to be about 3%.

4. Results

The normalized functions $I(S)$ of the scattered X-radiation obtained for the series of the liquids studied, figure 1, reveal a broad main maximum. The FWHM and height of this maximum increase with increasing length of the molecule.

On the basis of the positions and shape of the main maximum, it is possible to calculate the most frequently occurring and the most probable distances d_{Bragg} between the scattering centres and the approximate mean radii $\overline{R}$ of the first coordination sphere [26] in the liquids studied (table 3).

The shapes of the differential radial distribution functions (figure 2) provide information on the structure of liquids studied. These functions yield information about the difference between the observed and the average distribution of electron density. Coordination shells are delimited by the minima of DRDFs [27].

Assuming the rigid and planar conformation of the molecules of the compounds studied, models of their structure were proposed. The probable conformations of these molecules are shown in figure 3, where the mean intermolecular distances are marked.

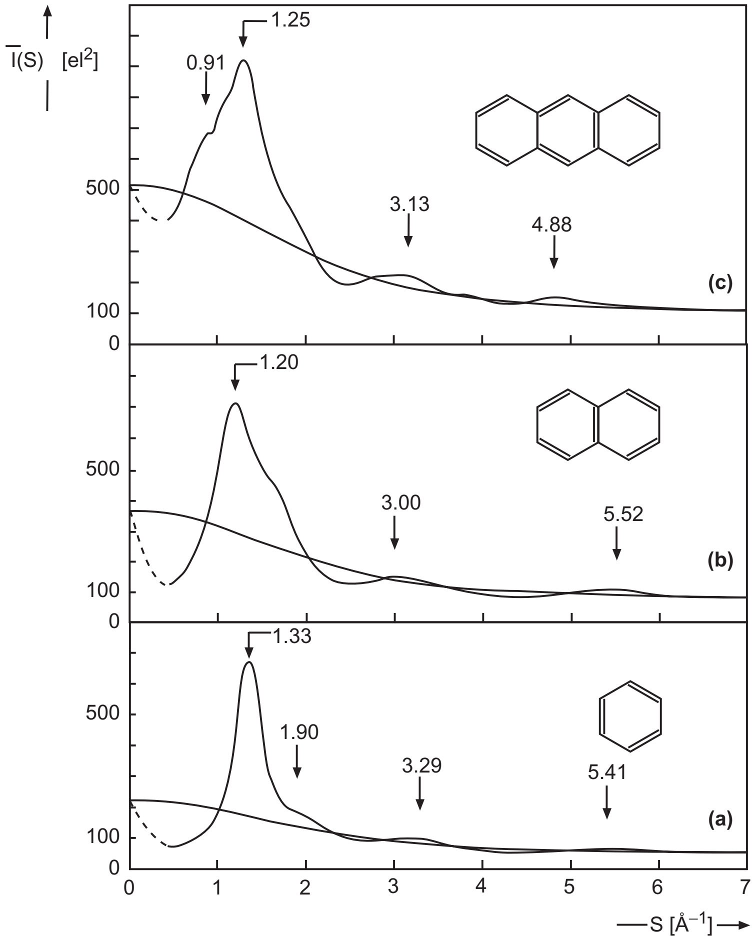


Figure 1. Scattered X-ray intensity distribution from liquid benzene (a), naphthalene (b), and anthracene (c).

Table 3. Maxima position S_{max} (Å) of angular-distribution functions, the corresponding mean distances d_{Bragg} (Å) between the scattering centres, and the mean radii $\overline{R}$ (Å) of the first coordination sphere in the liquids studied.

Liquid	S_{max} (Å^{-1})	d_{Bragg} (Å)	$\overline{R}$ (Å)
Benzene	1.33	4.72	5.51
Naphthalene	1.20	5.23	6.14
Anthracene	1.25	5.03	5.88

The mean diameter of the molecules studied $\overline{D}$ (table 4) was calculated assuming the Stuart–Briegleb model [28] describing the spatial distribution of atoms in the molecule. The greater the molecule volume V_0 the greater their polarizability α. The boiling point B_p of the compounds studied, under the same pressure, increases with introduction of subsequent benzene rings to the molecule (table 4).

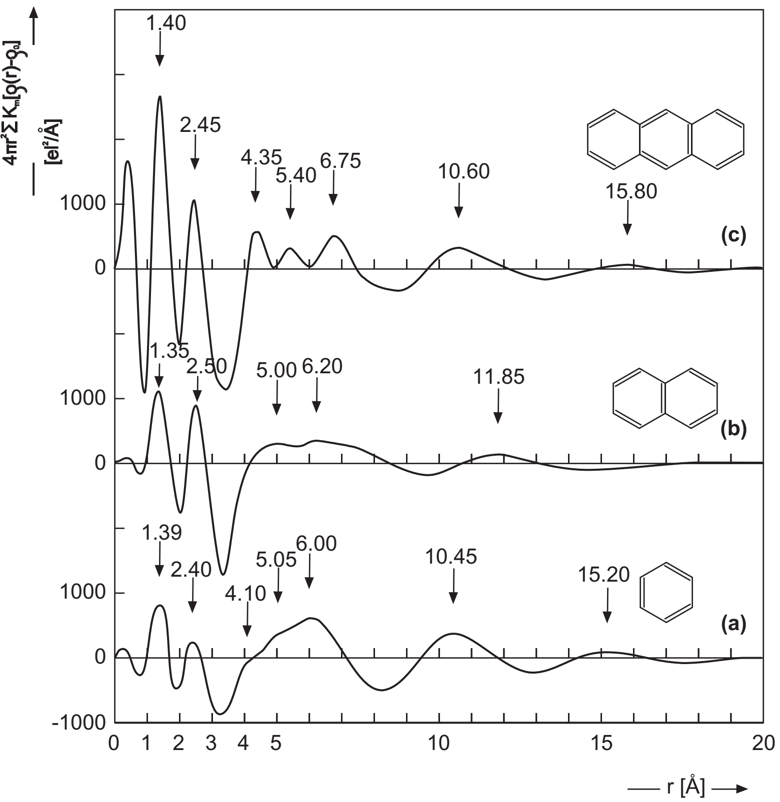


Figure 2. Differential function of radial distribution of electron density of liquid benzene (a), naphthalene (b), and anthracene (c).

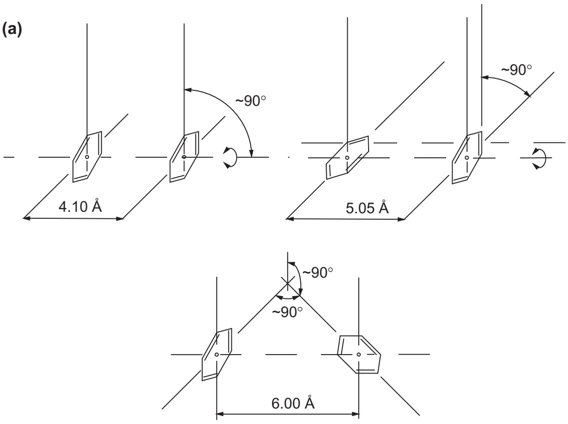


Figure 3. Models of probable conformations of molecules in benzene (a), naphthalene (b), and anthracene (c).

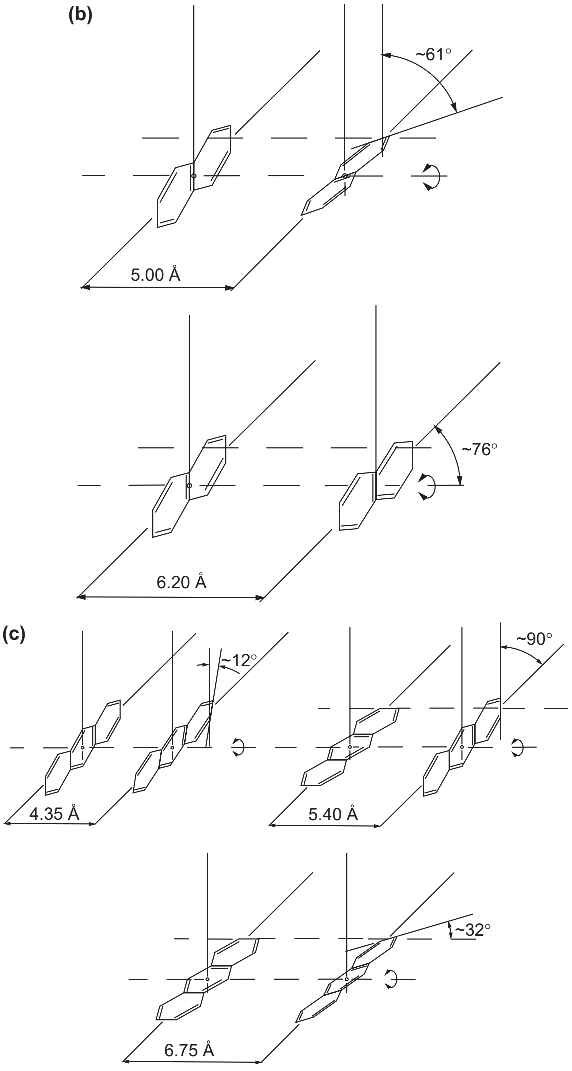


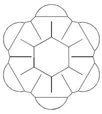
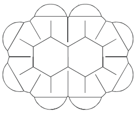
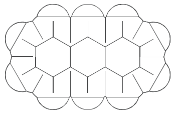
Figure 3. Continued.

5. Discussion

The first maxima of the DRDFs (figure 2) occurring as they do at $\bar{r} < 1\,\text{Å}$, are not adapted to a physical interpretation, and will not be considered [29]. The maxima $\approx 3.20 < \bar{r} \leq 20\,\text{Å}$ are ascribed to intermolecular diffraction.

With regard to the size of the molecules studied, the next two maxima can be assigned to intramolecular distances only. The maxima at $\bar{r} = 1.39$, 1.35, and 1.40 Å (figure 2) correspond to the intramolecular distance between nearest neighbouring carbon atoms (C_1–C_2) in benzene, naphthalene, and anthracene, respectively. The maxima occurring at $\bar{r} = 2.40$ to 2.50 Å, are attributed to the next inter-carbon distances $C_1 \cdots C_3$ in the molecule.

Table 4. Specific volume V_0 (Å^3), mean diameter $\overline{D}$ (Å) and polarizabilities of the molecules α (cm^3), and the boiling B_p (K) of the liquids studied.

			
Parameters	Benzene	Naphthalene	Anthracene
V_0 (Å^3)	88.2	134.4	180.6
$\overline{D}$ (Å)	5.63	6.36	6.76
$10^{-24}\alpha$ (cm^3)	10.4	18.2	30.8
B_p (K)	353	491	615

In liquid benzene, a molecule occupies on average a volume $\overline{V} = 148.4$ Å^3. The calculated mean, most often recurring least mutual distances between the molecules, as obtained by analysis of the radial distribution function, are respectively $\bar{r}_1 = 4.10$ Å, $\bar{r}_2 = 5.05$ Å and $\bar{r}_3 = 6.00$ Å. The mean intermolecular distance for $\bar{r}_1 = 4.10$ Å, figure 3(a), corresponds to the plane-parallel molecular arrangement. Existence of this configuration at a distance $\bar{r} \approx 4.10$ Å was also postulated by Narten [2]: however, only for a small number of molecular pairs. In the Narten model of liquid benzene: "The molecules pairs (...) fit together like six-toothed bevel gear wheels whose axes are almost at right angles" [2]. The range of intermolecular distances, corresponding to the main maximum of the DRDF for benzene, covers those characteristic of perpendicular arrangement of molecules both in the form of letters T and L. Such an arrangement of neighbouring molecules, resembling a letter L, helped interpretation of the maximum of the DRDF at $\bar{r}_3 = 6.00$ Å, figure 2(a). This is only perpendicular configuration in which the centres of neighbouring molecules are at a distance of about 6 Å; in the perpendicular configuration resembling a letter T this distance is $\bar{r}_2 = 5.05$ Å, figure 3(a) [30]. These values are in agreement with the model proposed by Lowden and Chandler [4]. The perpendicular configuration may be favoured in liquid benzene of the quadrupole moment of its molecule. Such a structure of liquid benzene was indicated by the Cotton–Mouton constant measurements [31], degree of depolarization of scattered radiation [32] and temperature dependence of the optical Kerr effect [33].

For naphthalene the position of the DRDF at $\bar{r} = 5.00$ Å corresponds to the skew orientation of the nearest neighbouring with $\alpha \approx 61^\circ$, while the position of the other one corresponds to the almost perpendicular molecular arrangement with $\alpha \approx 76^\circ$ (figure 3b) [6]. The significant broadening of the coordination spheres (table 5) testifies to the fact that molecular conformations of the nearest neighbours in naphthalene are much more complex than in benzene.

The mean distance between the anthracene molecules forming the first coordination sphere, determined from the intensity distribution, is $\overline{R} = 5.88$ Å, which is between the fourth and fifth DRDF maximum.

A clearly marked split of this maximum observed for anthracene corresponding to $\bar{r} = 4.35$, 5.40, and 6.75 Å, indicates the possibility of the presence of three probable arrangements in the first coordination sphere (figure 3c) [34]. The skew conformation is assumed because it is more energetically favourable [35].

Table 5. The range of coordination spheres and the number of molecules in each sphere for the studied liquids.

Liquid	Sphere I	Sphere II	Sphere III
Benzene	3.20–8.00 $N_1 \approx 10.6$	8.00–12.75 $N_2 \approx 36.2$	12.75–17.60 $N_3 \approx 95.3$
Naphthalene	3.25–10.15 $N_1 \approx 10.6$	10.15–15.05 $N_2 \approx 45.6$	15.05–19.20 $N_3 \approx 72.3$
Anthracene	3.45–8.80 $N_1 \approx 8.7$	8.80–13.30 $N_2 \approx 22.30$	13.30–17.95 $N_3 \approx 46.95$

6. Conclusions

A comparison of the results of structural analyses of benzene, naphthalene, and anthracene was made. The molecules are arranged in parallel, perpendicular, and coplanar configurations. In benzene the dominant one is the perpendicular conformation, in naphthalene and in anthracene it is the parallel one. Significant differences were noted in the character of differential functions obtained for the three compounds.

In the range to about 18.25 Å, three spheres of intermolecular ordering were distinguished. The maxima in the range $\approx 3.30 \leq \bar{r} < 5.35$ Å, are interpreted as due to intra- and intermolecular diffraction, whereas those for $\bar{r} > 5.35$ Å are due to intermolecular diffraction.

The closest packing of the naphthalene molecules occurs when the distances between their centres of gravity are $\bar{r} = 3.60$ Å and they lay flat one upon another. A significant split of the main maximum of the radial function in the range $\bar{r}$ $\langle 3.25\text{–}10.15 \rangle$ Å into two maxima at $\bar{r} = 5.00$ and 6.20 Å suggests that in liquid naphthalene, in the radial range studied, there are two most probable types of mutual arrangement of molecules interacting through van der Waals forces (London dispersion interaction) [36].

These distances according to the theory of X-ray scattering by liquids [4], correspond to short-range ordering and point to favoured distances between the centres of nearest neighbouring molecules.

Acknowledgement

This work was performed within research project No. 2P 302 006 04 of the Committee for Scientific Research (Republic of Poland).

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