

IN SITU CRYSTALLIZATION AND CRYSTAL STRUCTURE DETERMINATION OF CHLOROBENZENE[♦]

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The crystal structure of chlorobenzene, which is liquid at ambient conditions of pressure and temperature, was determined after *in situ* crystallization by using Optical Heating and Crystallization Device (OHCD) coupled to a single crystal X-ray diffractometer. Chlorobenzene crystallizes in the orthorhombic space group *Pbcn* with one symmetry-independent molecule in the asymmetric unit. In the crystal structure, type II Cl \cdots Cl interactions form zigzag chains that are assisted by C—H \cdots π interactions. Hirshfeld surface analysis revealed five types of intermolecular contacts.

Keywords: X-ray diffraction; optical heating crystallization device; halogen interactions; chlorobenzene

КРИСТАЛИЗАЦИЈА *IN SITU* И ОПРЕДЕЛУВАЊЕ НА КРИСТАЛНАТА СТРУКТУРА НА ХЛОРОБЕНЗЕН

Со примена на уред за оптичко загревање и кристализација (Optical Heating and Crystallization Device, OHCD) е определена кристалната структура на хлоробензен, супстанца којашто при собна температура и притисок е во течна состојба. Хлоробензенот кристализира во орторомбичната просторна група *Pbcn* со една симетриски независна молекула во асиметричната ќелија. Во кристалот Cl \cdots Cl интеракции од втор вид образуваат цик-цак ленти коишто се дополнително стабилизирани со C—H \cdots π интеракции. Со анализа на интермолекулските интеракции со хиршфелдовски површини се утврдени пет вида интермолекулски контакти.

Клучни зборови: кристална структура; рендгенска дифракција; уред за оптичко загревање и кристализација; халогенски интеракции; хлоробензен

1. INTRODUCTION

The *in situ* crystallization technique is an experimental approach to structure determination of compounds with low melting point where the crystallization is carried out in an X-ray diffractometer followed by single crystal structure determination [1]. An instrument, Optical Heating and Crystallization Device (OHCD), that was developed by Boese and coworkers [1–10] in the 1990s, is a convenient and commercially available accessory to a diffractometer to crystallize and deter-

mine crystal structures of gases, liquids, and small amounts of others materials with low melting points. The instrument utilizes the principles of the zone melting technique where a narrow region of the sample placed in an elongated container having a temperature gradient is melted and the molten zone is shifted along the material to remove impurities. With the OHCD, the material to be crystallized is first introduced in a glass or quartz capillary, which is then cooled with a nitrogen gas stream below the freezing point of the sample. Infrared radiation from a carbon dioxide laser is used

[♦] Dedicated to Academician Gligor Jovanovski on the occasion of his 70th birthday.

to melt a narrow zone of the solidified material, which can be moved along the capillary multiple times to repeat the crystallization-melting procedure until single crystal(s) is (are) obtained.

Pure chlorobenzene is a colorless liquid with almond-like odor and melting point $T = 228$ K. It is widely used as a solvent for reactions and as a precursor in chemical synthesis. There are two reports on the crystal structure of chlorobenzene. The first report [11] dates back to 1958 when S. G. Biswas determined the unit cell parameters (space group $Pm\bar{m}n$, $a = 13.72$ Å, $b = 11.32$ Å, $c = 7.75$ Å, $V = 1203.656$ Å³, density = 1.225 g cm⁻³) from Debye-Scherrer photographs of frozen chlorobenzene at 93 K. In 1971, the crystal structure of chlorobenzene was determined at high pressure (14.2 kbar, 392 K). The unit cell parameters were consistent with the earlier report (space group $Pbcn$, $a = 13.32(9)$ Å, $b = 11.08(3)$ Å, $c = 7.00(3)$ Å, $V = 1033$ Å³, density = 1.447 g cm⁻³, $Z = 8$) [12]. Although detailed crystal structure parameters of chlorobenzene are not available yet, the crystal structures of several dichlorobenzene isomers have been reported [13–19]. Herein, we describe the results of single crystal X-ray structure determination of chlorobenzene accomplished by using the *in situ* crystallization technique with OHCD.

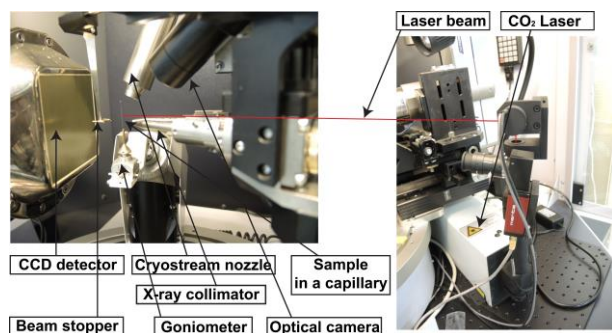


Fig. 1. APEX DUO diffractometer (Bruker) with an OHCD accessory

2. EXPERIMENTAL SECTION

The *in situ* crystallization was carried out according to the procedure described in the Results and Discussion section. The optical heating was carried out with SYNRAD CO₂ laser controlled by the OHCD III V64 software. Single crystal X-ray data collection was carried out with a Bruker APEX DUO diffractometer equipped with CCD area detector using monochromatic MoK α radiation ($\lambda = 0.71069$ Å) [20]. The temperature of the sample was maintained at 200 K with a low-temperature device (N-HeliX from Oxford Cry-

osystems). The diffraction data were collected and processed with the APEX 2 software [20] and the multi-scan absorption correction was applied to the data with SADABS [21]. The structure was solved by direct methods using SHELXS-97 [22] and refined with SHELXL-2014 [23]. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed at calculated positions. The Hirshfeld surface analysis was carried out with the software package Crystal Explorer (ver. 3.1) [24]. The crystallographic data were deposited within the Cambridge Structure Database (CCDC) and can be retrieved as reference 1050587.

3. RESULTS AND DISCUSSION

3.1. Crystallization

Liquid chlorobenzene was introduced into a Lindemann glass capillary with diameter 0.5 mm which was then flame-sealed and mounted vertically on the goniometer with the aid of a brass tip inside the Bruker APEX DUO single crystal X-ray diffractometer. A flow of cold nitrogen gas from N-HeliX low-temperature system (Oxford Cryosystems) was used to solidify the sample inside the capillary by maintaining the temperature at 200 K. The X-ray diffraction images confirmed that this solidified material was an amorphous (glassy) chlorobenzene. An IR beam from a CO₂ laser was then used to locally melt a narrow zone of the solidified sample. The molten zone was moved upwards with the help of the laser beam while maintaining the temperature of the other parts of the capillary at 200 K. The zone melting scan was carried out for several cycles while inspecting the crystalline nature of the material inside the capillary from the X-ray diffraction images. After several cycles, a single crystal of chlorobenzene was obtained inside the capillary and its crystallinity was confirmed with well-defined Bragg reflections (Fig. 2A).

3.2. Crystal structure of chlorobenzene

Chlorobenzene crystallized in the orthorhombic space group $Pbcn$ with one molecule in the asymmetric unit (unit cell parameters: $a = 13.6128(6)$ Å, $b = 11.3384(5)$ Å, $c = 7.4339(4)$ Å, $V = 1147.40(9)$ Å³, density = 1.303 g cm⁻³). It has similar crystal packing as bromobenzene and iodobenzene [25]. The C—C and C—Cl bond lengths as well as the C—C—C and C—C—Cl angles are listed in Figure 2B. In the structure, type II Cl \cdots Cl interactions ($d_{\text{Cl}\cdots\text{Cl}} = 3.6708(8)$ Å, $\theta_{\text{Cl}\cdots\text{Cl}\cdots\text{Cl}} = 138.2^\circ$ and $3.6672(9)$ Å, 146.7°) connect the chlo-

robenzene molecules to form zigzag chains along the *a* axis that are accompanied by C—H \cdots π interaction ($d_{\text{H6}\cdots\text{C1}} = 2.876 \text{ \AA}$, $d_{\text{C6}\cdots\text{C1}} = 3.544(2) \text{ \AA}$, $\theta_{\text{C6-H6}\cdots\text{C1}} = 129.9^\circ$). These zigzag chains are interconnected by another C—H \cdots π interaction ($d_{\text{H2}\cdots\text{C6}} = 2.971 \text{ \AA}$, $d_{\text{C2}\cdots\text{C6}} = 3.805(3) \text{ \AA}$, $\theta_{\text{C2-H2}\cdots\text{C6}} = 150.0^\circ$; Figure 3). The chlorobenzene molecules are not involved in $\pi\cdots\pi$ and Cl $\cdots\pi$ interactions.

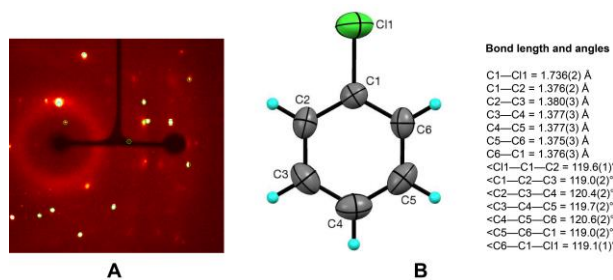


Fig. 2. (A) X-ray diffraction image recorded from chlorobenzene single crystal obtained by *in situ* crystallization. (B) ORTEP-type plot of the molecular structure of chlorobenzene in the crystal drawn with 50% probability ellipsoids. The C—C and C—Cl bond lengths and the corresponding angles are listed.

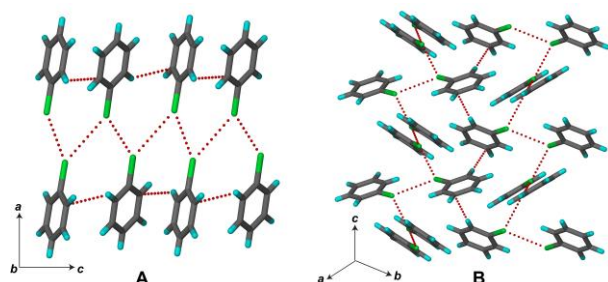


Fig. 3. (A) Cl \cdots Cl type II interactions accompanied by C—H \cdots π interaction form zig-zag chains of chlorobenzene molecules along the *c* axis. (B) The zig-zag chains are interconnected with each other by C—H \cdots π interaction along the *c* axis.

3.3. Hirshfeld surface analysis

The Hirshfeld surface analysis [26–28] provides a quantitative measure of intermolecular contacts in a crystal structure that can be conveniently visualized as three-dimensional contour plots and two-dimensional fingerprint plots. Distances from the Hirshfeld surface to the nearest nuclei inside and outside the surface are expressed by the distance functions d_i and d_e . The function d_{norm} represents the normalized contact distances and is defined as

$$d_{\text{norm}} = \frac{d_i - r_i^{\text{vdW}}}{r_i^{\text{vdW}}} + \frac{d_e - r_e^{\text{vdW}}}{r_e^{\text{vdW}}}, \quad \text{Eq. (1)}$$

where r_i^{vdW} and r_e^{vdW} represents Van der Waals radii of the nearest atoms inside and outside the surface, respectively. Mapping of the Hirshfeld surface with d_{norm} typically uses a color-coded scheme (red-white-blue) to distinguish short interactions (red, shorter than the sum of the Van der Waals radii) from medium long (white) and long (blue, longer than the sum of the Van der Waals radii) intermolecular contacts. The Hirshfeld surface of chlorobenzene with d_{norm} reflects the absence of strong intermolecular interactions, which is indicated by the lack of red-colored area on the surface (Fig. 4A, B). The Hirshfeld surface mapped with the function shape index (*S*) is also useful in the analysis of intermolecular contacts. The shape index is defined in terms of the principal curvatures (κ_1 and κ_2) as

$$S = \frac{2}{\pi} \arctan\left(\frac{\kappa_1 + \kappa_2}{\kappa_1 - \kappa_2}\right), \quad \text{Eq. (2)}$$

The presence of red spots on the plot representing the shape index indicates C—H \cdots π interactions (denoted by white arrows in Fig. 4C, D). Bifurcated Cl \cdots Cl interactions correspond to the flat light blue regions (denoted by black arrows in Figure 4D). The two-dimensional fingerprint plot of the Hirshfeld surface of chlorobenzene showed 5 different types of close contacts. The Cl \cdots Cl and C \cdots H contacts contribute with 6.2 and 32.3%, respectively, while the longer H \cdots Cl contacts ($\sim 3 \text{ \AA}$) contribute 25.9% to the Hirshfeld surface (Fig. 4E, F).

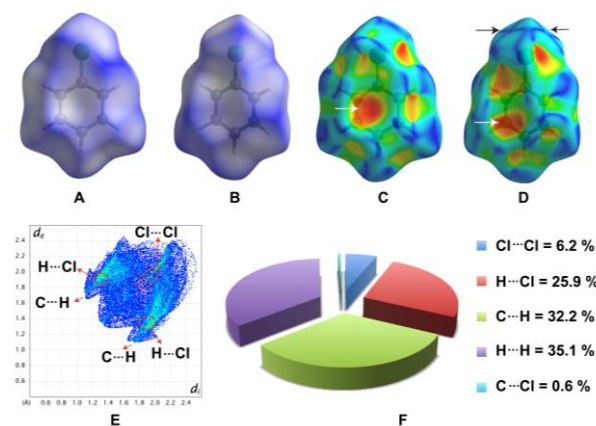


Fig. 4. (A, B) Two views of the Hirshfeld surface mapped with d_{norm} . (C, D) Two views of the color-coded Hirshfeld surface. (E) Two-dimensional fingerprint plot of the Hirshfeld surface where the Cl \cdots Cl, C \cdots H and H \cdots Cl interactions are indicated by red circles and arrows. (F) Distribution of the contributions from the five different intermolecular contacts in the crystal structure of chlorobenzene.

CONCLUSIONS

The crystal structure of chlorobenzene, which is liquid at ambient conditions, was determined by using the *in situ* crystallization method. The results show the convenience of this technique when applied with a commercially available setup for structure determination of samples that are available as small amounts of liquids at ambient conditions. The structure details of chlorobenzene could be important in establishing accurate structural parameters pertinent to the halogen bonding interactions.

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