Hindawi Publishing Corporation
Journal of Chemistry
Volume 2013, Article ID 634986, 5 pages
http://dx.doi.org/10.1155/2013/634986

Research Article

Spectral Characterization and Crystal Structure of 1,2-Bis-(1*H*-benzimidazol-2-yl)-ethane Dihydrochloride

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Received 29 October 2011; Accepted 31 December 2011

Academic Editor: Mohamed Farook

The crystal structure of 1,2-bis-(1*H*-benzimidazol-2-yl)-ethane dihydrochloride (**1**) was determined by X-ray diffraction at room temperature. The structure of **1** was also characterized by mass, elemental analysis, FT-IR, and NMR spectroscopy techniques. The title compound crystallizes in triclinic system and space group P-1, $a = 7.1350$, $b = 9.6299(1)$, $c = 15.3340(7)$ Å, $\alpha = 80.67(2)$, $\beta = 79.66(2)$, $\gamma = 68.395(11)^{\circ}$, $V = 958.33(10)$ Å^3, $Z = 2$. Owing to the *anti* conformations of $-CH_2-$ groups, the entire molecule is relatively flat. ^{1}H-NMR spectra of **1** show AA′XX′ system characteristics.

1. Introduction

Bis-benzimidazoles are known to be strong chelating agents coordinating through the C=N nitrogen atoms and form stable complexes with various transition metals [1–9]. On the other hand, bis-benzimidazoles give metallic or nonmetallic thermal stable polymer structures [10, 11]. Also, bis-(2-benzimidazoles) have received much attention for their wide-rang biological activity [12–14] and their importance in selective ion-exchange resins [15, 16].

1,2-Bis-(1*H*-benzimidazol-2-yl)-ethane shows optical brightening characteristics in various textile materials [17, 18]. Also, it was reported that it exhibits antipoliovirus [19, 20] and *antifungal* effects [21].

In the literature, the crystal structure of 1,2-bis-(1*H*-benzimidazol-2-yl)-ethane dihydrochloride tetrahydrate, an axle-type compound, was reported [22]. Perchlorate salt tetrahydrate of 1,2-bis-(1*H*-benzimidazol-2-yl)-ethane crystal structure was reported (see also [23]). On the other hand, the crystal structures of $Co(NCS)_2$ [24], $CuBr_2$ [25, 26], Cu(II), and Ni(II) perchlorate [27] complexes of 1,2-bis-(1*H*-benzimidazol-2-yl)-ethane were investigated. It was reported that the ligand coordinated to M(II) ions through two N atoms of C=N groups to give chelate complexes.

In the present study, the structure of **1** ($C_{16}H_{16}N_4Cl_2$, Figure 1), a symmetric molecule, is investigated by FT-IR, NMR, mass spectroscopy, and X-ray diffraction.

2. Experimental

2.1. Materials. All chemicals and solvents were reagent grade and were used as purchased without further purification.

^{1}H- and ^{13}C-NMR (APT) spectra were run on a Varian Unity Inova 500 NMR spectrometer. The residual DMSO-d_6 signal was also used as an internal reference. FT-IR spectra were recorded in KBr disks on a Mattson 1000 FT-IR spectrometer. The ESI (electron spray ionization) MS analyses were carried out in positive ion modes using a Thermo Finnigan LCQ Advantage MAX LC/MS/MS. FT-IR spectra were recorded in KBr disks on a Mattson 1000 FT-IR spectrometer.

2.2. Synthesis of **1**. The title compound was synthesized from a 1:2 molar ratio of succinic acid (1.18 g, 10 mmol) and *o*-phenylenediamine (2.16 g, 20 mmol) in 5.5 N HCl (20 mL) according to the literature [28].

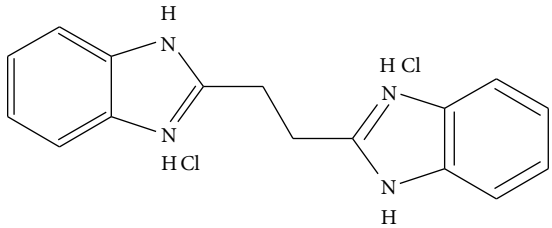

Figure 1: Chemical diagram of the title compound.

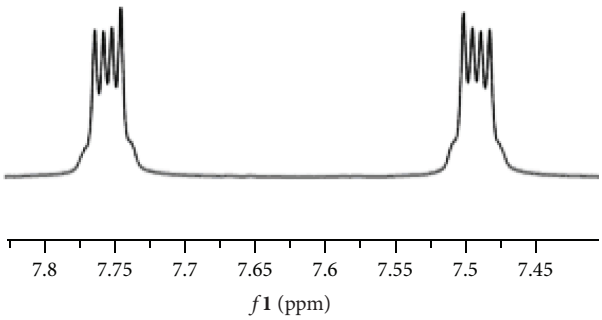

Figure 2: AA′XX′ system in the ^{1}H-NMR spectra of **1**.

The crystals suitable for X-ray diffraction were obtained from ethanol : HCl (5%) (90 : 10, v : v) solution at room temperature. The yield of the colourless crystals is 1.91 g yield (73%). M.p. 270–294°C. Found: C, 57.12; H, 4.61; N, 16.54. Calc. for $C_{16}H_{16}N_4Cl_2$ (MW : 335 g/mol); C, 57.33; H, 4.81; N, 16.71%. IR (KBr, cm^{-1}); 3054 m, br; ν(arom. CH), 2894 m, 2760 m; ν(aliph. CH), 1773 w, 1620 m; ν(arom. C=C), 1594 m; ν(C=N), 1549 m, 1455 s, 1438 s, 1313 m, 1277 s, 1231 m, 1155 s, 1039 m, 913 m, 884 m, 752 s; oop(Ar-CH). ^{1}H-NMR (499.83 MHz, DMSO-d_6): δ_H, 7.75 (AA′XX′ system, 4H, J = 6.34; $CH_{arom.}$), 7.49 (AA′XX′ system, 4H, J = 6.34; $CH_{arom.}$), 3.86 (4H, s, CH_2); ^{13}C-NMR (125.68 MHz, DMSO-d_6): δ_C, 152.28 (C=N) , 132.23 (aromatic C), 125.98, 114.58 (aromatic CH), 24.48 (CH_2). Mass spectra, (ESI+) *m/z* 335.2 (100%) (M^+), 263.3 (47%) ([MH-2HCl]$^+$).

2.3. Crystallography. Diffraction measurements were carried out at 20 ± 1°C on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-*Kα* radiation (λ = 0.71070 Å), at the 127.40 mm distance between the crystal and the detector (Istanbul University Advanced Analyses Laboratory).

For the structure solution, 47668 reflections were collected, 3414 were unique (R_{int} = 0.109); equivalent reflections were merged. An empirical absorption correction was applied, which resulted in transmission factors ranging from 0.63 to 1.00. The data were corrected for Lorentz and polarization effects.

The structure of **1** was solved by SIR92 [29] and refined with CRYSTALS [30]. The nonhydrogen atoms were refined anisotropically. H atoms were treated as riding, with C–H = 0.95(6) Å and U_{iso}(H) = 1.2U_{eq}(C), and were constrained with refinement. All calculations were performed using the CrystalStructure [31] crystallographic software package.

Table 1: Crystal and experimental data for the title compound.

Empirical formula	$C_{16}H_{16}N_4Cl_2$
Formula weight	335.24
Temperature (K)	293
Wavelength (Å)	0.71070
Crystal system	Triclinic
Space group	*P*-1
Unit cell dimensions	a = 7.1350 Å b = 9.6299(1) Å c = 15.3340(7) Å α = 80.67(2)° β = 79.66(2)° γ = 68.395(11)°
Cell volume (Å^3)	958.33(10)
Z	2
Calculated density (g cm^{-3})	1.162
Crystal size (mm)	0.40 × 0.30 × 0.10
Linear absorption coefficient (μ)	3.39 cm^{-1}
No. of observations ($I > 3.00\ \sigma(I)$)	2886
Goodness of fit indicator	1.125
Index ranges	$-8 \le h \le 8$, $-11 \le k \le 11$, $-18 \le l \le 18$
θ range for data collection (°)	2.7–25.0
R ($I > 3.00\ \sigma(I)$)	0.0840
R_w ($I > 3.00\ \sigma(I)$)	0.2190

3. Results and Discussions

3.1. Spectroscopy. ^{1}H-NMR and APT spectra of **1** are shown in Figures 2 and 3, respectively. The NMR data of the title compound is very informative for the symmetrical structure. In the ^{1}H-NMR spectrum, two double-doublets of AA′XX′ system at δ_H 7.75 (4H) and 7.49 (4H) ppm are distinguished, which are attributed to the benzene protons (Figure 2). In the APT spectra, five carbon atom signals are observed as expected. The 152.28 ppm signal belongs to the carbon atom that attached to the two imidazole nitrogen atoms. The 132.23 ppm signal is assigned to the two aromatic quaternary carbon atoms. The hydrogen atoms bonded aromatic carbons appear at the 125.98 and 114.58 ppm values (Figure 3).

3.2. Crystal Description. The details of the X-ray data collection, structure solution, and structure refinements are given in Table 1. Selected bond distances and angles are listed in Table 2. Selected torsion angles are given in Table 3. Table 4 contains the hydrogen bond geometry parameters. ORTEP-III view of the molecular structure of the title compound is given in Figure 4; crystal packing diagram of **1** is given in Figure 5.

The average bond distances and angles for the benzimidazole ring are in agreement with those of the similar

Table 2: Selected bond lengths (Å) and bond angles (°).

Bond	Distance	Bond	Distance	Bond	Distance
N1–C7	1.34(2)	N1–C2	1.39(1)	C8–C9	1.61(2)
N2–C1	1.39(2)	N2–C7	1.30(2)	C3–C4	1.34(2)
C1–C2	1.34(2)	C1–C6	1.41(2)	C5–C6	1.39(2)
C7–C8	1.52(1)	C2–C3	1.43(2)	C5–C4	1.40(2)
Angle	(°)	Angle	(°)	Angle	(°)
C7–N1–C2	109(1)	C10–N3–C11	104.9(9)	C1–N2–C7	110(1)
C16–N4–C10	106.7(8)	C2–C1–N2	107(1)	C6–C1–N2	130(1)
C8–C7–N1	124(1)	C8–C7–N2	127(1)	N1–C7–N2	107(1)
C3–C2–N1	129(1)	C3–C2–C1	124(1)	N1–C2–C1	105(1)
C9–C8–C7	105.6(9)	C4–C3–C2	113(1)	C6–C5–C4	124(1)
C1–C6–C5	112(1)	C3–C4–C5	121(1)		

Table 3: Selected torsion angles (°).

C2–N1–C7–C8	−172(1)	C7–N1–C2–C3	178(1)
C7–N2–C1–C6	175(1)	C7–C8–C9–C10	174(1)
C1–N2–C7–C8	171(1)	N4–C10–C9–C8	−120(1)
N2–C1–C2–C3	−178(1)	C6–C1–C2–C3	5(2)
N2–C1–C6–C5	176(1)	N1–C7–C8–C9	−95(1)
N3–C10–C9–C8	69(1)		

Table 4: Hydrogen bond lengths (Å) and bond angles (°).

D–H ⋯ A	D–H (Å)	H ⋯ A (Å)	D ⋯ A (Å)	D–H ⋯ A (°)
N1–H5 ⋯ $Cl2^{i}$	0.86(2)	2.29(1)	3.13(1)	163.1(0)
N3–H11 ⋯ $Cl1^{i}$	0.86(1)	2.354(8)	3.146(8)	153.1(0)

Symmetry code: (i) $+x, +y, +z$.

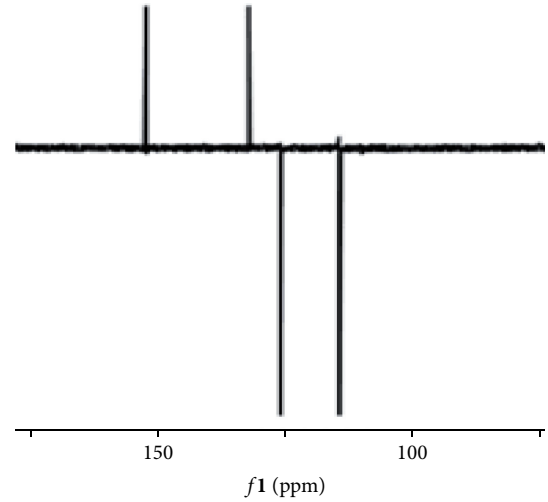

Figure 3: APT spectra of **1** in the 75–175 ppm region.

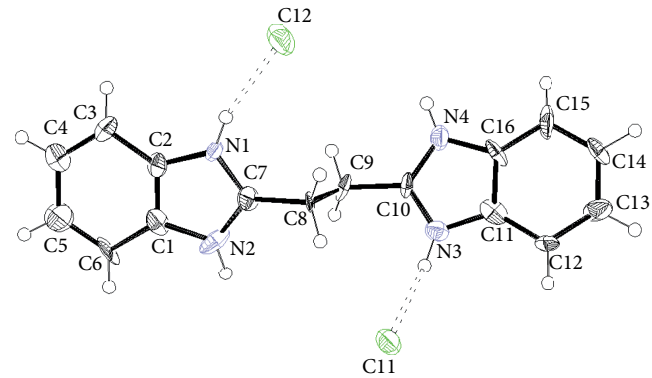

Figure 4: The molecular structure of compound **1**. Displacement ellipsoids are plotted at the 50% probability level. Hydrogen bonds are shown as dashed lines.

bis(benzimidazolyl)-substituted compounds [22, 23, 32–34]. Only C8–C9 bond length is different (1.61 Å) from that of the literature (e.g., 1.504 Å) [23]. Hydrogen bonding and bond angle values are in agreement with the literature [22, 23, 35]. The crystal structure of **1** is stabilized by intermolecular H⋯Cl⋯H interactions, which lead to the formation of a two-dimensional layer (Figure 5).

The C–N bond lengths in the imidazole ring are in the range 1.30(1)–1.40(1) Å; these are shorter than the single-bond length of 1.480 Å and longer than the typical C=N distance of 1.280 Å, indicating partial double-bond character. This can be interpreted in terms of conjugation in the heterocycle; the dihedral angles between the six- and five-membered rings are 1.24 and 6.77 (1)°, showing no exact co-planarity.

As expected, the benzimidazole moieties of the molecule are planar; the displacements of all nine atoms contained in the rings are less than 0.0065(1) Å from the least-squares plane. Planarity of the benzimidazole ring system is usually observed. In the solid state, the conformations of the $-CH_2-$ groups of **1** are all *anti*. Owing to the *anti* conformations, the entire molecule is relatively flat, the largest deviation from planarity being reflected in the torsion angle C7–C8–C9–C10 =174(1)° [35] and the planes of the C1–C6 and C11–C16 benzene rings are inclined towards each other at angle of 27.68(1)°. (See Supplementary

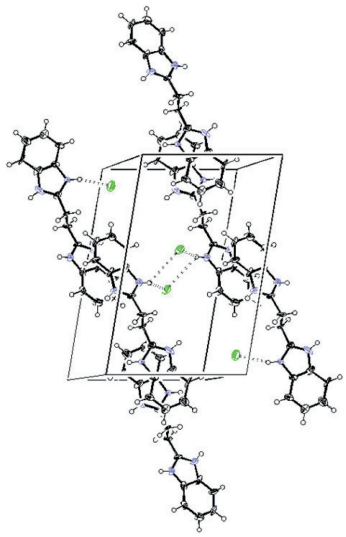

Figure 5: Unit cell packing diagram for compound **1**. Molecular overlap view from the a-axis.

materials available online at http://dx.doi.org/10.1155/2013/634986.)

4. Conclusion

The crystal structure of 1,2-bis-(1*H*-benzimidazol-2-yl)-ethane dihydrochloride (**1**) was determined by X-ray diffraction at room temperature. The structure of **1** was also characterized by mass, elemental analysis, FT-IR, and NMR spectroscopy techniques. ^{1}H-NMR spectra of **1** shows AA′XX′ system characteristics. Owing to the *anti* conformations of $-CH_2-$ groups, the entire molecule is relatively flat. The crystal structure of **1** is stabilized by intermolecular H⋯Cl⋯H interactions, which lead to the formation of a two dimensional layers.

Acknowledgment

This work was supported by the Research Fund of Istanbul University.

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