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Synthesis and Crystal Structure of a New Hydrated Benzimidazolium Salt Containing Spiro Structure

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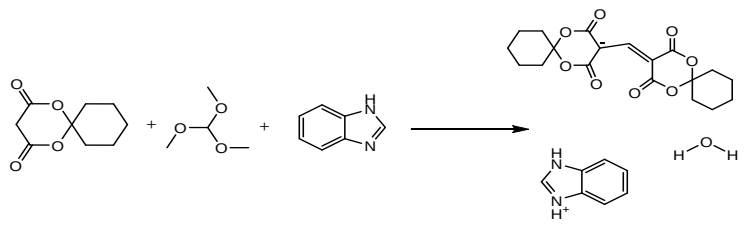
Abstract: A new hydrated benzimidazolium salt containing spiro structure was obtained when benzimidazole is added to ethyl alcohol of 1,5-dioxaspiro[5.5]undecane-2,4-dione and trimethoxymethane. The title compound $(C_{19}H_{21}O_8)$ $(C_7H_7N_2)$ $(0.5H_2O)$ was characterized by elemental analysis, IR, UV-Vis, and single-crystal X-ray diffraction. The result shows that it belongs to the triclinic system, space group P-1, with a = 11.017(2) Å, b = 11.424(2) Å, c = 11.650(2) Å, α = 70.60(3)°, β = 71.00(3)°, γ = 67.64(3)°, Mr = 505.51, V = 1245.2(5) Å, Z = 2, Dc = 1.348 g/cm^3, F(000) = 534, μ(MoKa) = 0.102 mm^{-1}. There exist two types of hydrogen bonds in the crystal. $(C_{19}H_{21}O_8)^-$ anions and $(C_7H_7N_2)^+$ cations are linked by N–H···O hydrogen bonds, while $(C_{19}H_{21}O_8)^-$ anions and free water are linked by O–H···O hydrogen bonds. All of the above hydrogen bonds form a one-dimensional (1D)-chained structure. The 1D chains further links the molecule into a three-dimensional (3D)-layered structure.

Keywords: synthesis; crystal structure; benzimidazolium

1. Introduction

Heterocyclic compounds occupy an important position in medicinal chemistry and in the pharmaceutical industry. As an important type of heterocycles, spiro compounds that contain one common atom have also shown prominent biological and pharmacological properties, such as antimicrobial [1,2], anticancer [3,4], antioxidant [5], anti-tubercular agents [6], protease activated receptor-1 (PAR1) antagonist [7], antineoplastic [8], and so on. In the last decade, the researchers' interests are now shifted to the salts of heterocyclic compounds in order to increase their solubility and efficacy. Therefore, numerous benzimidazolium salts have been reported due to a wide application in various fields such as catalysis [9], medicine [10,11], fluorescent probes [12], and liquid electrolyte [13]. Considering that two biological active organic moieties are combined into different ionic parts might augment their biological activities, a new hydrated benzimidazolium salt containing spiro structure was synthesized. Its crystal structure was determined by single-crystal X-ray diffraction analysis (Scheme 1):



Scheme 1. The synthesis route of a new hydrated benzimidazolium salt containing spiro structure.

2. Results and Discussion

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1567471. Copies of availablematerial can be obtained, free of charge, on application tothe Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: 44-(0)-1223-336033) or e-mail: deposit@ccdc. cam.ac.uk).

2.1. Crystal Structure

The selected molecular structure parameters of the title compound are listed in Table 1. Figure 1 shows the molecular structure of ($C_{19}H_{21}O_8$) ($C_7H_7N_2$) ($0.5H_2O$), and Figure 2 depicts its crystal packing in the unit cell.

Table 1. Selected molecular structure parameters.

Bond	Distances (Å)	Bond	Distances (Å)
N(1)−C(7)	1.316(3)	N(2)−C(7)	1.315(2)
N(1)−C(1)	1.386(3)	N(2)−C(6)	1.379(2)
C(14)−C(15)	1.446(2)	C(18)−C(19)	1.457(2)
C(15)−C(17)	1.386(2)	C(19)−C(20)	1.456(2)
C(15)−C(16)	1.445(2)	O(2)−C(8)	1.4422(2)
C(17)−C(19)	1.380(2)	O(1)−C(8)	1.4381(2)
O(7)−C(24)	1.439(2)	O(8)−C(24)	1.438(2)
Angle	(°)	Angle	(°)
C(19)−C(17)−C(15)	131.18(1)	C(17)−C(15)−C(16)	124.55(1)
C(17)−C(19)−C(18)	116.84(1)	C(17)−C(15)−C(14)	117.487(1)
C(20)−C(19)−C(18)	117.55(2)	C(16)−C(15)−C(14)	117.16(2)
O(8)−C(24)−O(7)	108.89(1)	O(1)−C(8)−O(2)	108.72(1)
Torsion	(°)		(°)
O(3)−C(14)−C(15)−C(17)	−11.9(2)	C(17)−C(19)−C(20)−O(6)	20.5(3)
O(2)−C(14)−C(15)−C(17)	170.22(1)	O(5)−C(18)−C(19)−C(17)	−16.7(3)
O(3)−C(14)−C(15)−C(16)	158.38(2)	C(17)−C(19)−C(20)−O(8)	−165.71(1)
C(15)−C(17)−C(19) −C(18)	−167.65(2)	C(14)−C(15)−C(17)−C(19)	−170.89(2)

Symmetry transformations used to generate equivalent atoms:A: −x + 1,−y + 2,−z.

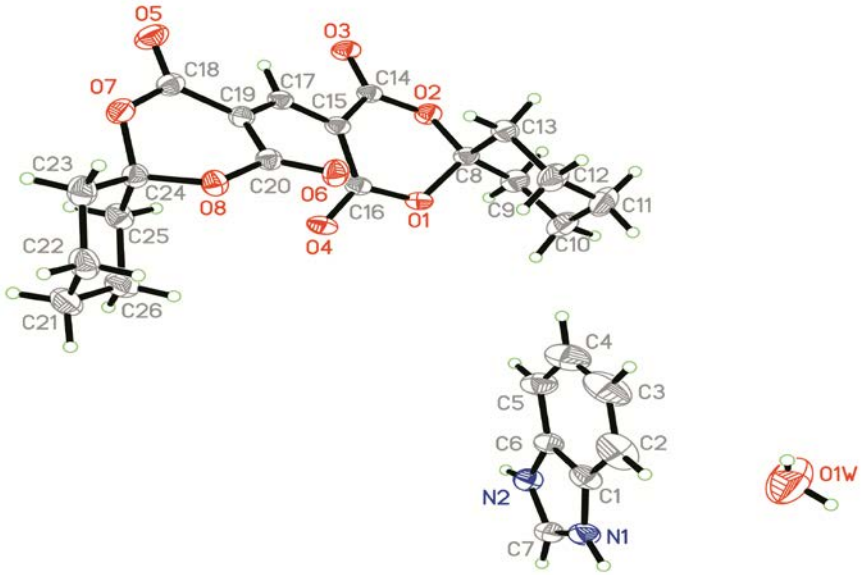


Figure 1. The molecular structure of ($C_{19}H_{21}O_8$) ($C_7H_7N_2$) ($0.5H_2O$), showing 30% probability displacement ellipsoids and the atomic numbering scheme.

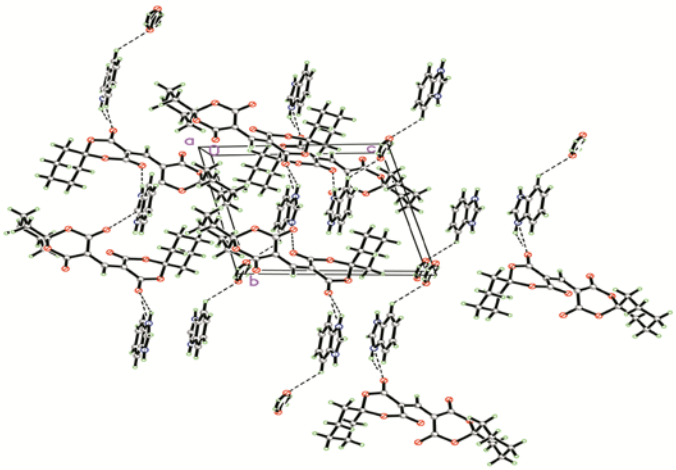


Figure 2. The packing arrangement down the a axis of $(C_{19}H_{21}O_8)$ $(C_7H_7N_2)$ $(0.5H_2O)$.

The molecular structure consists of $(C_7H_7N_2)^+$ cation, $(C_{19}H_{21}O_8)^-$ anion, and water molecule (Figure 1). As shown in Figure 3, one water molecule is shared by two $(C_{19}H_{21}O_8)^-$ anions. In addition, water molecule is found to be disordered positions and the occupancy of each H_2O is 0.5. It is possible that the volume of water molecule is small and it is a free state in hydrated benzimidazolium salt. The central C(17) atom of $(C_{19}H_{21}O_8)^-$ anion is bridged by two 1,5-dioxaspiro[5.5]undecane-2,4-dione groups. The bond lengths C17–C15 (1.386(2) Å) and (C17–C19) (1.380(2) Å) are different with other spiro structures reported (C=C double bond C(10)–C(2) 1.367(7) Å, single bond C(10)–C(11) 1.433(8) Å) [14], which indicates C(15)–C(17)=C(19) is allyl anion. The bond angle of C(15)–C(17)–C(19) 131.19(1)° in the structure is little smaller than C(11)–C(10)–C(2)137.9(5)° in reference [14]. The title compound is not planar. The C(15)−C(17)−C(19)−C(18), C(14)−C(15)−C(17)−C(19), O(5)−C(18)−C(19)−C(17), O(3)−C(14)− C(15) −C(17) torsion angles are −167.65(2)°, −170.89(2)°, −16.7(3)° and −11.9(2)°, respectively. The two cyclohexane rings both exhibit a chair-like configuration, with puckering parameters for ring 1 (C8−C13): Q = 0.565 (6) Å, q2 = 0.025 Å, q3 = −0.565 Å, ϑ = 177.5°, φ = 69.43°; ring 2 (C21−C26): Q = 0.556 Å, q2 = 0.037 Å, q3 = −0.555 Å, ϑ = 176.2°, φ = 168.05° [15].

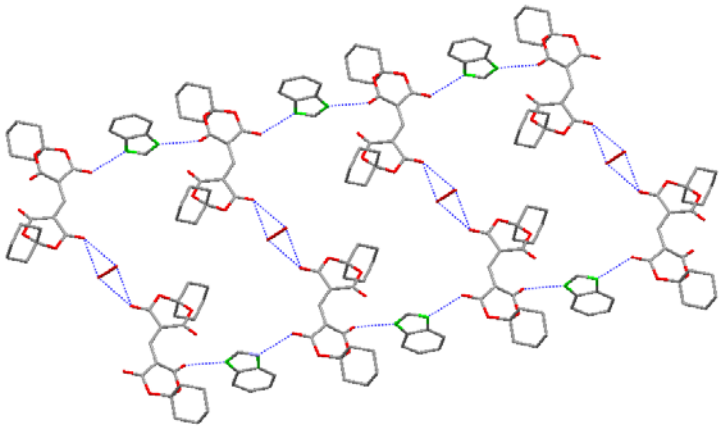


Figure 3. One-dimensional (1D)-chained structure by N–H···O and O–H···O intermolecular interactions.

As can be seen from Figure 3, there are N–H···O and O–H···O two types of hydrogen bonds in the crystal. $(C_{19}H_{21}O_8)^-$ anions and $(C_7H_7N_2)^+$ cations are linked by N–H···O hydrogen bonds, the donor, and acceptor distances are 2.728(1) Å for N(1)–H(1A)···O(4), 2.718(1) Å for N(2)–H(2)···O(3), respectively. While $(C_{19}H_{21}O_8)^-$ anions and free water are linked by O–H···O hydrogen bonds, the donor and acceptor distances are 2.875(1)Å for O1W−H1W1···O(5), 2.994(1)Å for O1W−H1W2···O(5), respectively (Table 2). A one-dimensional (1D)-chained structure is assembled by intermolecular hydrogen bonds. The molecule further forms a three-dimensional (3D)-layered structure by the 1D chains (Figure 4).

Table 2. Hydrogen bond distances and angles for the title compound.

D–H···A	Symmetry	D–H(Å)	H ... A(Å)	D ... A(Å)	∠D–H···A (°)
N(1)–H(1A)···O(4)	−x + 1, −y + 1, −z + 1	0.899	1.832	2.728	173.53
N(2)–H(2)···O(3)	−x + 1, −y, −z + 1	0.851	1.925	2.717	154.53
O1W−H1W1 ... O(5)	x + 1, y + 1, z − 1	0.854	2.064	2.878	159.30
O1W−H1W2 ... O(5)	−x, −y + 1, −z + 1	0.853	2.307	2.985	136.62

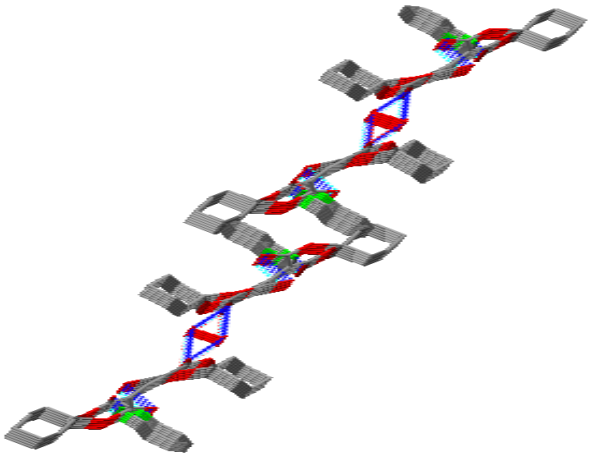


Figure 4. Three-dimensional (3D)-layered structure of $(C_{19}H_{21}O_8)$ $(C_7H_7N_2)$ $(0.5H_2O)$.

2.2. Spectroscopic Properties

As shown in Figure 5, the two bands at 2937 cm^{-1} and 2856 cm^{-1} are assigned to the C–H stretching vibration of the benzimidazolum ring. The strong bands at 1675 cm^{-1} and 1218 cm^{-1} are attributed to the stretching vibrations of C=O and C–O bands of 1,3-dioxane ring, which conforms to our earlier report [16,17]. The title compound exhibits strong bands at 1493 cm^{-1} (C=C), 1441 cm^{-1}(C=N), 779 cm^{-1}($\upsilon_{C\text{-}H}$ benzene ring) and 744 cm^{-1}($\upsilon_{C\text{-}H}$ imidazole ring) for the benzimidazolum group [18]. These are in accordance with the results of crystal structure analysis.

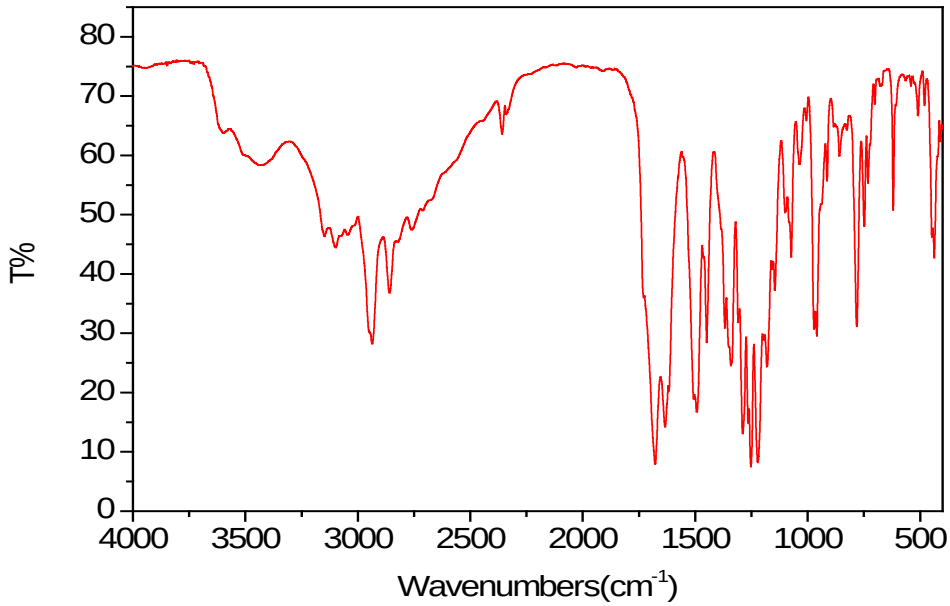


Figure 5. Infrared spectrum of the title compound.

As shown in Figure 6, the molecule exists three bands, which were observed at 210 nm, 243 nm and 384 nm in EtOH. The absorption band at 243 nm is assigned to $\pi \rightarrow \pi^*$ transition of the benzimidazole group. The absorption band at 384 nm is attributed to $\pi \rightarrow \pi^*$ electron transition of enolate form (HO–C=C–C=O).The absorption band at 210 nm is possibly affected by the nitrogen atom and the solvent polarity. These values are similar to those found in related structure compound [14,18].

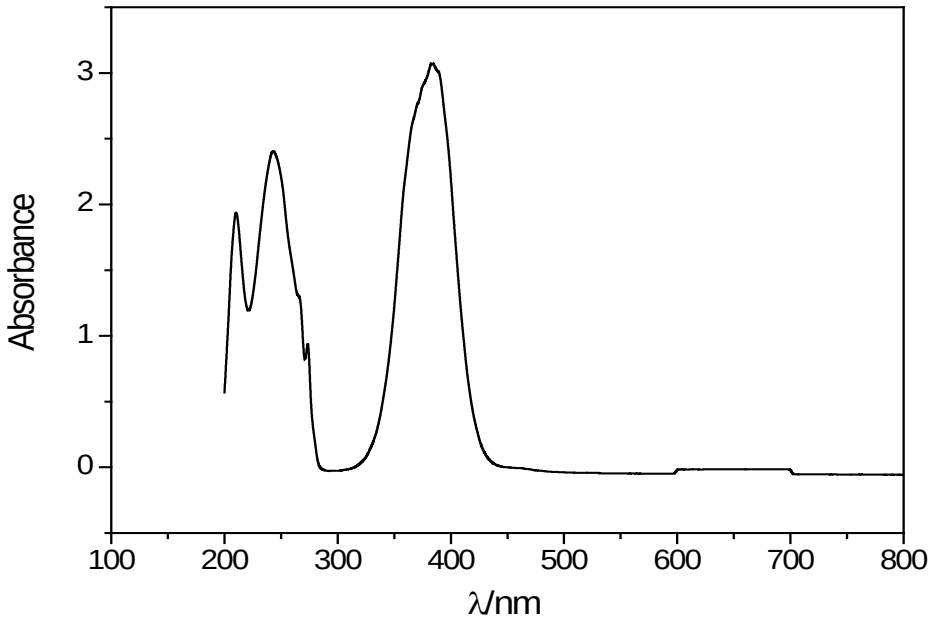


Figure 6. UV-Vis spectra of the title compound.

3. Experimental Section

3.1. Materials and Methods

Elemental analyses were obtained using a Vario ELIII analyzer (Elementar, Hanau, Germany). Fourier transform infrared spectra were determined on FT-IR 510P (Nicolet, Madison, WI, USA). UV-visible absorption spectra were carried out on a UV3100 pectrometer (Shimadzu, Kyoto, Japan).

3.2. Preparation of the Title Compound

1,5-dioxaspiro[5.5]undecane-2,4-dione (1.84 g, 0.01 mol) was reacted with trimethoxymethane (1.27 g, 0.024 mol) in ethyl alcohol (30mL) solution. After refluxing 2.5 h, benzimidazole (1.18 g, 0.01 mol) was addedand the mixture was refluxed for another 5 h. The red precipitate was recovered by filtration and dried. Yield 18.2 %. m.p.: 176.5–177.3 °C. Elemental analysis Calcd. (%) For $C_{26}H_{29}N_2O_{8.50}$: C, 61.77; H, 5.78; N, 5.54. Found: C, 61.54; H, 5.66; N, 5.67. Red block-shaped crystals were obtained by recrystallization from the solution of ethanol.

3.3. Crystallography

The crystal of $(C_{19}H_{21}O_8)$ $(C_7H_7N_2)$ $(0.5H_2O)$ with dimensions of 0.40 mm × 0.38 mm × 0.37 mm was mounted a spider**II**diffractometer using MoKα radiation at 293(2) K. Its structure was solved by SHELXS-97 [19]. The final cycle of refinement included 334 parameters gave R = 0.0481 and wR = 0.1268 with $w = 1/[\sigma^2(F_o^2) + (0.0721P)^2 + 0.2939P]$, where $P = (F_o^2 + 2F_c^2)/3$. Further details of crystallographic data are shown in Table 3.

Table 3. Selected crystal data and details of the structure determination for the title compound.

Formula	**$(C_{19}H_{21}O_8)$ $(C_7H_7N_2)$ $(0.5H_2O)$**
Formula Weight	505.51
Crystal System	Triclinic
Space group	P-1
Crystal Size(mm^3)	0.40 × 0.38 × 0.37
Wavelength (Å)	0.71073
a(Å)	11.017(2)
b(Å)	11.424(2)
c(Å)	11.650(2)
α(°)	70.60(3)
β(°)	71.00(3)
γ(°)	67.64(3)
V($Å^3$)	1245.2(4)
Z	2
F(000)	534
D/g·cm^{-3}	1.348
−h, h/−k, k/−l, l	−13:14; −14:14; −15:15
Reflections collected	12207
Independent reflections	5629[R(int) = 0.0345]
Reflections observed(I > 2σ(I))	4279
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5629/0/342
Goodness-of-fit on F^2	1.081
Final R indices [I > 2sigma(I)]	R_1 = 0.0481, wR_2 = 0.1265
R indices (all data)	R_1 = 0.0650, wR_2 = 0.1490
Largest diff. peak and hole (e $Å^{-3}$)	0.373, –0.218

4. Conclusions

A new hydrated benzimidazolium salt containing spirostructure was synthesized. Its structure was characterized by elemental analysis, IR, UV-Vis, and single-crystal X-ray diffraction. The title

compound consists of $(C_7H_7N_2)^+$ cations, $(C_{19}H_{21}O_8)^-$ anions, and water molecule. The result shows that it belongs to the triclinic system, space group P-1. In the crystal, $(C_{19}H_{21}O_8)^-$ anions and $(C_7H_7N_2)^+$ cations are linked by N–H···O hydrogen bonds, while $(C_{19}H_{21}O_8)^-$ anions and free water are linked by O–H···O hydrogen bonds. All of the abovehydrogen bonds form a 1D-chained structure. The 1D chains further link the molecule into a 3D-layered structure.

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Author Contributions: Jinhe Jiang synthesized the title compound. Wulan Zeng conceived and designed the experiments and wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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