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ORIGINAL PAPER

# Synthesis and Crystal Structure of Hydrate Adduct of 6-Benzylaminopurine and 5-Sulfosalicylic Acid $[(C_{12}H_{12}N_5)(C_7H_5O_6S)\cdot H_2O]$

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**Abstract** The crystal structure of hydrate adduct of 6-benzylaminopurine and 5-sulfosalicylic acid $[(C_{12}H_{12}N_5)(C_7H_5O_6S)\cdot H_2O]$ **1** is studied. It crystallizes in monoclinic system space group $P2_1/n$ with $a = 6.2128(9)$ Å, $b = 20.762(3)$ Å, $c = 15.675(2)$ Å, $\beta = 92.040(2)°$, $V = 2{,}020.6(5)$ Å$^3$, $Z = 4$, $R_{gt}(F) = 0.0494$, $wR_{ref}(F^2) = 0.1112$, and $T = 173(2)$ K. Single-crystal X-ray diffraction analysis reveals that the asymmetric unit of **1** contains one 6-benzylaminopurine molecule and one 5-sulfosalicylic acid molecule, as well as one lattice water molecule. In **1**, hydrogen bonds link the two monomers into one-dimensional double chain, two-dimensional layer network, and further a 3-D supramolecular network. Short ring-interactions with intra-chain $\pi$–$\pi$ stacking are observed (distances between ring centroids are 3.964, 3.796 and 3.571 Å, and the dihedral angle between planes are 6.97°, 5.55°, and 5.66°, respectively).

**Keywords** Crystal structure · 6-Benzylaminopurine · 3-D supramolecular network · $\pi$–$\pi$ Conjugate effects

## Introduction

6-Benzylaminopurine (6-BA) is the type of adenine derivative with 6-substituted group. 6-benzyl-amino substituent has a higher activity, which made it play an important role in the tissue culture, gene expression regulation, stress resistance, anti-aging and anti-heavy metal pollution, etc. Metal ions in life processes can lead to body lesions, so the research of the complexation reaction of purine compounds with metal ions has an important significance in the life sciences [1–4]. Up to date, there are few reports on the 6-benzyl-amino-purine derivative. In this paper, we introduce a hydrate adduct of 6-benzylaminopurine and 5-sulfosalicylic acid $[(C_{12}H_{12}N_5)(C_7H_5O_6S)\cdot H_2O]$ **1**, in which there are lots of the strong hydrogen bonds and $\pi$–$\pi$ interactions. Its structure was determined using the X-ray diffraction method and characterized with spectroscopic techniques.

## Experimental Section

### General Procedures and Materials

All chemicals purchased were reagent grade and used without further purification. IR spectrum was recorded on an AVATAR360 spectrophotometer with range 4,000–400 cm$^{-1}$ using KBr pellets. Elemental analyses were performed using an Optima-2000DV elemental analyzer.

### Synthesis of Hydrate Adduct of 1

Compound **1** was synthesized by the reaction of 6-benzylaminopurine 0.0226 g (0.1 mmol) and 5-sulfosalicylic acid 0.05 g (0.2 mmol) in methanol 8 mL. Mixture was placed in a 15 mL test tube for 10 days at room temperature. The crystalline of **1** (colorless club-shaped) was collected by vacuum filtration and dried in air (yield 53%).

Elemental analysis calcd. for $C_{19}H_{25}N_5O_7S$ (%): C 49.41, H 4.12, N 15.17, O 24.27; Found: C 49.39, H 4.08, O 24.31, N 15.22. IR data (cm$^{-1}$): 3403(w), 3131(w),

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3031(w), 1749(w), 1724(m), 1658(s), 1610(m), 1475(w), 1398(m), 1353(w), 1234(w), 1174(s), 1124(m), 1079(w), 1035(s), 885(w), 840(w), 784(w), 721(w), 665(w), 593(m), 484(w).

### X-ray Structure Determination of 1

The crystal and instrumental parameters used in the unit-cell determination and data collection are summarized in Table 1. Diffraction measurements were made at room temperature on a Bruker SMART APEX II X-ray diffractometer using graphite-monochromated Mo K$\alpha$ radiation using $\omega/2\theta$ scan mode. Unit-cell dimensions were determined and refined in the $1.96° < \theta < 26.00°$ range. The structure was solved by the direct methods using SHELXS-97 and refined by full-matrix least-squares techniques on $F^2$ with SHELXL-97 [5, 6]. The empirical absorption corrections were applied by the multi-scan method via X-RED software. All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were included in their idealized positions and refined isotropically. ORTEP drawing [7] of the molecule with 50% probability displacement thermal ellipsoids and atom-labeling scheme are shown in Fig. 1. Selected bond distances (Å) and angles (°) for compound are list in Table 2.

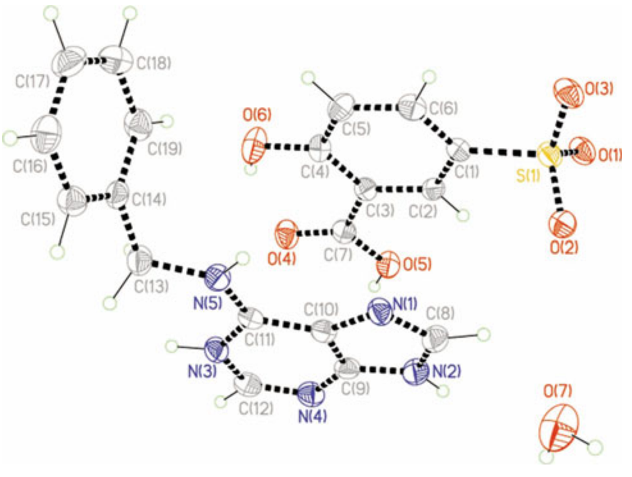

**Fig. 1** ORTEP drawing of the molecule with 50% probability displacement thermal ellipsoids

**Table 1** Crystal data and structure refinement for **1**

| | |
|---|---|
| CCDC no. | 753471 |
| Empirical formula | $C_{19}H_{19}N_5O_7S$ |
| Formula weight | 461.45 |
| $T$ (K) | 173 (2) |
| Radiation ($\lambda$, Å) | Mo K$\alpha$ (0.71073) |
| Crystal system, space group | Monoclinic, $P2_1/n$ |
| Unit cell dimensions (Å, °) | |
| $a$ | 6.2128(9) |
| $b$ | 20.762(3) |
| $c$ | 15.675(2) |
| $\beta$ | 92.040(2) |
| $Z$ | 4 |
| $V$ (Å$^3$) | 2,020.6(5) |
| $D_{\text{calc.}}$ (g cm$^{-1}$) | 1.517 |
| $\mu$ (mm$^{-1}$) | 0.215 |
| $F(000)$ | 960 |
| Crystal size (mm) | 0.30 × 0.25 × 0.15 |
| $\theta$ Range for data collection (°) | 1.96–26 |
| Index ranges | $-7 \le h \le 7$, $-25 \le k \le 22$, $-19 \le l \le 19$ |
| Reflections/unique ($R_{\text{int}}$) | 14785/3920 ($R_{\text{int}} = 0.0670$) |
| Data/parameters | 3920/295 |
| $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0494$, $wR_2 = 0.1112$ |
| Goodness of fit indication | 1.021 |
| Largest difference peak and hole (e Å$^{-3}$) | 0.294 and −0.368 |

## Results and Discussion

### Description of the Crystal Structure of Hydrate Adduct of 6-Benzylaminopurine and 5-Sulfosalicylic Acid $[(C_{12}H_{12}N_5)(C_7H_5O_6S)\cdot H_2O]$ 1

Single-crystal X-ray diffraction analysis reveals that the asymmetric unit of **1** contains one 6-benzylaminopurine molecule and one 5-sulfosalicylic acid molecule, as well as one lattice water molecule (Fig. 1). The exocyclic bond length C(3)–C(7) and C(13)–C(14) are elongated to 1.466(4) Å and 1.498(3) Å, longer than the cyclic those of C–C bonds (average 1.388 Å). The bond lengths N–C are average 1.349 Å, except for exocyclic N(5)–C(11) (1.313(3) Å) and N(5)–C(13) (1.475(3) Å). The C(4)–O(6) bond length (1.351(3) Å) is long than C(7)–O(4) and C(7)–O(5) bond lengths (1.250(3) Å and 1.293(3) Å, respectively). The bond lengths S–O are average 1.454(2) Å.

The molecular unit **1** as a whole, ignoring the lattice water molecule, contains three six-membered rings and one five-membered ring, N1–C8–N2–C9–C10 marked P1, N3–C11–C10–C9–N4–C12 marked P2, C14–C15–C16–C17–C18–C19 marked P3 and C1–C2–C3–C4–C5–C6 marked P4. The one 6-benzylaminopurine molecule and one 5-sulfosalicylic acid molecule, join together through hydrogen bonds. The corresponding hydrogen bonds are O(5)–H(5A)···N(1) (2.553 Å, 169.0°), N(5)–H(5B)···O(4) (2.877 Å, 168°) and intra-hydrogen bond O(6)–H(6A)···O(4) (2.619 Å, 146°). The molecular units $(\mathbf{1})_n$, as a basic building unit, are connected with each other by hydrogen bonds, N(3)–H(3)···O(1) (2.763 Å, 148.0°), C(12)–H(12)···O(3)

**Table 2** Selected bond lengths (Å) and angles (°) for **1**

| | | | | | |
|---|---|---|---|---|---|
| C(1)–C(2) | 1.380(3) | C(7)–O(4) | 1.250(3) | C(13)–N(5) | 1.475(3) |
| C(1)–C(6) | 1.395(3) | C(7)–O(5) | 1.293(3) | C(13)–C(14) | 1.498(3) |
| C(9)–C(10) | 1.380(3) | C(8)–N(1) | 1.323(3) | C(14)–C(15) | 1.377(4) |
| C(2)–C(3) | 1.392(3) | C(8)–N(2) | 1.344(3) | C(14)–C(19) | 1.404(4) |
| C(3)–C(4) | 1.406(3) | C(9)–N(2) | 1.352(3) | C(15)–C(16) | 1.382(4) |
| C(3)–C(7) | 1.466(4) | C(9)–N(4) | 1.355(3) | C(16)–C(17) | 1.382(4) |
| C(4)–O(6) | 1.351(3) | C(10)–N(1) | 1.377(3) | C(17)–C(18) | 1.378(4) |
| C(4)–C(5) | 1.385(4) | C(11)–N(5) | 1.313(3) | C(18)–C(19) | 1.384(4) |
| C(5)–C(6) | 1.380(4) | C(11)–N(3) | 1.372(3) | O(1)–S(1) | 1.4669(2) |
| C(10)–C(11) | 1.408(3) | C(12)–N(4) | 1.300(3) | O(2)–S(1) | 1.4473(2) |
| C(1)–S(1) | 1.767(3) | C(12)–N(3) | 1.369(3) | O(3)–S(1) | 1.4475(2) |
| C(2)–C(1)–C(6) | 119.3(2) | N(1)–C(8)–N(2) | 112.7(2) | C(15)–C(16)–C(17) | 120.0(3) |
| C(2)–C(1)–S(1) | 119.29(2) | N(2)–C(9)–N(4) | 126.4(2) | C(18)–C(17)–C(16) | 119.9(3) |
| C(6)–C(1)–S(1) | 121.3(2) | N(2)–C(9)–C(10) | 105.8(2) | C(17)–C(18)–C(19) | 120.2(3) |
| C(1)–C(2)–C(3) | 121.2(2) | N(4)–C(9)–C(10) | 127.8(2) | C(18)–C(19)–C(14) | 120.2(3) |
| C(2)–C(3)–C(4) | 118.9(2) | N(1)–C(10)–C(9) | 110.1(2) | C(8)–N(1)–C(10) | 104.0(2) |
| C(2)–C(3)–C(7) | 119.9(2) | N(1)–C(10)–C(11) | 131.4(2) | C(8)–N(2)–C(9) | 107.3(2) |
| C(4)–C(3)–C(7) | 121.1(2) | C(9)–C(10)–C(11) | 118.6(2) | C(12)–N(3)–C(11) | 123.8(2) |
| O(6)–C(4)–C(5) | 118.2(2) | N(5)–C(11)–N(3) | 121.6(2) | C(12)–N(4)–C(9) | 111.6(2) |
| O(6)–C(4)–C(3) | 122.1(2) | N(5)–C(11)–C(10) | 125.7(2) | C(11)–N(5)–C(13) | 123.8(2) |
| C(5)–C(4)–C(3) | 119.7(2) | N(3)–C(11)–C(10) | 112.7(2) | O(2)–S(1)–O(3) | 113.81(1) |
| C(6)–C(5)–C(4) | 120.5(2) | N(4)–C(12)–N(3) | 125.5(3) | O(2)–S(1)–O(1) | 111.28(1) |
| C(5)–C(6)–C(1) | 120.3(2) | N(5)–C(13)–C(14) | 111.4(2) | O(3)–S(1)–O(1) | 112.44(1) |
| O(4)–C(7)–O(5) | 123.2(2) | C(15)–C(14)–C(19) | 118.7(2) | O(2)–S(1)–C(1) | 106.73(1) |
| O(4)–C(7)–C(3) | 121.8(2) | C(15)–C(14)–C(13) | 121.2(2) | O(3)–S(1)–C(1) | 106.67(1) |
| O(5)–C(7)–C(3) | 115.0(2) | C(19)–C(14)–C(13) | 120.1(2) | O(1)–S(1)–C(1) | 105.25(1) |
| C(14)–C(15)–C(16) | 121.1(3) | | | | |

(3.220 Å, 155.0°), C(13)–H(13A)···O(3) (3.445 Å, 148.0°) and C(15)–H(15)···O(1) (3.478 Å, 157.0°), to extend into a 1-D double chain along the *b*-axis (Fig. 2). The structure of **1** extends from 1-D double-chain to 2-D supramolecular layer under the interactions of hydrogen bonds in the *bc* plane (Fig. 3). The corresponding hydrogen bond distance and angle, C(8)–H(8)···O(2), are 3.240 Å and 132.0°. Within layer, the weak $\pi$–$\pi$ packing interactions in face-to-face for P2-P3 and P4-P1 and offset face-to-face for P1-P3 (distance between rings centroids are 3.964/3.796 Å and 3.571 Å, and the dihedral angle are 6.97°/5.55° and 5.66°, respectively), further reinforce supramolecular structural stability. At last, a 3-D supramolecular network is further constructed via hydrogen bonds C(17)–H(17)···O(3) (3.496 Å, 163.0°) and C(19)–H(19)···O(6) (3.387 Å, 161.0°), as well as hydrogen bonds formed by lattice water molecules (Fig. 4). The parameters of the hydrogen bonds are listed in Table 3.

The packing diagram of **1** (Fig. 3) shows the stronger $\pi$–$\pi$ conjugate effects stacking in face-to-face and offset face-to-face alignment mode along the *x*-axis. The stacking interactions are best propitious to stabilize the structure, as well charge transfer [8–10]. As a sequential work, we now further consider the new studies with other substituents and investigate effect on the biological activity derived of inter- and/or intramolecular interactions.

The UV–visible absorption spectrum of **1** in ethanol is shown in Fig. 5. The bands centered at 270.9 and 334.9 nm. Result reveals that the absorption band 270.9 nm is red-shifted due to the protonation character of 6-BAP, in comparison to that of the parent 6-BAP (267.5 nm), but the above 334.9 nm may be much more likely resulted in $\pi$–$\pi$ conjugation effect.

IR spectrum of the compound **1** was recorded in the 4,000–400 cm$^{-1}$ region (Fig. 6). The bands centered at 3,403 cm$^{-1}$ (N–H and O–H), 3,243 cm$^{-1}$ (N–H) and 3,131 cm$^{-1}$ (N–H) could be assigned to N–H and O–H stretching vibrations, which peaks shifted towards lower wavenumber under the information of the hydrogen-bonding and/or $\pi$–$\pi$ conjugation effect, comparing with free 6-BAP (3,444, 3,257, 3,207 cm$^{-1}$) and free –OH (about 3,650 cm$^{-1}$) [11]. The band located at 3,031 cm$^{-1}$

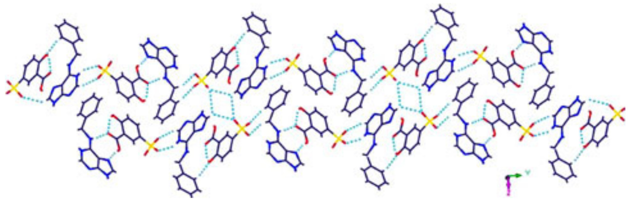

**Fig. 2** The 1-D hydrogen-bonded double chain of **1** along the *b*-axis. Hydrogen bonds are drawn as *blue dotted lines*. (Color figure online)

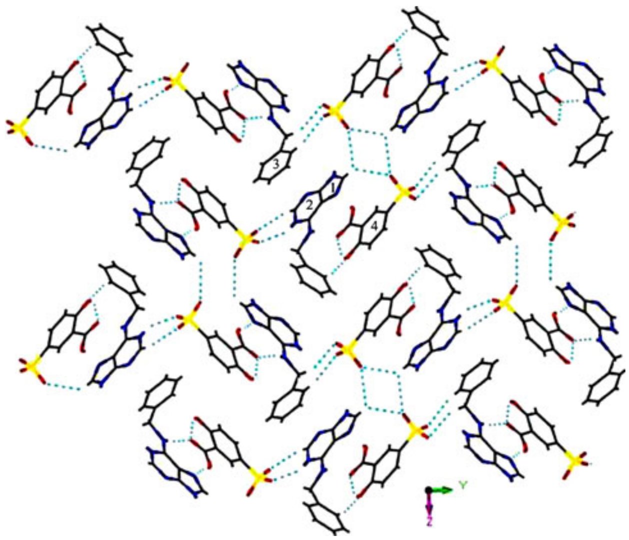

**Fig. 3** The 2-D hydrogen-bonded layer of **1** in the *bc* plane, as well as $\pi$–$\pi$ interactions. Hydrogen bonds are drawn as *blue dotted lines*. (Color figure online)

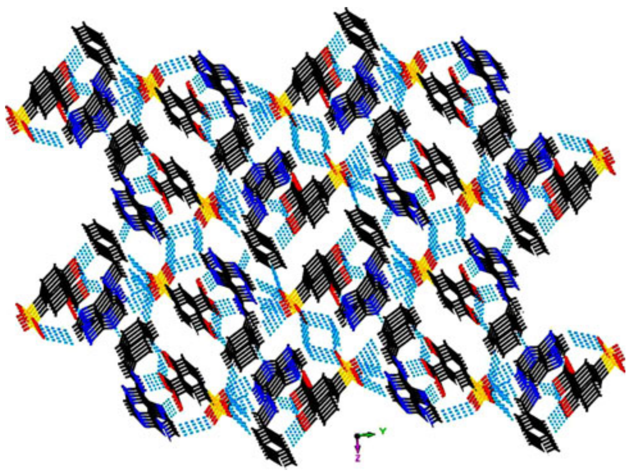

**Fig. 4** The 3-D supramolecular network built from hydrogen bonds. Hydrogen bonds are drawn as *blue dotted blue lines*. (Color figure online)

could be assigned to C–H stretching vibration of aromatic ring. The asymmetric and symmetric stretching vibrations of the carboxyl group are centered at 1,724 and

**Table 3** Intra- and inter-molecular hydrogen bond distances (Å) and angles (°) for **1**

| D–H···A | d(D–H) | d(H···A) | d(D···A) | <(DHA) |
|---|---|---|---|---|
| N2–H2A···O7#1 | 0.8800 | 1.8200 | 2.6895 | 171.00 |
| N3–H3···O1#2 | 0.8800 | 1.9800 | 2.7631 | 148.00 |
| O5–H5A···N1#1 | 0.8300 | 1.7400 | 2.5534 | 169.00 |
| N5–H5B···O4#3 | 0.8800 | 2.0100 | 2.8769 | 168.00 |
| O6–H6A···O4 | 0.8300 | 1.8900 | 2.6188 | 146.00 |
| O7–H7A···O1#4 | 0.8300 | 2.0300 | 2.8272 | 160.00 |
| O7–H7B···O2#5 | 0.8700 | 2.0500 | 2.8258 | 148.00 |
| C8–H8···O2 | 0.9500 | 2.5300 | 3.2404 | 132.00 |
| C12–H12···O3#2 | 0.9500 | 2.3400 | 3.2203 | 155.00 |
| C13–H13A···O3#6 | 0.9900 | 2.5700 | 3.4450 | 148.00 |
| C15–H15···O1#6 | 0.9500 | 2.5800 | 3.4782 | 157.00 |
| C17–H17···O3#7 | 0.9500 | 2.5800 | 3.4957 | 163.00 |
| C19–H19···O6 | 0.9500 | 2.4800 | 3.3867 | 161.00 |

Symmetry transformations used to generate equivalent atoms: #1 $x-1, y, z$ #2 $-x+1/2, y-1/2, -z+3/2$ #3 $x+1, y, z$ #4 $-x+1, -y+2, -z+1$ #5 $-x+2, -y+2, -z+1$

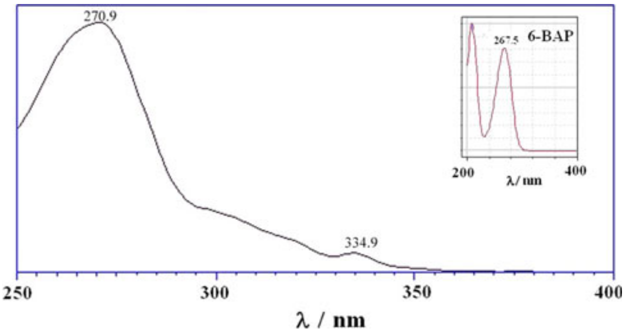

**Fig. 5** UV–vis absorption spectrum of **1** in ethanol at room temperature. *Inset* UV-vis spectrum of 6-BAP in ethanol at room temperature

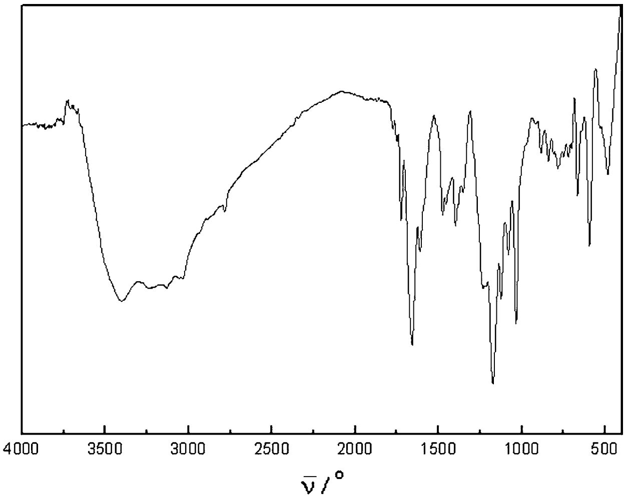

**Fig. 6** IR spectrum of **1**

1,398 $cm^{-1}$, respectively. The bands observed between 1,658 and 1,610 $cm^{-1}$ may be assigned to the C–N stretching vibrations of the heterocyclic ring. The bands from 1,234 to 1,035 $cm^{-1}$, can be attributed to the stretching vibrations of the S=O and S–O groups, respectively.

## Supplementary Material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 753471. Copies of this data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting. The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033.

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