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REVIEW PAPER

Synthesis and Crystal Structure of Tetrabutylammonium 4-(2-Bromothiophene-5-Sulfanilamide)-Benzoate

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Abstract Tetrabutylammonium 4-(2-bromothiophene-5-sulfanilamide)-benzoate crystallizes in $C_{2/C}$ lattice with $a = 18.3389(17)$, $b = 16.540(16)$, $c = 15.8280(15)$ Å, $\beta = 116.959(2)$, $V = 4279.5(7)$ Å^3, $Z = 4$, and $R = 0.0560$. In the structure a very short centrosymmetric hydrogen bond and C=O···Br halogen bond interactions, together with N–H···O and C–H···O hydrogen bonds give a three-dimensional network.

Keywords Sulfanilamide · C=O···Br interaction · Short O···H···O hydrogen bonds

Introduction

Week interactions are used to design and manipulation of supramolecular system [1]. One of these kinds of the interactions is hydrogen bond, which plays a crucial role in many chemical processes. Although conventional hydrogen bond such as O–H···O, N–H···O have been explained sufficiently, it seems the nature of strong O–H···O bond needs more detailed study [2]. This short hydrogen bond is frequently observed in salts containing carboxylate group [3–5]. In the strong O–H···O hydrogen bonds, the location of the proton is uncertain. It may be located precisely at: (i) the centre of the O···O distance; (ii) close to one O atom; (iii) closer to one O atom but jumps between the two O atoms [6].

Besides hydrogen bond, another interaction, halogen bonding, has raided great interest. Because its parallelism potency with hydrogen bond, such interaction is considered as an effective and reliable tool in crystal engineering at the disposal of the supramolecular chemist [7] and even may constitute some unique supramolecular motif [8].

For possible antimicrobial activity, 4-(2-bromothiophene-5-sulfonamido) benzoic acid, which are of interest since the biological activity of both sulfanilamide [9, 10] and thiophene [11, 12] was condensed in our library, and the title complex was obtained. The X-ray analysis demonstrates that the C=O···Br halogen bond and extremely short O–H···O hydrogen bond play important roles in forming complex.

Experimental

The melting points were taken on a WRS-1A melting point apparatus. The IR spectra were recorded on a Perkin-Elmer 2000 spectrophotometer as a KBr pellet. The NMR spectra of the crystalline complexes were recorded on a Bruker AM-300 spectrometer operating at 25 °C, using DMSO-d as the solvent and TMS as the internal standard. All reagents were commercial products and were utilized without further purification. Differential scanning calorimetry and thermogravimetric analysis (DSC–TGA) analyses were carried out on a Universal V4.1D TA Instruments (SDT Q600), at a heating rate of 10 °C/min under a nitrogen atmosphere.

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A solution of ethyl acetate (30 mL) with 5-bromothiophene-2-sulfonyl chloride (10 mmol) was dropped into a sodium carbonate (30 mmol, 3.1 g) solution (30 mL) with 4-amino-benzoic acid (10 mmol) and tetrabutylammonium bromide (10 mmol) at room temperature. Then the pH of the solution was adjusted to 2 after 6 h, then followed with filtration and extraction, and a colorless single crystal was obtained after 3 days. Melting point: 210 °C, IR (KBr): 3448(s), 3095, 2955, 2869, 1679(s), 1605(s), 1510, 1403(s), 1332(s), 1222, 1153(s), 936, 782, 590(s). Analysis for the title complex: C:47.21%, H:5.35%, N:4.37%; calcd for [$C_{38}H_{51}Br_2N_3O_8S_4$]: C:47.25%, H:5.32%, N:4.35%. ^{1}HNMR (300MH$_Z$, DMSO-d): 8.66(s,1H, NH), 7.56(d, 2H, Ar–H, $J = 8.7$ Hz), 6.97(d,1H, BrC=CH, $J = 3.7$ Hz), 6.75(d,1H, C=CH, $J = 3.7$ Hz), 6.67(d, 2H, Ar–H, $J = 8.7$ Hz), 3.24–1.33(m, 24H, CH_2 of tetrabutylammonium), 0.93(t, 12H, CH_3 of tetrabutylammonium, $J = 7.2$ Hz); ^{13}CNMR: 190, 152.5, 130.5, 127.6, 115.4, 133.5, 128.3, 126.2, 112.4, 61.3, 26.5, 21.3, 13.7.

Table 1 Crystal data and details of the structure determination of the title complex

CCDC number	675799
Formula	$C_{38}H_{51}Br_2N_3O_8S_4$
Formula weight	965.90
Crystal system	Monoclinic
Space group	C $_{2/C}$
a, *b*, *c* [Å]	18.3389(17) 16.5409(16) 15.8280(15)
α, β, ν [°]	90.00, 116.959(2), 90.00
V [Å^3]	4279.5(7)
Z	4
D(calc) [g/cm^3]	1.498
Mu(MoKa) [/mm]	2.142
F(000)	1988
Crystal size [mm]	0.39 × 0.16 × 0.12
Data collection	
Temperature (K)	293
Radiation [Å]	
Theta min–max [°]	1.75, 25.02
Data set	−21:21; −16:19; −17:18
Total, unique data, *R*(int)	3778, 2909, 0.0266
Observed data [I > 2.0 σ(I)]	2909
Refinement	
*N*ref, *N*par	3778,251
R, *wR*$_2$, *S*	0.0560, 0.1499, 1.030
$w = 1/[\sigma_c^2 (Fo^2) + (0.0650P)^2 + 1.9900P]$ where $P = (Fo^2 + 2Fc^2)/3$	
Max. and av. shift/error	0.00, 0.00
Min. and max. resd. dens. [eÅ^{-3}]	−1.186, 1.992

The structure of the title complex was determined by single crystal X-ray diffraction method. The intensity data were collected on a Bruker Smart-Apex CCD diffraction diffractometer using MoKα radiation at room temperature. The structure was solved by direct methods, and refined by SHELXS program package. Detailed of data collection and those of refinement procedure are given in Table 1. The selected conformational parameters and hydrogen bond interactions are summarized in Tables 2 and 3, respectively.

Results and Discussion

The DSC−TGA measurement demonstrates the title complex is remarkable stability. As shown in Fig. 1, it decomposes at 300 °C, and lost 93.3% of its weight.

The title complex crystallizes in the space group C$_{2/C}$ with two anions and one cation in the asymmetric unit of the cell. The conformation of sulfonamide group is consistent with the result of a previous research [13]. The length of S–N bond is 1.613(3) Å and the torsion angle of C4–S2–N1–C5 is 76.1°. As shown in Fig. 2, the plane of the thiophene ring and the phenyl ring are almost perpendicular, which is indicated by the dihedral angle between them at 96.7°. This structure is the same as that in the case

Table 2 Selected bond lengths (Å) or angles (°) for the title complex

Atoms involved	Data	Atoms involved	Data
C5–C6	1.378(6)	C9–C10	1.377(6)
C6–C7	1.376(6)	O3–C11	1.287(5)
C7–C8	1.382(5)	O4–C11	1.230(5)
C8–C9	1.383(6)	Br1–C1	1.875(5)
S2–O1	1.428(3)	N1–C5	1.418(5)
S2–O2	1.426(3)	C8–C11	1.501(5)
C5–N1–S2	128.2(3)	C3–C4–S2	125.9(4)
N1–S2–C4	105.35(19)	S1–C4–S2	121.3(2)
O4–C11–O3	124.2(4)		

Table 3 Distance (Å) and angles (°) of hydrogen bond interactions

Atoms involved	Symmetry	Distance		Angle
D–H···A		D···A	H···A	
O(3)–H(3O)···O(3)	x + 3/2, y + 3/2, z + 1	2.481(4)	1.24	180
N(1)–H(1)···O(4)	x, −y + 1, +z − 1/2	2.793(6)	1.96	164
C(10)–H(10)···O(10)	x, y, z	3.021(5)	2.42	122
C(9)–H(9)···O(2)	x, −y + 1, +z + 1/2	3.270(7)	2.52	138
C(6)–H(6)···O(4)	x, −y + 1, +z − 1/2	3.268(6)	2.55	135

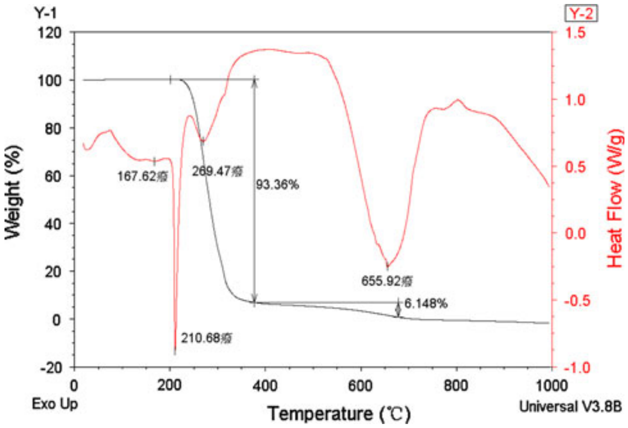

Fig. 1 DSC–TGA curvers of the title complex

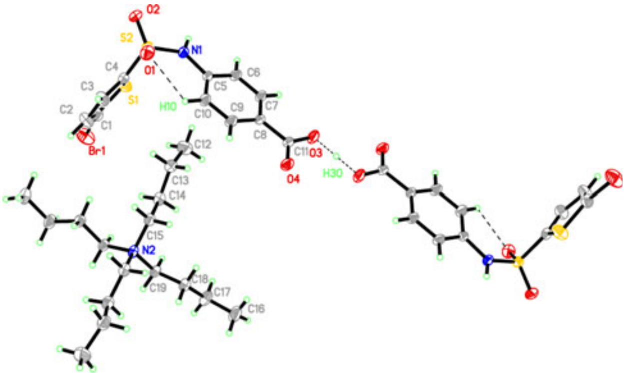

Fig. 2 An illustration of the inclusion compound, showing 30% probability displacement ellipsoids

of its analogous compound [14]. The intramolecular C(10)–H(10)···O(10) hydrogen bonds interactions serve as a barrier of S(2)–N(1) single bond rotation and stabilize the perpendicular conformation formed by thiophene ring and phenyl ring.

A very short O(3)–H(3O)···O(3)(x + 3/2, y + 3/2, z + 1) distance[2.481(4) Å] is observed between the two neighboring 4-(2-bromothiophene-5-sulfanilamide)-benzoate (BZT). The H(3O) is fixed with 0.5 occupancy at the crystallographic inversion center and bridge two groups of BZT to form an anion dimer. Such a location of the acidic proton means that the short O···O hydrogen bond between the carboxylate groups is characterized by a symmetrical double-minimum potential curve [15]. The dimer is centrosymetric and planar, and has the two BZT groups in trans orientation [C(11)–O(3)···O(3A)–C(11A) 180°, Fig. 2] regarding the O(3)···H···O(3) line as axis, such hydrogen bonding could be described by graph set of $D_2^1(3)$ [16]. For comparison, in solid state, carboxylic acids tend to be tied via O–H···O hydrogen bond to form dimmer, where the hydrogen binding graph set could be indicated by $R_2^2(8)$ [17]. The very short hydrogen bond cause a shift of the carbonyl absorption in the IR spectrum to lower frequency of about 20 cm^{-1} at 1679 cm^{-1}.

As shown in Fig. 3, the BZT anion dimers are linked together with its inversion equivalent BZT at (−x + 1/2, −y + 3/2, −z + 1) by N–H···O hydrogen bond. As a result rows of BZT anion dimer are formed. Further rows are connected to form the "wall". The walls are associated by C(11)–O(3)···Br(1) with the O(3)···Br(1) halogen bond length of 3.120(3) Å and an angle of 116.2°, the bond length is shorter than the sum of their Van der Waals radii (3.35 Å) [18]. In general, this non-covalent contact is considered as a result of the specific attractive force which is in analogy to the transfer of charge from Lewis base to a Lewis acid [19]. While Price et al. [20] argued that the highly directional short intermolecular contacts are

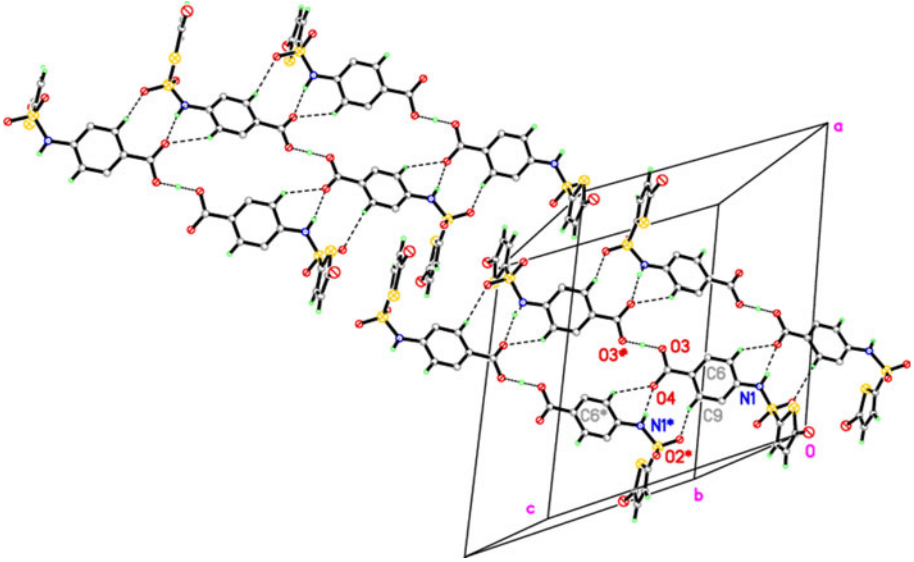

Fig. 3 A view of the hydrogen bonding that links to neighboring carboxylate dimmer. Hydrogen bonds are shown as *dashed lines*. Atom lableled with an *asterisk* (*) or *hash* (#) are at the symmetry positions of (−x + 1/2, −y + 3/2, −z + 1) and (x + 3/2, y + 3/2, z + 1)

observed as a result of close packing of atoms with non-spherical atoms charge distribution. Here the length of the Br···O bond agreed well with the previous observed constructions [21, 22]. In addition, weekly hydrogen bonds, C(9)–H(9)···O(2) and C(6)–H(6)···O(4), are observed to stabilize the comformation. In the title complex, the cation tetrabutylammonium remains in its fully extension form, and is inserted in the wall of the BZT anions with a narrow range. There are week C–H···Br [3.045(5) Å] interaction between the Br atom of the anion and the H atom of the cation, which increasing the stability of the complex.

In conclusion, we have prepared a complex with interesting structure featuring a very short centrosymmetric hydrogen bond [O···O distance 2.481(4) Å] and C=O···Br halogen bond interactions, together with N–H···O and C–H···O hydrogen bond in its crystal. The result indicates that very short O···O and O···Br interactions should be considered for the crystal design.

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