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Quantitative analysis of weak interactions by Lattice energy calculation, Hirshfeld surface and DFT studies of sulfamonomethoxine

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ABSTRACT

Sulfamonomethoxine, 4-Amino-*N*-(6-methoxy-4-pyrimidinyl) benzenesulfonamide ($C_{11}H_{12}N_4O_3S$), is investigated by single crystal X-ray diffraction technique. Pair of N–H···N and C–H···O intermolecular interactions along with π···π interaction are responsible for the stability of the molecular packing of the structure. In order to understand the nature of the interactions and their quantitative contributions towards the crystal packing, the 3D Hirshfeld surface and 2D fingerprint plot analysis are carried out. PIXEL calculations are performed to determine the lattice energies correspond to intermolecular interactions in the crystal structure. Ab initio quantum chemical calculations of sulfamonomethoxine (SMM) have been performed by B3LYP method, using 6-31G** basis set with the help of Schrodinger software. The computed geometrical parameters are in good agreement with the experimental data. The Mulliken charge distribution, calculated using B3LYP method to confirm the presence of electron acceptor and electron donor atoms, responsible for intermolecular hydrogen bond interactions hence the molecular stability.

1. Introduction

Sulfamonomethoxine, 4-Amino-*N*-(6-methoxy-4-pyrimidinyl) benzenesulfonamide, one of the novel members of sulfonamide family, is long acting, anti-infective and antibacterial sulfonamides [1–4]. It is active against both gram positive and gram negative bacteria. Fig. 1(a) displays the chemical structure of sulfamonomethoxine. The sulfamonomethoxine ($C_{11}H_{12}N_4O_3S$) (SMM) is synthesized earlier but the crystal structure of is not yet reported. It crystallizes in monoclinic space group $P2_1/n$. The three dimensional crystal structure of sulfamonomethoxine has been worked out for systematic study and quantification of the intermolecular interactions and molecular geometry which contribute to molecular stability.

The stability of crystal structure can be understood by studying the nature of its intermolecular interactions. Hirshfeld surface (HS) is graphical tool which illustrates the surface characteristics of the molecule consisting of all the interactions of crystal structure with a due recognition of characteristic interactions for the molecular structure [5]. The geometry of a Hirshfeld surface reflects the relationship between different atoms and intermolecular contacts in a crystal. The Hirshfeld surfaces are supported by the 2-D fingerprint plots which quantitatively summarize the nature and type of intermolecular contacts experienced by molecules in the crystal. The contribution of the intermolecular interactions is further supported by the lattice energies associated with each such interaction. The total interaction energy contribution is divided into coulombic, polarization, dispersion and repulsion contributions in the PIXEL method. It gives better explanation of the involvement of intermolecular interactions to the stability of crystal packing [6,7]. At this context, the present work focus on the Hirshfeld surface analysis and lattice energy calculation of the molecule to reveal the presence of weak but combined effect of intermolecular forces on molecular conformation.

2. Experimental details

Sulfamonomethoxine is procured from Sigma-Aldrich with high purity (<99%) and used without further purification. The diffraction quality transparent crystals of SMM are obtained from n-butanol under control evaporation at room temperature. The intensity data of transparent single crystals are collected using graphite monochromated MoK_α radiation of wavelength 0.7073 Å on Kappa Apex-II CCD-4 single crystal X-ray diffaractometer at room temperature.

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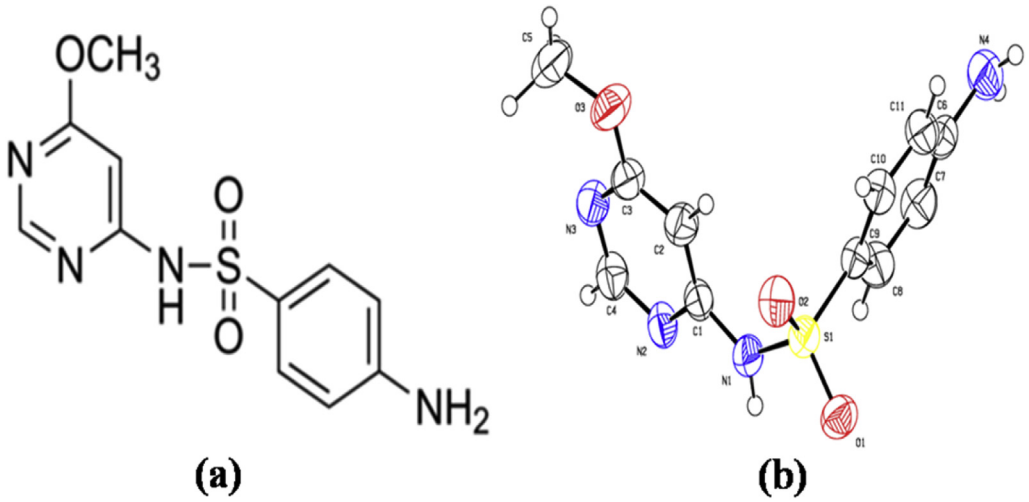

Fig. 1. (a) Chemical Structure and (b) The ORTEP diagrams of the molecule with 50% probability ellipsoidal area of Sulfamonomethoxine (SMM).

Table 1
Crystallographic data and Refinement Parameter.

Empirical formula	$C_{11}H_{12}N_4O_3S$
Formula weight	280.31 gm/mol
Temperature (K)	296.15
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	9.1712 (4)
b (Å)	6.1925 (3)
c (Å)	22.0197 (9)
α (°)	90°
β (°)	99.550 (3)°
γ (°)	90°
Volume (Å^3)	1233
Z	4
Density (Mg cm^{-3})	1.51
Absorption coefficient (mm^{-1})	0.27
F (000)	584
2Θ range for data collection	1.9–27.5°
Index ranges	$-11 \le h \le 11$, $-8 \le k \le 7$, $-28 \le l \le 28$
Reflections Measured/Independent	10612/2835
Data/restraints/parameters	2835/2/220
Goodness-of-fit on F^2	1.05
R [int] & R [F2 > 2σ(F2)]	0.025 & 0.038
Largest diff. peak/hole (e Å^{-3})	0.35/-0.36

Table 2
Selected bond lengths (Å) and bond angles involving non hydrogen atoms (°) of SMM.

	X-ray	B3LYP		X-ray	B3LYP
Bond lengths (Å)					
S1–O2	1.435 (2)	1.458	N3–C3	1.335 (2)	1.3357
S1–O1	1.435 (3)	1.458	N1–C1	1.361 (2)	1.3797
S1–N1	1.620 (5)	1.659	C8–C7	1.383 (3)	1.3879
S1–C9	1.756 (2)	1.769	C2–C3	1.386 (2)	1.3936
N2–C4	1.756 (2)	1.334	O3–C3	1.340 (2)	1.3413
N4–C6	1.398 (2)	1.398	O3–C5	1.438 (3)	1.4396
Bond angles (°)					
O2–S1–O1	117.9 (8)	119.9	C3–O3–C5	117.6 (2)	117.4
O2–S1–N1	111.6 (8)	110.37	C4–N3–C3	114.4 (6)	114.8
O1–S1–N1	104.0 (8)	102.78	C11–C6–N4	120.2 (2)	120.4
O2–S1–C9	107.8 (8)	107.81	C10–C11–C6	120.8 (2)	120.8
O1–S1–C9	109.1 (8)	109.77	N1–C1–N2	113.4 (5)	113.9
N1–S1–C9	105.8 (8)	105.21	N1–C1–C2	128.1 (6)	125.3
C1–N1–S1	124.2 (3)	127.18	C10–C9–S1	119.3 (3)	118.6
Torsional Angles (°)					
O2–S1–N1–C1	44.6 (2)	−44.1	C9–S1–N1–C1	−72.4 (2)	71.93
O1–S1–C9–C8	66.9 (2)	64.79	C5–O3–C3–N3	5.2 (3)	−4.87
Dihedral angle (°)					
Phenyl and pyrimidine ring (C6–C7–C8–C9–C10–C11 & C1–C2–C3–N3–C4–N2)				89.85 (8)	86.40°

Table 3
Intermolecular interactions of title molecule.

Hydrogen bond interactions					
D–H···A	d (D–H) Å	d (H–A) Å	d (D–A) Å	(D–H···A)°	
N1–H1···N2 (ii)	0.88 (3)	1.97 (3)	2.851 (2)	178 (4)	
C4–H4···O1 (ii)	0.958 (19)	2.422 (19)	3.142 (2)	131.8 (15)	
N4–H4A···N3 (iii)	1.07 (4)	2.50 (4)	3.530 (3)	161 (3)	
C11–H11···O1 (iv)	0.97 (2)	2.59 (2)	3.438 (2)	146.1 (15)	
C2–H2···O2 (i)	0.985 (19)	2.392 (19)	3.010 (2)	120.2 (14)	
C10–H10···O2(i)	0.886 (19)	2.521 (19)	2.910 (2)	107.3 (14)	
π … π interaction					
Cg(I)···Cg(J)	Cg(I)···Cg(J)Å	α	β	γ	Cg(I)···P Å
Cg (1)···Cg (1) (v)	4.6504 (10)	0	39.6	39.6	3.5856 (7)
Y–X…π interaction					
Y–X(I)···Cg (J)	**d(H–Cg) Å**	**d(Y–Cg) Å**	**Y–X···Cg°**	**γ°**	**H···P Å**
S1–O2···Cg (1) (v)	3.2752 (14)	3.8853 (8)	104.23 (6)	24.8	32.8

Cg(1) represents the centroid of pyrimidine ring (C1–C2–C3–N2–C4–N3).
Symmetry code: (i) x, y, z; (ii) -x+2, -y+1, -z+2; (iii) x-1/2, -y+1/2, z-1/2; (iv) -x+3/2, y-1/2, -z+3/2; (v) -x+/2, -y, -z+2.
D–H represents the bond between Donor and hydrogen H–A that of between hydrogen and Acceptor.

The SMM crystallizes in monoclinic space group $P2_1/n$ with crystallographic parameters a = 9.1712 Å, b = 6.1925 Å, c = 22.0197 Å, α = 90.00°, β = 99.55and γ = 90.00°. Direct method [8] is used to solve the crystal structure of title molecule and SHELX-97 [9] program to refine by full-matrix least square technique on F^2. All non hydrogen atoms are refined anisotropically. All the hydrogen atoms are located from the difference Fourier map and the crystal structure of SMM is refined to R = 0.038 for the 2835 reflections having I > 2σ(I) value and S = 1.05. Molecular packing diagram and the various molecular interactions are calculated using programs PLATON [10], PARST [11] and Mercury [12]. All the crystallographic data along with important refinement parameters are listed in Table 1.

2.1. Computational studies

Density functional theory, with Becke's three-parameter hybrid exchange functional with Lee- Yang-Parr correlation functional utilizing 6-31G** basis set (B3LYP method) [13–15], has been used to calculate all quantum chemical calculations performed using JAGUAR [16] utility from Schrodinger software package. Hirshfeld surfaces and the associated 2-D fingerprint plots are generated