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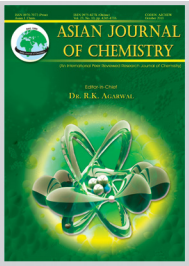

Synthesis, Structure and DFT Calculation of Chlorimuron-ethyl

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The commercial herbicide chlorimuron-ethyl ($C_{15}H_{15}ClN_4O_6S$, Mr = 414.82) was synthesized and its structure was studied by X-ray diffraction. The crystals are triclinic, space group P-1 with a = 7.831(3), b = 12.324(5), c = 20.242(8) Å, α = 94.941(7), β = 97.426(7), γ = 93.658(7)°. Theoretical calculation of chlorimuron-ethyl was carried out with B3LYP/6-31G (d,p). The full geometry optimization was carried out using 6-31G(d,p) basis set and the frontier orbital energy. This result is in accord with the result analyzed by the Frontier molecular orbital theory.

Key Words: Therotical calculations, Crystal structure, ALS, Chlorimuron-ethyl.

INTRODUCTION

Sulfonylureas, a unique group of herbicides, are extensively used to control a range of weeds and some grasses in a variety of crops and vegetables. Because of lack of acetolactate synthase (ALS) in mammals, so these herbicides are safety to human[1]. Until now, many commercial sulfonylureas were developed, such as chlorsulfuron, metsulfuron, chlorimuron, ethametsulfuron, bensulfuron, thifensulfuron, tribenuron, nicosulfuron, cinosulfuron, pyrazosulfuron, sulfometuron, *etc*.

The structure of the yeast acetolactate synthase-chlorimuron ethyl complex reveals that the two substituents on the heterocyclic ring make hydrophobic contacts with the protein. However, the herbicide is involved in numerous other interactions so the requirement for both substituents is not apparent. Lu *et al*.[2] reported single crystal of the compounds. In view of these facts and also as a part of our work on the development of bioactive compounds[3,4], herein we report the synthesis, crystal structure and DFT study of chlorimuron-ethyl.

EXPERIMENTAL

Crystallographic data of the compound collected on a Bruker SMART 1000 CCD diffractometer.

Crystal structure determination: The crystal of title compound with dimensions of 0.26 mm × 0.24 mm × 0.16 mm was mounted on a Bruker SMART[5,6] 1000 CCD area-detector diffractometer with a graphite-monochromated MoK_α radiation (λ = 0.71073Å) by using a phi and scan modes at 294(2) K in the range of $1.02° \le \theta \le 25.01°$. The crystal belongs to triclinic system with space group P-1 and crystal parameters of a = 7.831(3) Å, b = 12.324(5) Å, c = 20.242(8) Å, α = 94.941(7)°, β = 97.426(7)°, γ = 93.658(7)°, V = 1924.5 (12) A^3, D_c = 1.432 g/cm^3. The absorption coefficient μ = 0.346 mm^{-1} and Z = 4. The structure was solved by direct methods with SHELXS-97[7] and refined by the full-matrix least squares method on F^2 data using SHELXL-97. The empirical absorption corrections were applied to all intensity data. H atom of N-H was initially located in a difference Fourier map and were refined with the restraint Uiso(H) = 1.2 Ueq(N). Other H atoms were positioned geometrically and refined using a riding model, with d(C---H) = 0.93-0.97 Å and Uiso(H) = 1.2 Ueq(C) or 1.5 Ueq(Cmethyl). The final full-matrix least squares refinement gave R = 0.0799 and wR = 0.2135 ($w = 1/[s^2(F_o^2) + (0.1242P)^2 + 2.1624P]$, where $P = (F_o^2 + 2F_c^2)/3$, S = 1.02, $(\Delta/\sigma)_{max} < 0.005$, $\Delta\rho_{max}$ = 0.4700 e $Å^3$ and $\Delta\rho_{min}$ = -0.55 e $Å^3$.

Therotical calculations: On the basis of the above crystal structure, a isolated molecule was selected as the initial structure, while DFT-B3LYP/6-31G (d,p)[8,9] methods in Gaussian 03 package[10] were used to optimize the structure of the title compound. Vibration analysis showed that the optimized structures were in accordance with the minimum points on the potential energy surfaces. All the convergent precisions were the system default values and all the calculations were carried out on the Nankai stars supercomputer at Nankai University.

Synthesis: To a stirred suspension of 4-chloro-6-methoxy-pyrimidin-2-amine (3 mmol) in 12 mL of anhydrous acetonitrile

at room temperature, ethyl 2-(isocyanatosulfonyl) benzoate (3 mmol) was added. The mixture was stirred for 24 h. Then the product were separated by filtration, washed with acetonitrile and recrystallized from acetonitrile.

RESULTS AND DISCUSSION

Structure of chlorimuron-ethyl: The selected bond lengths and bond angles are presented in Table-1. The molecular structure of chlorimuron-ethyl is shown in Fig. 1. The molecular packing of the molecule is shown in Fig. 1. The π-π stacking is shown in Fig. 2.

TABLE-1
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (º) AND THEROTICAL CALCULATIONS FOR THE TITLE COMPOUND

Bond lengths (Å)			Bond angles (º)		
Bond lengths	X-ray Crystal	DFT	Bond angles	X-ray Crystal	DFT
S(1)-O(4)	1.421(5)	1.441	O(4)-S(1)-O(3)	119.4(3)	127.2
S(1)-N(1)	1.639(5)	1.651	O(3)-S(1)-N(1)	104.2(3)	111.4
S(1)-C(1)	1.765(6)	1.754	O(4)-S(1)-C(1)	107.7(3)	98.4
Cl(1)-C(14)	1.718(8)	1.720	N(1)-S(1)-C(1)	106.0(2)	105.4
O(1)-C(7)	1.317(9)	1.353	C(10)-N(1)-S(1)	122.9(4)	122.4
O(2)-C(7)	1.204(9)	1.209	C(10)-N(2)-C(11)	130.3(5)	124.7
O(5)-C(10)	1.222(6)	1.211	C(11)-N(3)-C(12)	116.3(6)	123.2
O(6)-C(12)	1.368(8)	1.366	C(2)-C(1)-S(1)	116.8(5)	119.1
N(1)-C(10)	1.372(7)	1.395	O(2)-C(7)-O(1)	121.6(9)	117.5
N(2)-C(10)	1.369(7)	1.392	O(2)-C(7)-C(6)	126.6(7)	120.4
N(2)-C(11)	1.383(6)	1.352	O(5)-C(10)-N(2)	121.4(5)	123.6
N(3)-C(11)	1.331(7)	1.264	N(2)-C(10)-N(1)	116.8(5)	115.4
N(4)-C(14)	1.343(8)	1.265	N(3)-C(11)-N(4)	127.2(5)	122.5
			N(3)-C(11)-N(2)	118.3(5)	117.5
			N(3)-C(12)-O(6)	119.2(6)	121.3

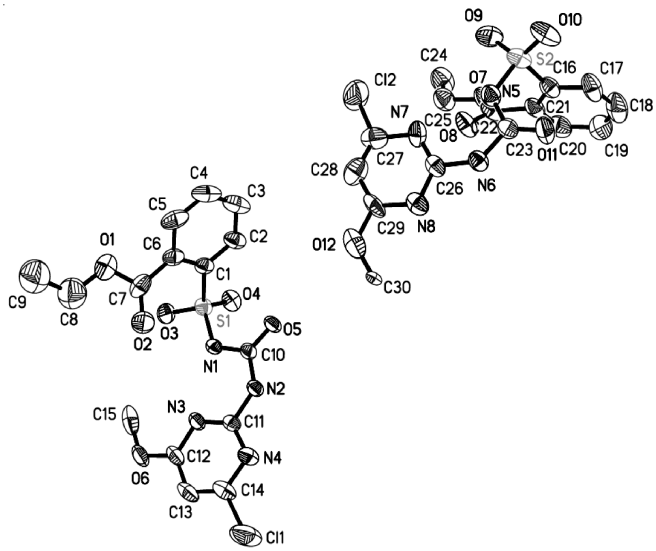

Fig. 1. Molecular structure of the title compound

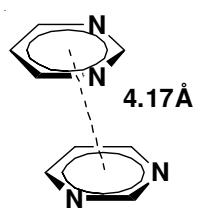

Fig. 2. π-π stacking of pyrimidine ring

The molecular structure was discussed. There are two different planes in the molecule and each of them has a conjugated system. In the crystal there exist two different configurations, in which the intermolecular hydrogen bonds and π-π interactions result in the dimeric crystal structure. It is according with the other crystals of sulfonylurea compounds.

Generally, the average bond lengths and bond angles of ring systems (benzene ring and pyrimidine ring) are normal ranges. The C10-N1 bond [1.37 Å] is shorter than a normal C-N single bond (1.47 Å), which shows that C10-N1 is conjugated with the O5-C10 double bond. However, the C11=N3 bond [1.33 Å] is similar with the general C=N double bond length of 1.27 Å. Chlorimuron-ethyl also presents intermolecular hydrogen bonds formed by the nitrogen atom of NH group and the hydrogen atom of the NH group or SO_2 group. The distances of these hydrogen bonds are 1.93(N1-H1--N3), 2.79(N1-H1--O2). The torsion angles of these rings are close to 0º or 180º respectively.

As shown in Fig. 1, the phenyl ring (C1, C2, C3, C4, C5, C6) (pyrimidine rings (C9, C10, C11, C12, C13, C16) is fairly planar with plane equation 2.493x + 11.409y + -2.666z = 5.1424 (6.705x + -1.147y + 8.127z = 10.9272) and the largest deviation from the least squares plane is 0.0054 nm (0.0067 nm). Meanwhile, the angles of the phenyl ring and the pyrimidine ring is 76.4 °.

The intermolecular face-to-face π-π stacking appears between the two pyrimidine rings in another adjacent molecule (Fig. 2), in which the distance of the centroid of pyrimidine ring is 4.17 Å. These interactions can help to further stabilize the crystal structure.

Molecular total energies and frontier orbital energy analysis: Molecular total energy and frontier orbital energy levels are listed in Table-2. It is seen that the results of HF methods have good consistency. Energy gap between HOMO and LUMO calculated by B3LYP.

TABLE-2
TOTAL ENERGY, FRONTIER ORBITAL ENERGY

	DFT
E_{total}/hartree[b]	-2109.24
E_{HOMO}/hartree	-0.011
E_{LUMO}/hartree	0.032
ΔE[a]/hartree	0.043

[a]$\Delta E = E_{LUMO} - E_{HOMO}$; [b]1 hartree = $4.35974417 \times 10^{-18}$ J = 27.2113845 eV

According to the frontier molecular orbital theory, HOMO and LUMO are the most important factors that affect the bioactivity. HOMO has the priority to provide electrons, while LUMO can accept electrons firstly[5]. Thus study on the Frontier orbital energy can provide useful information about the biological mechanism. Taking DFT result for example, the geometry of the frame of the title compound is hardly influenced by the introduction of either pyrimidyl ring, urea bridge or phenyl ring (Fig. 3). The HOMO of the title compound is mainly located on the pyrimidyl ring and urea bridge. While, the LUMO of the title compound is located on the pyrimidyl ring, urea bridge, benzene ring, ester group. The fact that the title compound has strong affinity suggests the importance of the frontier molecular orbital in the π-π stacking or hydrophobic

interactions. This also implies that the orbital interaction between chlorimuron-ethyl and the aromatic ring or some other side of residue chains of AHAS receptors is dominated by π-π or hydrophobic interaction among the frontier molecular orbitals.

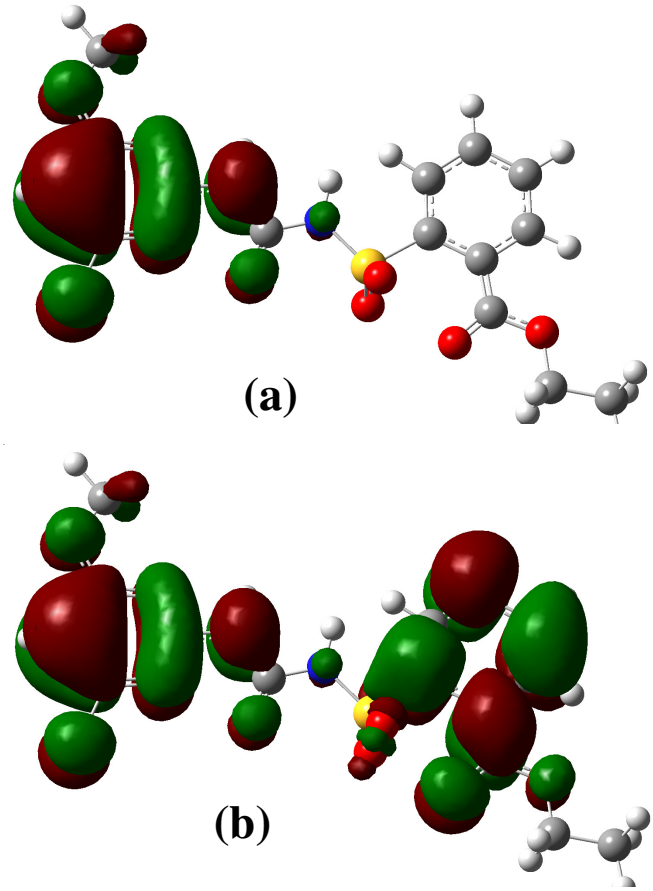

Fig. 3. Frontier molecular orbitals of title compound: (a) HOMO of the title compound; (b) LUMO of the title compound.

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