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Article

Synthesis, Crystal Structure and DFT Studies of 8-chloro-3-((3-chlorobenzyl)thio)-[1,2,4]triazolo[4,3-*a*]pyridine

Jin-Xia Mu [1], Ming-Yan Yang [2], Zhao-Hui Sun [2], Cheng-Xia Tan [2], Jian-Quan Weng [2], Hong-Ke Wu [2] and Xing-Hai Liu [2,*]

[1] Department of Environmental Engineering, China Jiliang University, Hangzhou 310018, China; E-Mail: mujinxiajl@sina.com

[2] College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, China; E-Mails: yangmingyanzjut@126.com (M.-Y.Y.); esunzhaohui@126.com (Z.-H.S.); tanchengxia@zjut.edu.cn (C.-X.T.); jqweng@zjut.edu.cn (J.-Q.W.); wuhk910@gmail.com (H.-K.W.)

* Author to whom correspondence should be addressed; E-Mail: xhliu@zjut.edu.cn; Tel./Fax: +86-571-8832-0832.

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Abstract: 8-chloro-3-((3-chlorobenzyl)thio)-[1,2,4]triazolo[4,3-*a*]pyridine was synthesized and recrystallized from EtOH. The compound was characterized by ^{1}H NMR, ^{13}C NMR, FTIR, MS, elemental analysis and X-ray diffraction. The compound was crystallized in the monoclinic space group *P2(1)/c* with *a* = 8.1992(5), *b* = 21.7731(12), *c* = 7.8454(6) Å, α = 90, β = 108.421(7), γ = 90°, *V* = 1328.81 (15)Å^3, *Z* = 4 and *R* = 0.0351. Theoretical calculation of the title compound was carried out with B3LYP/6-31G. The full geometry optimization was carried out by using the 6-31G basis set. The frontier orbital energy and atomic net charges were discussed. The experimental results of the compound have been compared with theoretical results and it was found that the experimental data shows good agreement with the calculated values.

Keywords: 1,2,4-triazolo[4,3-*a*]pyridine; hydrazine; synthesis; crystal structure; theoretical calculation

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1. Introduction

The drug discovery of novel structures has attracted many chemists. Within current research, heterocycles are key to drug discovery. 1,2,4-Triazole compounds are classic nitrogen containing heterocycles [1,2]. They display antifungal [3–5], herbicidal [6,7], anti-mycobacterial [8] and antioxidant activities [9]. Pyridine is another important nitrogen-containing heterocycle with various bioactivities [10–13]. Heterocycles which are obtained by the fusing of 1,2,4-triazole and pyridine ring show an obvious increase of biological activity [14,15]. For instance, 1,2,4-triazolo[4,3-*a*]pyridine derivatives possess outstanding biological activities, such as mGlu2 receptor PAM activity [16], antifungal activity [17], antibacterial activity [18], and so on.

In our previous work, some interesting heterocyles were synthesized and they showed various activities [19–24]. In this paper, a novel 1,2,4-triazolo[4,3-*a*]pyridine was synthesized and characterized by ^{1}H NMR, ^{13}C NMR, FTIR, MS and elemental analysis. The single crystal structure of the title compound was determined by X-ray diffraction.

2. Results and Discussion

2.1. Synthesis and Spectra Analysis

The synthetic procedure for the title compound is shown in Scheme 1. The starting material 3-chloro-2-hydrazinylpyridine was synthesized according to the method in our previous papers [14,15]. The key intermediate 8-chloro-[1,2,4]triazolo[4,3-*a*]pyridine-3(2*H*)-thione was obtained according to the method which was reported by Chen [25]. 3-Chloro-2-hydrazinylpyridine was used to react with thiourea under microwave irradiation to afford the key intermediate. The target compound 2 was obtained by the reaction between intermediate 1 and 1-chloro-3-(chloromethyl)benzene under microwave irradiation at the alkaline condition. The thioamide (-NH-C(=S)) structure showed in the key intermeadiate can exist either as the thione, or thiol tautomeric form. The ^{1}H NMR of intermediate and the final compound indicated that the substitution of 8-chloro-[1,2,4]triazolo[4,3-*a*]pyridin-3(2*H*)-thione occurred at the sulfur atom instead of the nitrogen atom, as expected for thiol. With regard to the mass spectra, the title compound showed an M-H signal.

2.2. Frontier Orbital Energy Analysis and Molecular Total Energies

Molecular total energy and frontier orbital energy levels are listed in Table 1.

Table 1. Total energy and frontier orbital energy.

--	DFT
E_{total}/Hartree [a]	−1983.14769316
E_{HOMO}/Hartree	−0.24453
E_{LUMO}/Hartree	−0.06468
ΔE [b]/Hartree	0.1229

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

The energy gap between HOMO and LUMO was calculated by B3LYP. 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 first. Thus, the study on the frontier orbital energy can provide useful information about the biological mechanism. As shown in Figure 1, the geometry of title compound was optimized by using DFT method. The LUMO of the title compound is mainly located on the 1,2,4-triazolo[4,3-*a*]pyridine ring. However, the HOMO of the title compound is located on the1,2,4-triazolo[4,3-*a*]pyridine ring, benzene ring and thioether group. Therefore, the electrons transit from the benzene ring to the 1,2,4-triazolo[4,3-*a*]pyridine ring via thioether bridge, while the energy gap between the HOMO and LUMO is 0.17985 Hartree.

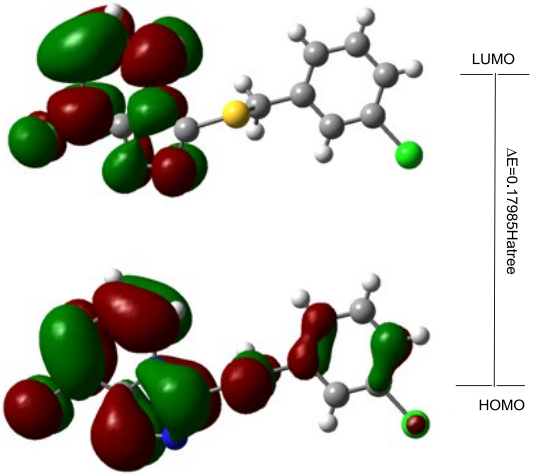


Figure 1. Frontier molecular orbitals of 2.

2.3. Crystal Structure

The selected bond lengths, bond angles and torsion angles are shown in Table 2. The molecular structure of the title compound is shown in Figure 2.

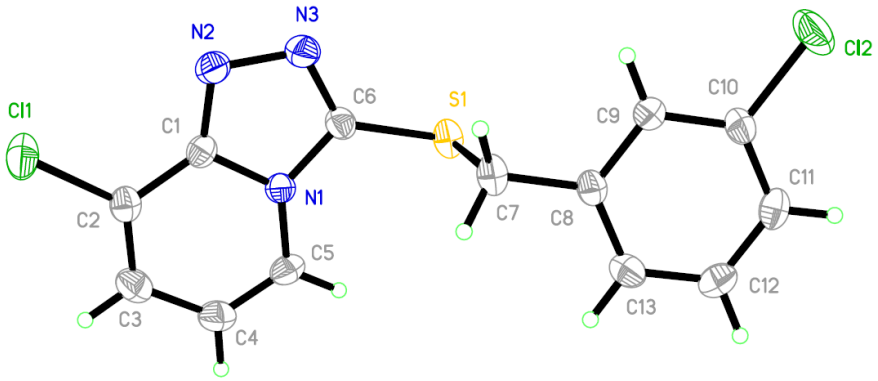


Figure 2. The molecular structure of the title compound.

The title compound consists of pyridine ring, 1,2,4-triazole ring and benzene ring according to X-ray single-crystal structure determination. Generally, the average bond lengths and bond angles of these rings are in normal ranges [26–29]. In 1,2,4-triazole and pyridine ring system, the C5–N1,

C1–N1 and C6–N3 bonds are significantly longer than C=N bond (1.28 Å) [30], which indicates significant electron delocalization in the fused ring system. The torsion angle of C6-S1-C7-C8 is 176.69(18)°, which indicates that the two rings are co-planar. The experimental values correlate with the theoretical values.

Table 2. Selected bond lengths [Å], angles [°] and theoretical calculations for the title compound.

Bond	X-ray Crystal	DFT	Angle	X-ray Crystal	DFT
S1-C6	1.743(3)	1.74330	C6-S1-C7	98.57(11)	98.55541
S1-C7	1.837(3)	1.83750	C5-N1-C1	123.3(2)	123.28802
Cl1-C2	1.718(3)	1.71782	C5-N1-C6	132.2(2)	132.15746
Cl2-C10	1.742(2)	1.74147	C1-N2-N3	106.84(19)	106.81997
N1-C5	1.377(3)	1.37688	N2-C1-N1	110.3(2)	110.31368
N1-C1	1.378(3)	1.37831	N1 C1 C2	117.5(2)	117.48357
N1-C6	1.384(3)	1.38396	N3-C6-S1	127.63(18)	127.62512
N2-C1	1.323(3)	1.32294	N1-C6-S1	122.75(18)	122.74936
N2-N3	1.382(3)	1.38169	C8-C7-S1	108.99(17)	108.96455
N3-C6	1.310(3)	1.30950	C13-C8-C9	119.0(2)	118.99908
C1-C2	1.417(3)	1.41733	C11-C10-Cl2	119.06(19)	119.07111
C7-C8	1.502(3)	1.50164	C3-C2-Cl1	123.4(2)	123.37263
C8-C13	1.383(3)	1.38280	C2-C3-C4	119.9(2)	119.90145

As it shown in Figure 2, the 1,2,4-triazolo[4,3-*a*]pyridine ring is nearly parallel with benzene ring in a quite small dihedral angle (θ) of 14.7°. The 1,2,4-triazolo[4,3-*a*]pyridine ring (C1, C2, C3, C4, C5, N2, N3, C6, N1) and benzene ring (C8, C9, C10, C11, C12, C13) are fairly co-planar according to plane equation −0.586x + 8.623y + 6.991z = 9.2949 and −0.617x + 3.270y + 7.524z = 5.8229, and the largest deviation from the least squares plane are 0.0067 nm and 0.0046 nm. The title compound has an extensive network of hydrogen bonds. The parameters of intramolecular and intermolecular bonds are given in Table 3. They are linked together by C–H•••N hydrogen bonds (Figure 3). The hydrogen bonds strengthen the integration of the 3D networks.

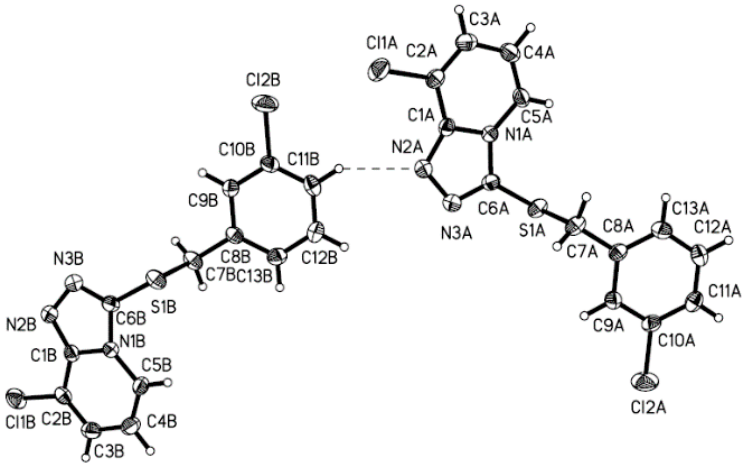


Figure 3. The pack of title compound.

Table 3. Hydrogen-bond parameters (Å) of the title compound.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(11B)-H(11B)•••N2A	0.93	2.60	3.419(3)	147.7

2.4. Mulliken Atomic Charges and ESP

Table 4 exhibits the calculated Mulliken atomic charges except for atoms H.

Table 4. Mulliken atomic chargesexcept for atoms H (e).

Atom	DFT
S1	0.413
N1	−0.694
N2	−0.292
N3	−0.243
Cl1	0.222
Cl2	0.128
C1	0.456
C2	−0.272
C3	−0.037
C4	−0.105
C5	0.222
C6	0.052
C7	0.565
C8	0.102
C9	−0.045
C10	−0.290
C11	−0.029
C12	−0.052
C13	−0.088

Taking DFT as an example again (Figure 4), all the nitrogen atoms are the most negatively charged ones, which can easily interact with the positively charged part of the receptor. Therefore, we supposed that this compound can combine with the amino-acid residue on its surface by interacting with the 1,2,4-triazolo[4,3-a]pyridine ring, which may be responsible for the bioactivity.

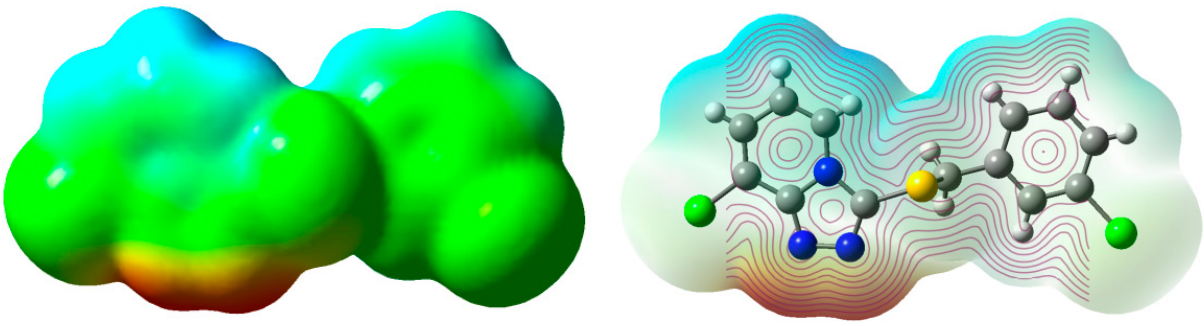


Figure 4. Electrostatic potential mapping on the electron density (isovalue = 0.04).

3. Experimental Section

3.1. Instruments

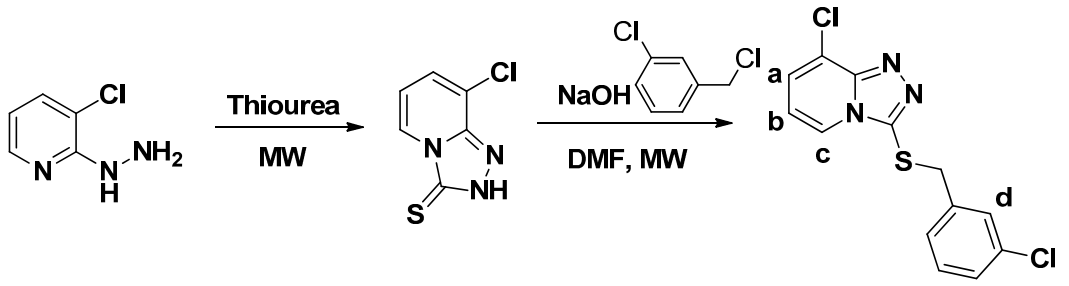
Melting points were determined by using an X-4 apparatus and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AV-400 or ANANCE III (500 M) instrument by using TMS as an internal standard and $CDCl_3$ or DMSO-d_6 as the solvent. FT-IR was determined on a Nicolet AVATAR instrument. Elemental analyses were performed on a Vario EL elemental analyzer. Crystallographic data of the compound was collected on a Rigaku Saturn diffractometer. All the reagents are of analytical grade or freshly prepared before using.

3.2. Therotical Calculations

According to the above crystal structure, a crystal unit was selected as the initial structure, while DFT-B3LYP/6-31G methods in Gaussian 03 package [31] 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, which means no virtual frequencies. It proved that the optimized structures were stable. All the convergent precisions were the system default values, and all the calculations were carried out on a DELL computer.

3.3. General Procedure

The title compounds were synthesized according to the route shown in Scheme 1, and the yields were not optimized.



1 2

Scheme 1. The synthetic route of title compound.

Preparation of **2**: The 3-chloro-2-hydrazinylpyridine (143 mg, 1 mmol) and thiourea (3 mmol) were exposed to CEM Discover Focused Synthesizer at 180 °C for 30 min. Then the mixture was poured into water (40 mL), filtered and recrystallized to give the key intermediate 8-chloro-[1,2,4]triazolo[4,3-*a*]pyridin-3(*2H*)-thione. ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 6.22(s, 1H, SH), 6.66(t, J = 5.0 Hz, 1H, Pyridine-H), 7.48(d, J = 7.6Hz, 1H, Pyridine-H$_a$), 8.11(d, J = 4.9 Hz, 1H, Pyridine-H$_c$). 8-Chloro-[1,2,4]triazolo[4,3-*a*]pyridin-3(2*H*)- thione (1 mmol), DMF (5 mL), 1-chloro-3-(chloromethyl)benzene (1.1 mmol) and NaOH (0.05 g, 1.2 mmol) was irradiated at 90 °C for 15 min. After the reaction was completed, the mixture was poured into crushed ice and the target compound **2** was collected and recrystallized. The crude product was purified by column

chromatography. The result was a white yellow crystal, yield 91%, m.p.280–281 °C; ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 4.33(s, 2H, SCH_2), 6.99(t, J = 6.9 Hz, 1H, Pyridine-H_b), 7.15(s, 1H, Phenyl-H_d), 7.24–7.25(m, 3H, Phenyl-H), 7.64(d, J = 7.1 Hz, 1H, Pyridine-H), 7.82(d, J = 6.8Hz, 1H, Pyridine-H). ^{13}C NMR ($CDCl_3$, 125 MHz), δ: 39.49, 113.69, 121.33, 122.72, 126.36, 126.98, 128.08, 128.84, 130.01, 134.58, 138.42, 138.73, 149.08; FT-IR(KBr, cm^{-1}) υ: 1624, 1475, 1419, 1362, 1314, 1077, 1049, 940, 857, 803, 779, 745, 721, 683; MS (ESI), m/z: 332$(M + Na)^+$, 314$(M + 3)^+$, 311$(M + 1)^+$, 310$(M)^+$, 185, 126. Elemental anal. For $C_{13}H_9Cl_2N_3S$ (%), calculated: C, 50.33; H, 2.92; N, 13.55; found: C, 50.25; H, 3.17; N, 13.65.

3.4. Structure Determination

The cube-shaped single crystal of the title compound was obtained by recrystallization from EtOH. The crystal with dimensions of 0.20 mm × 0.18 mm × 0.12 mm was mounted on a Rigaku Saturn diffractometer with a graphite-monochromated MoKα radiation (λ = 0.71073Å) by using a Phi scan modes at 293 (2) K in the range of $2.9° \leq \theta \leq 26.3°$. A total of 5808 reflections were collected, of which 2708 were independent (R_{int} = 0.018) and 2149 were observed with $I > 2\sigma(I)$. The calculations were performed with SHELXS-97 program [32] and the empirical absorption corrections were applied to all intensity data. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were determined by theoretical calculations and refined isotropically. The final full-matrix least squares refinement gave R =0.043 and wR = 0.103 ($w = 1/[\sigma^2(F_o^2) + (0.038P)^2 + 0.670P]$ where $p = (F_o^2 + 2F_c^2)/3$), S = 1.05, $(\Delta/\sigma)_{max} < 0.001$, $\Delta\rho_{max} = 0.036$ and $\Delta\rho_{min} = -0.23$ e Å^{-1}.

4. Conclusions

In summary, a new 1,2,4-triazolo[4,3-*a*]pyridine derivative with 3D infinite chain structures was synthesized and characterized by ^{1}H NMR, ^{13}C NMR, FTIR, MS, elemental analysis and X-ray single diffraction.

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Author Contributions

Jin-Xia Mu, Ming-Yan Yang and Zhao-Hui Sun carried out experimental work, Jin-Xia Mu prepared the manuscript and did the theoretical calculation, Cheng-Xia Tan, Jian-Quan Weng and Hong-Ke Wu discussed the experimental data. Xing-Hai Liu designed the material and supervised the project. All authors have read and approved the final manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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