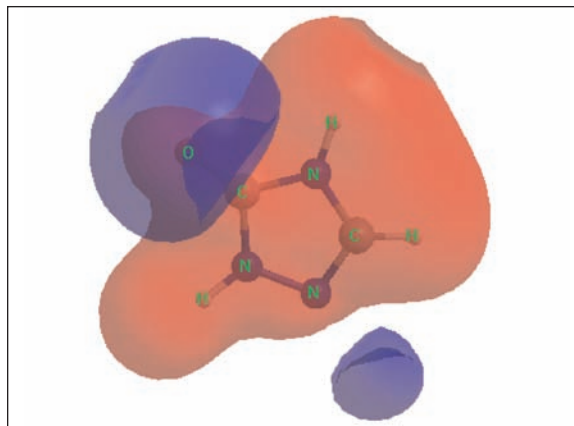


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1,2,4-Triazol-5-one (TO) was synthesized by reacting semicarbazide hydrochloride with formic acid and its single crystal was grown by the slow evaporation method. Its molecular structure and crystal structure were determined by X-ray single crystal diffraction technique. The obtained results show that the crystal belongs to Crystal system of Monoclinic, space group Pn. It was characterized by elemental microanalysis and FT-IR techniques. Based on the crystal data, we had also carried quantum chemistry calculations on the title compound using the B3LYP and MP2 method with cc-pVTZ basis set. The calculation results further demonstrate the crystal structure of title compound and its other related properties.

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1. Introduction.

1,2,4-Triazol-5-one is a known compound, commonly referred to as TO and useful as an intermediate in the production of explosives that are relatively insensitive to shock, impact, and friction, and in the synthesis of fine chemicals [1,2]. In practice, the TO intermediate is nitrated to produce 3-nitro-1,2,4-triazol-5-one (NTO) which is used in explosive compositions [3-6].

Much attention has been paid to TO as a new kind of high nitrogen containing material that possesses many excellent features, such as higher nitrogen content, higher enthalpy and lower sensitivity. The preparation, molecular structure and thermal decomposition mechanism of its various energetic coordination compounds have been also studied in our previous works [7-10].

In this paper, in order to examine the structure of TO, we have synthesized TO and tried to grow single crystal with different solvents by the natural evaporation method. It is characterized by elemental microanalysis and FT-IR techniques. We have also carried out quantum chemistry calculations using the B3LYP and MP2 methods with cc-pVTZ basis set. We have obtained some physicochemical properties of the title compound such as bond distances, bond angles, frequencies and molecular electrostatic potential. And at the same time, for better understanding, we have compared the experimental results with the calculated data.

2. Experimental Section and Computational Method.

2.1. Reagents and the Instruments.

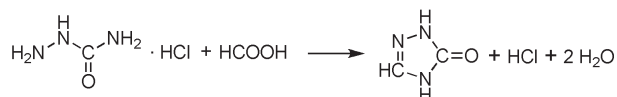
Semicarbazide hydrochloride (AR) and formic acid (AR) are commercially available and have been used without additional purification.

Flash EA 1112 full-automatic microanalyser was used for elemental analysis. Bruker Equinox 55 infrared spectrometer was used for FT-IR analysis, using KBr pellet in the range of 4000-400 cm^{-1} with the resolution of 8 cm^{-1} . In the determination of the structure with single crystal, X-ray intensities are recorded by a Siemens P4 automatic diffractometer with graphite-monochromatized Mo K_{α} radiation, $\lambda = 0.70713 \text{ \AA}$. It scans in the form of ω mode with the range of $2.24^{\circ} < \theta < 31.25^{\circ}$.

2.2. Synthesis of TO and its Single Crystal.

TO was prepared by the method which is described by Boudakian [11] and Rothegey [12]. We introduced formic acid to make the cyclic semicarbazide. The reaction principle for making the title compound is shown in Scheme 1.

Scheme 1



Semicarbazide hydrochloride (45.0 g, 0.4 mol) suspended in 25.0 ml of formic acid (85%) are initially introduced into a 100 mL four-neck flask with a contact thermometer, stirrer, dropping funnel, short column and reflux divider. While stirring, the mixture is reacted at 90~95 °C for 3 h in an oil bath and then heated to a weak reflux at 106 °C in the course of 4 hours. After complete reaction, precipitate is formed lately and cooled. The mixture is then concentrated to dryness under reduced pressure and the residue is recrystallized from 100 ml of alcohol to give 28 g (about 82% yield based on semicarbazide hydrochloride) of TO of melting point 239.0~240.0 °C.

After that, the 4 g of TO obtained is dispersed into the 40 mL of distilled water and heated to 50 °C, then filtrated. The filtrate is deposited into the culture box at the constant temperature of 20 °C, then colorless transparent single crystals for X-ray measurement appeared after about 14 days.

2.3. Determination of the Crystal Structure.

Dimensions of the single crystal used for the X-ray measurement are 0.46×0.24×0.24 mm³. Cell parameters are determined from 34 reflections in the 2 θ range of 5.88°< θ <20.20°. At the temperature of 299(2) K, the data are collected by ω scans in the range of 2.24°< θ <31.25°, h : 0~5, k : 0~13, l : -7~7, and 719 reflections are collected which included 651 independent reflections are obtained, among which 527 with $I > 2\sigma(I)$ are used for the determination of crystal structure and refinement.

The coordinates of all of the non-hydrogen atoms in the molecule are obtained by direct method. The hydrogen atom is obtained by the Fourier method. All calculations are carried out with Siemens SHELXS 97 program [13] on a personal computer. Refinement is performed by block-diagonal least-square method using SHELXL 97 program [14]. Final R indices for the data of $I > 2\sigma(I)$ is $R_1 = 0.0327$, $wR_2 = 0.0812$, and the R indices for all data is $R_1 = 0.0400$, $wR_2 = 0.0841$, and the goodness-of-fit on F^2

is 0.983 with the extinction coefficient 0.12(6), $\omega = 1/[s^2(F_0^2) + (0.0546P)^2]$, $P = (F_0^2 + 2F_c^2)/3$. The largest difference peak and hole is 0.141 e·Å⁻³ and -0.176 e·Å⁻³.

The obtained results showed that the crystal belongs to Crystal system of Monoclinic, space group Pn with crystal parameters of $a = 3.633(1)$ Å, $b = 9.081(3)$ Å, $c = 5.361(2)$ Å, $\beta = 95.29(1)^\circ$, $V = 176.1(2)$ Å³, $Z = 2$, $D_c = 1.604$ g/cm³, $\mu = 0.132$ mm⁻¹, $F(000) = 88$.

Crystallographic data for the structure has been deposited with the Cambridge Crystallographic Data Center as supplementary publication, CCDC No. 272496. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (Fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

2.4. Quantum Chemistry Calculation.

In order to acquire reliable structures, we employ three sophisticated methods to optimize the geometries, namely, the DFT B3LYP method [15,16] and the second-order Møller-Plesset perturbation method (MP2) [17-19]. The basis set employed for optimization and frequencies analysis is Dunning's correlation consistent polarized valence double-zeta basis set [20-22], *i.e.*, the cc-pVDZ basis set. The harmonic vibrational frequencies and infrared intensity are also predicted at the B3LYP/cc-pVDZ and MP2/cc-pVDZ levels of theory. All calculations are performed using the Gaussian 98 program packages[23].

3. Results and Discussion.

3.1. Elemental Analysis and Infrared Absorption Spectra Analysis.

Elemental analysis for TO. Calcd.: C 28.24%, H 3.53%, N 49.41%; Found: C 28.31%, H 3.55%, N 49.26%.

By the analysis of IR spectra for TO, the main results are as follows: $\nu_{N-H}^s = 3091$ cm⁻¹, $\nu_{C-H}^s = 2846$ cm⁻¹, $\nu_{C=O}^s = 1704$ cm⁻¹, $\delta_{N-H}^1 = 1568$ cm⁻¹, $\delta_{N-H}^{o.p} = 713$ cm⁻¹, $\nu_{C=N}^s = 1568$ cm⁻¹, $\nu_{C-N}^s = 1258$ cm⁻¹; 952 cm⁻¹ and 746 cm⁻¹ are assigned for the skeletal vibrations of triazole framework.

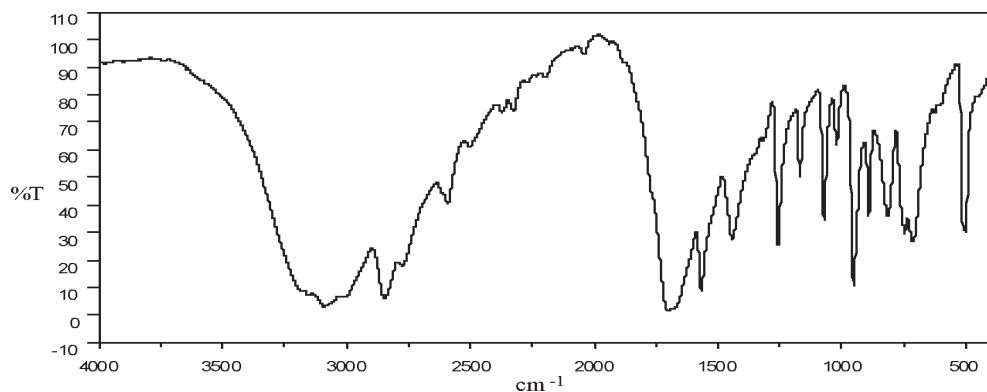


Figure 1. The typical of IR absorption curve for 1,2,4-triazol-5-one (TO).

The typical of IR absorption curve for TO is illustrated in Figure 1.

3.2. The Molecular Structure and Crystal Structure of TO.

The obtained atoms coordinates and thermal parameters are summarized in Table 1. The molecular structure and atom labels are shown in Figure 2 and the packing of the molecule in crystal lattice is illustrated in Figure 3.

is longer than the general lengths (1.270 Å). So the bond lengths of N-N, C-N, C=N tend to homogeneous value, which is result from the form of Π -bond of the TO molecule and the conjugate effect. On the base of the bond angles data of the TO, since the oxygen atom of the carbonyl involved in the conjugate effect, the internal angle of TO molecule all are close to 108.0° (the internal angle of the pentagon), in which the biggest error is less than 4.2° .

The analytic results indicate that one TO molecular is

Table 1
The Obtained Atoms Coordinates ($\times 10^4$) and the Thermal Parameters ($\times 10^2$)

Atoms	x	y	z	$U_{eq}/\text{\AA}^2$
O	8993(5)	3605(1)	10008(3)	4.4(1)
N(1)	7166(6)	1462(2)	7890(3)	3.6(1)
N(2)	5369(5)	1088(2)	5595(3)	4.0(1)
N(3)	5713(4)	3494(2)	6017(3)	3.3(1)
C(1)	7481(6)	2938(2)	8186(4)	3.1(1)
C(2)	4524(6)	2343(2)	4549(4)	3.6(1)
H(2)	3249	2443	2973	4.3
H(1N)	8200(60)	810(20)	8900(40)	4.2(7)
H(3N)	5320(70)	4417(13)	5780(50)	4.6(8)

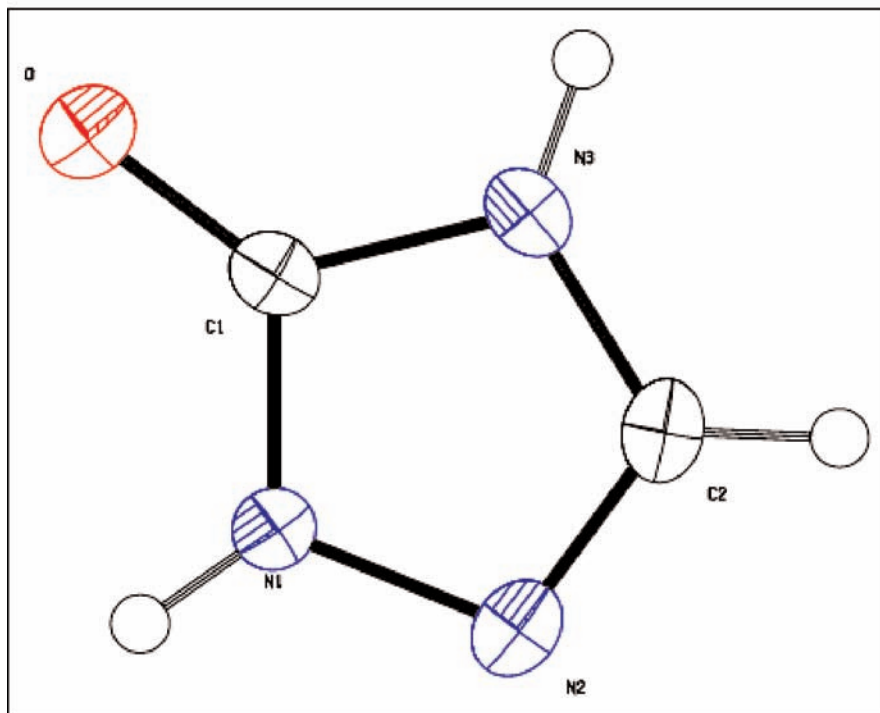


Figure 2. The molecular structure and atom label of 1,2,4-triazol-5-one (TO).

The obtained bond lengths and bond angles of TO are summarized in Table 2. According to the bond lengths data, it can be conclude that the average bond lengths value of the N-N and C-N are 1.381 and 1.360 Å, which are shorter than the general lengths (1.450 and 1.470 Å). At the same time, the bond lengths of C=N is 1.295 Å, which

planar. According to the packing of the molecule in crystal lattice, it may be found that many H-bonds existing in the intermolecular of 1,2,4-triazol-5-one in one layer, which is showed in Table 3.

In TO there are three kinds of intermolecular H-bonds. The first kind is the H-bond of N1-H(1N)...N2, which is

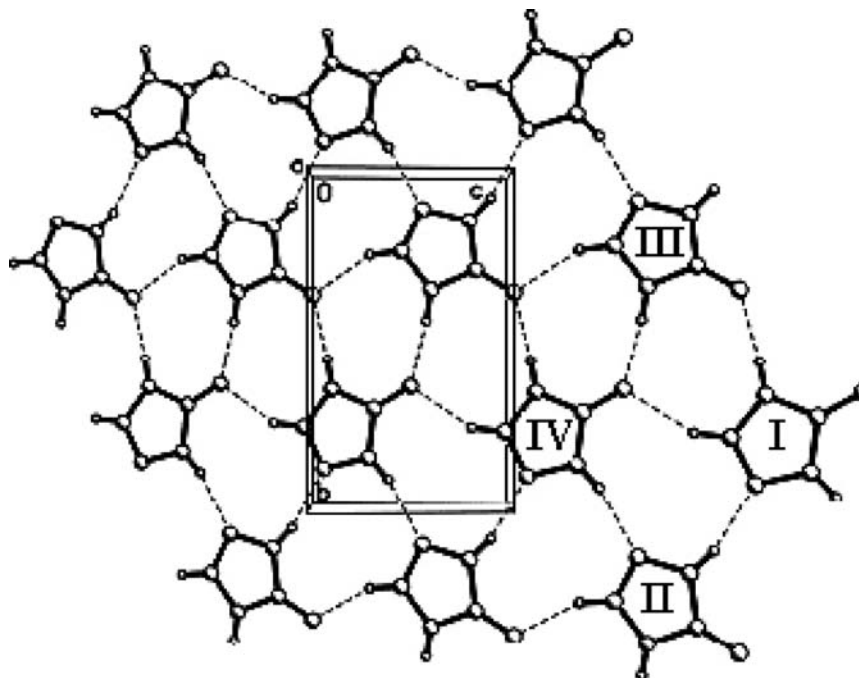


Figure 3. The packing of the molecule in crystal lattice of 1,2,4-triazol-5-one (TO).

Table 2
Selected Bond Lengths (Å) and Bond Angles (°)

Bond	Parameters		
	Exp.	B3LYP/cc-pVTZ	MP2/cc-pVTZ
Bond Length			
O-C(1)	1.235(2)	1.212	1.217
N(1)-C(1)	1.353(2)	1.377	1.377
N(1)-N(2)	1.381(2)	1.374	1.366
N(1)-H(1N)	0.863(1)	1.003	1.004
N(2)-C(2)	1.295(3)	1.292	1.305
N(3)-C(2)	1.355(3)	1.371	1.366
N(3)-C(1)	1.372(2)	1.399	1.396
N(3)-H(3N)	0.858(1)	1.003	1.004
C(2)-H(2)	0.930(1)	1.076	1.074
Bond Angle			
C(1)-N(1)-N(2)	112.1(2)	114.2	114.9
C(1)-N(1)-H(1N)	125.0(2)	125.4	125.0
N(2)-N(1)-H(1N)	122.4(2)	120.4	120.0
C(2)-N(2)-N(1)	104.0(2)	104.0	103.4
C(2)-N(3)-C(1)	107.9(2)	108.8	109.1
C(2)-N(3)-H(3N)	129(2)	128.0	127.9
C(1)-N(3)-H(3N)	123(2)	123.2	123.0
O-C(1)-N(1)	127.3(2)	130.2	130.2
O-C(1)-N(3)	129.0(1)	128.9	129.1
N(1)-C(1)-N(3)	103.7(2)	100.9	100.6
N(2)-C(2)-N(3)	112.2(2)	112.1	111.9
N(2)-C(2)-H(2)	123.9(2)	123.9	123.8
N(3)-C(2)-H(2)	123.9(2)	123.9	124.3

produced by N1-H(1N) of TO (II), and the N2 of the next TO (I) molecule that lies in the same layer. The second one is the H-bond of N3-H(3N)...O1b, which is formed between the N3-H(3N) of TO (I) molecule and the O of the next TO (III). The last one is the H-bond of C2-H(C2)...O that is engendered between the C2-H(C2) of TO (I) molecule and the oxygen O of the next TO (IV) lied the same layer. (Note: I, II, III and IV respectively denote the difference 1,2,4-triazol-5-one molecules in the packing of the molecules in the crystal lattice).

The hydrogen bonds formed among molecules are the main force forming the crystal. Many of the H-bonds effect result in the all crystal form di-dimension structure and enhance the stability of the compound.

3.3. Quantum Chemistry Calculation.

The calculated data are shown in the Table 2. We can find the computational results obtained at B3LYP/cc-pVTZ and MP2/cc-pVTZ level of theories are very similar. Comparing the data of experiment and computation, we can find that the bond lengths and the bond angles have subtle differences. The DFT calculations give a remarkably good description of the molecular geometry, in which all bond distances deviate by less than 0.02 nm from experimental values, and the largest bond-angle error is 1.5°. The calculated dihedral angles are 0° or 180°, so the molecule is a planar.

The harmonic vibrational frequencies and their infrared intensity of TO have been calculated and are predicted at both levels of theory mentioned above, and yield real fre-

Table 3
H-Bond Lengths and Bond Angles

Atom D	Atom H	Atom A	D-H/ Å	H...A/ Å	D...A/ Å	D-H...A/°
N1	H(1N)	N2	0.863(10)	2.073(12)	2.917(2)	166(2)
N3	H(3N)	O	0.858(10)	1.895(11)	2.7497(19)	174(3)
C2	H(C2)	O	0.93	2.36	3.221(3)	153.6

Table 4
Full Vibrational Assignment of 1,2,4-Triazol-5-one Based on the B3LYP/cc-pVTZ Level of Theory

V	Energy (cm-1)	Intensity (kM/Mole)	Assignment
1	223	7.0	Triazole ring framework out of plane bend
2	434	7.9	N _{1,3} -H out of plane bend
3	482	8.3	C ₁ =O in plane bend
4	511	195.9	N _{1,3} -H in plane bend
5	669	9.5	Triazole ring framework out of plane bend
6	743	5.9	Triazole ring framework out of plane stretch
7	754	6.9	Triazole ring framework out of plane wag and C-H wag
8	841	18.5	C ₂ -H out of plane wag
9	929	30.9	Triazole ring framework torsion
10	999	22.9	C ₁ -N _{1,3} stretch
11	1051	22.4	C ₁ -N ₁ , N ₁ -N ₂ and C ₂ -N ₃ stretch,
12	1115	2.6	N ₁ -N ₂ , C ₂ -N ₃ stretch, and N ₃ -H wag
13	1218	30.4	C ₁ -N ₁ stretch and C ₂ -H wag
14	1324	14.3	C ₁ -N ₃ stretch and N ₃ -H, C ₂ -H wag
15	1382	3.7	C ₁ -N ₁ stretch and N ₁ -H wag
16	1419	33.5	C ₂ -N ₃ stretch and N ₃ -H wag
17	1613	33.4	C ₂ =N _{2,3} stretch and N ₁ -H wag
18	1828	666.5	C ₁ =O stretch
19	3258	33.5	C ₂ -H stretch
20	3676	88.5	N ₁ -H stretch
21	3685	86.5	N ₃ -H stretch

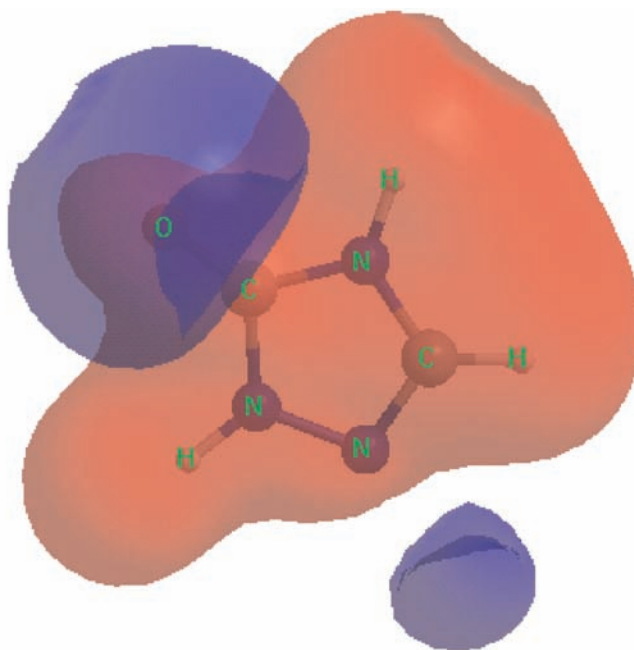


Figure 4. The MESP surface for 1,2,4-triazol-5-one molecule calculated at B3LYP/cc-pVTZ level of theory.

quencies. The predicted frequencies and intensities for TO are listed in Table 4 at the B3LYP/cc-pVTZ level of theory. All theoretical frequencies reported here are listed as calculated, as no scale factor is available for the B3LYP/cc-pVTZ level of theory. We assigned the main vibrational frequencies of some function groups. The vibrational frequencies are identical on the whole between theoretical calculation and the experimental result.

In order to study the possible coordination sites in TO molecule under formation of complex compounds, quantum chemistry calculations of molecular electrostatic potential (MESP) in TO have been carried out. In some cases, calculations of MESP allow to predict successfully the coordination sites in molecules [24]. The MESP surface for TO molecule calculated at B3LYP/cc-pVTZ level of theory is given in Figure 4. The highest negative values of the electrostatic potential are located near the N2 atom of the triazole ring and O atom of the carbonyl group of the TO molecule. It is also evident that the minima close to the N2 atom of the tetrazole ring and O atom of the carbonyl group are much deeper than those close to N1 and N3. Furthermore, in the case of the experimental structure of $[\text{Ag}(\text{TO})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$, [8] $[\text{Cu}(\text{TO})_2(\text{H}_2\text{O})_4](\text{PA})_2$ [9] and $\{[\text{Cu}(\text{TO})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2\}_n$ complex [10], the most preferable coordination sites in TO molecule would be the N2 atom of the tetrazole ring and O atom of the carbonyl group.

Thus, as a whole the results of quantum chemical calculations are in agreement with the experimental data on structure of 1,2,4-triazol-5-one (TO) complex.

4. Summary.

The molecule structure and crystal structure of 1,2,4-triazol-5-one was determined by X-ray single crystal diffraction analysis. Quantum-chemical calculations of molecular electrostatic potential for 1,2,4-triazol-5-one using MP2/cc-pVTZ and B3LYP/cc-pVTZ levels of theory showed that the N2 atom of the tetrazole ring and O atom of the carbonyl group are preferable sites for metal coordination. This is in agreement with the X-ray structure results of the 1,2,4-triazol-5-one complex [8-10].

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