

The Structure and Ab Initio Studies of Thiourea Dioxide

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The crystal and molecular structure of thiourea dioxide, $(\text{NH}_2)_2\text{CSO}_2$, was determined by x-ray single crystal diffraction techniques. Lattice constants are $a=10.669(2)$, $b=10.119(2)$, and $c=3.9151(5)$ Å with the space group $Pnma$ and $Z=4$. The thiourea portion of the molecule has a planar conformation. When the two oxygen atoms are included, the sulfur atom is at the apex of a trigonal pyramid formed with the two oxygen atoms and the carbon atom as the base. The crystal structure is stabilized by strong intermolecular hydrogen bonds. *Ab initio* calculations were performed to investigate the bonding features and reactivity of thiourea dioxide. The calculated bond order of S-C is only 0.481. The hydrogen bond energy was computed to be 22.3 kcal/mol for dimer. MEP analysis reveals that the sites on nucleophilic reactions are S and C atoms.

Introduction

The classical Lewis base ligands can be coordinated to the transition metal in unidentate and multidentate types, depends on the number of lone pairs of electron, and donor atoms on the ligands. There are many ligands that have all of oxygen, sulfur, and nitrogen atoms acting as ligand sites. Thiourea-dioxide is one of such candidates, and has been studied crystallographically, and theoretically.¹⁻³ However, more precise charge distribution of atoms was still under speculations. In this work single crystal diffraction studies and quantitative *ab initio* calculations have been carried out to investigate the bonding and reactivity of thiourea dioxide.

Experimental

White single crystals were obtained by slow recrystallization in acetone. A small crystal was selected for lattice constant determination and subsequent intensity data collection. Crystal data are given in Table 1.

The intensity data were reduced using Lorentz and polarization correction factors but no absorption correction was made. From this stage to the final refinement the NRCVAX computer software was used.⁴ The direct methods software, SOLVER, gave several sign sets with very good Figure of Merit and Residual values. All sign sets were investigated. The ones with good Figures of Merit gave trial models from E-maps that had many similar features. The Patterson map was computed and gave peaks consistent with the placement of the sulfur atom from several of the E-maps. With the confidence that the trial model was correct and the knowledge, the locations of the remaining non-hydrogen atoms were determined from difference maps.

Once the atoms were refined with anisotropic thermal parameters, the two independent hydrogen atoms were located. They were included in the model and allowed to refine isotropically. Positional parameters are given in Table 2. Bond distances and angles are given in Table 3. Figure 1 illustrates

Table 1. Summary of crystal data, intensity collection and least-squares refinement statistics of $(\text{NH}_2)_2\text{CSO}_2$

	Crystal data
$(\text{NH}_2)_2\text{CSO}_2$	MoK α radiation
Mr=108.11	$\lambda=0.71069$ Å
Orthorhombic	Cell parameters from 25 reflections
$Pnma$	$\theta=11.32-13.80^\circ$
$a=10.669(2)$ Å	$\mu=0.59$ mm ⁻¹
$b=10.119(2)$ Å	T=293 K
$c=3.9151(5)$ Å	Rectangular
$V=422.7(1)$ Å ³	$0.13\times 0.2\times 0.1$ mm
Z=4	colourless
$D_x=1.70$ mgm ⁻³	
	Data collection
Enraf-Nonius CAD4	$\theta_{\text{max}}=24$
diffractometer	$h=0\rightarrow 12$
ω -2 θ scan	$k=0\rightarrow 11$
Absorption correction: none	$l=0\rightarrow 4$
446 measured reflections	2 stand reflections
313 independent reflections	frequency: 180 min
244 observed reflections [$F>3\sigma(F)$]	intensity decay: 0.71%
	Refinement
Refinement on F	$\omega=1/\sigma(F)$
R=0.038	$(\Delta/\sigma)_{\text{max}}=0.026$
$\omega R=0.030$	$\Delta/\rho_{\text{max}}=0.31$
S=2.25	$\Delta\rho_{\text{min}}=-0.27$
244 reflections	Atomic scattering factors from NRCVAX program
39 parameters	All H-atom parameters refined isotropically

tes the molecular array around a molecule and Figure 2 the packing of the molecules.

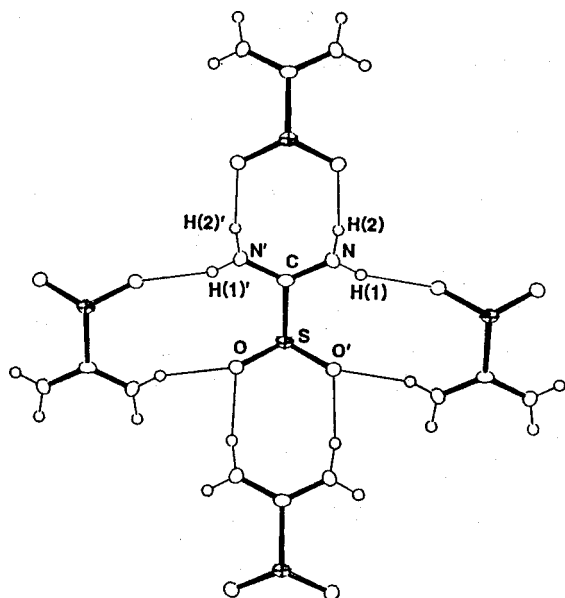
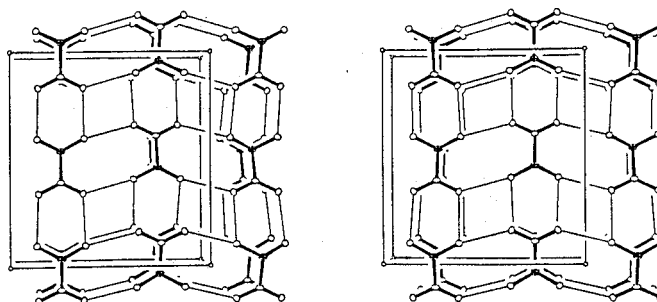
The *ab initio* calculations were carried out with the GAUS-

Table 2. Fractional atomic coordinates and anisotropic(isotropic) displacement parameters ($\text{\AA}^2 \times 100$) for $(\text{NH}_2)_2\text{CSO}_2$

Atom	x	y	z	u11	u22	u33	u12	u13	u23
S	.4599(2)	.75	.6355(5)	1.81(10)	3.71(11)	3.81(11)	0.00	0.27(11)	0.00
O	.4007(3)	.8719(3)	.4916(9)	2.03(19)	2.74(19)	6.25(25)	0.37(17)	0.14(18)	-0.46
N	.6633(5)	.6363(4)	.3990(14)	2.5(3)	1.73(25)	6.5(4)	0.45(23)	1.4(3)	0.0(3)
C	.6121(6)	.75	.3998(18)	1.2(4)	4.7(5)	2.4(4)	0.0	-0.4(4)	0.0
H(1)	.629(5)	.565(4)	.376(13)	4.3(17)					
H(2)	.739(5)	.623(4)	.250(12)	4.5(17)					

Table 3. Selected geometric parameters (\AA°)

S-O	1.496(3)	N-H(1)	0.82(4)
S-O(1)	1.496(3)	N-H(2)	0.89(5)
S-C	1.867(7)	C-N(1)	1.296(5)
N-C	1.296(5)		
O-S-O ⁽¹⁾	111.1(2)	S-C-N	117.2(4)
O-S-C	100.4(2)	N-C-N(1)	125.2(6)
C-N-H(1)	123(3)	C-N-H(2)	126(3)
H(1)-N-H(2)	110(4)		
Intermolecular hydrogen bonds (H atoms from difference maps)			
D-H...A	D...H	H...A	D-A
N-H(1)-O ⁽²⁾	.82(4)	2.04(4)	2.840(6)
N-H(2)-O ⁽³⁾	.89(5)	1.97(5)	2.845(6)
Symmetry code			
(1) x 1.5 - y z (2) $1-x$ $-0.5+y$ $1-z$ (3) $0.5+x$ $0.5-y$ $0.5-z$			

**Figure 1.** ORTEP(Johnson, 1971) drawing of the molecule with atom-labelling scheme (the displacement ellipsoids are drawn at 50% probability). Hydrogen bonds are indicated by thin lines.**Figure 2.** Stereoview of a unit cell packing. Origin, lower left; b-axis, horizontal; a-axis, vertical.

Results and Discussion

A mirror plane parallel to c-axis passes through the S and C atoms so that O and O', and N and N' atoms respectively are related by mirror symmetry.

As was reported in the earlier investigation, the S-C single bond, 1.867(7) \AA , is rather long compared with a 1.81 ± 1 \AA reported for paraffinic carbon-sulfur bonds in the International Tables.⁷ At the same time the C-N bond, 1.296(5) \AA is rather short compared with that of normal C-N single bonds (1.472 ± 5 \AA). The S-O bond is close to the average value reported for sulfate S-O bonds (1.49 \AA) and not far from those found in the gas phase sulfur dioxide (1.432 ± 3 \AA ave.). The geometric parameters in Table 3 show that the S, C, N, N' atoms in the thiourea portion of the molecule (Figure 1) are planar while the angle sum of 311.9° around the sulfur atom in the sulfur dioxide part of the molecule indicates that the lone-pair electron density of the sulfur atom is located at the apex of a trigonal pyramid extending toward the plane of SO_2 .

The thiourea dioxide molecule is hydrogen bonded through $\text{NH}\cdots\text{O}$ (dioxide) interaction with neighbouring molecules (see Table 3). Taking the bonding radii of hydrogen, nitrogen and oxygen to be 0.24, 1.32, and 1.21 \AA , respectively,⁸ the short intermolecular contacts are indicative of strong hydrogen bonds (the N-O distance in a hypothetical N-H-O molecular species would be $1.32 + 0.24 + 1.21 = 2.77$ \AA). As shown in Figure 2, all molecules are bound together by the hydrogen bonds. The importance of hydrogen bonding in the solid may be seen clearly from this figure. The rather high value of the density, 1.70 mgm^{-3} , also suggests very efficient packing for a small organic molecule.

Ab Initio Calculations. The long bond distance of C-S bond in crystal structure accounts for the ease of breaking this bond. This compound is suggested to be existed

SIAN 92, 94⁵ and GAMESS⁶ packages on a Cray Y-MP C916 and Indigo 2 workstation. Molecular geometries were optimized at 3-21G* and 6-31G* basis sets. The optimum 3-21G* geometry was used in computing the molecular electrostatic potential (MEP) and bond orders.

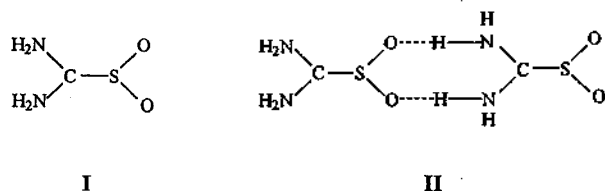
Table 4. Optimized Geometries and Total Energies (a.u.) for monomer and dimer of thiourea dioxide at 6-31G* and 3-21G*. The bond distances are in angstroms and the angles in degrees. The values in parentheses are for 3-21G* basis sets

	Monomer	Dimer
S-C	1.905 (1.930)	1.883 (1.886)
S-O	1.468 (1.468)	1.477 (1.482)
C-N	1.303 (1.303)	1.301 (1.301)
O...H ^a		2.003 (1.855)
∠S-C-N	117.9 (117.3)	117.3 (116.6)
∠O-S-C	97.1 (96.6)	97.8 (97.3)
∠O-S-O	117.1 (117.6)	114.7 (115.2)
∠N-C-N	124.1 (125.5)	125.4 (126.9)
SCF E.	-696.23872 (-692.75806)	-1392.51301 (-1385.56806)

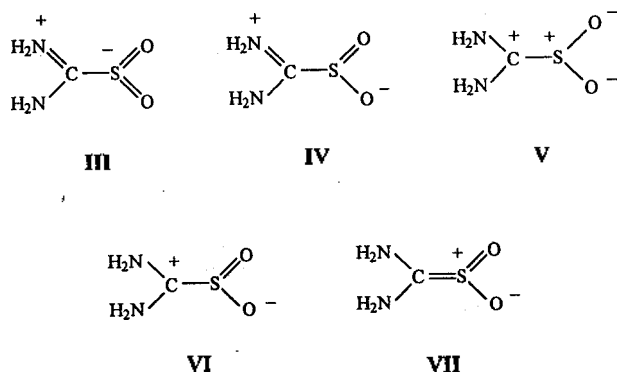
^aO...H bond length is for hydrogen bonding.

as zwitterion form in which the approximately planar (H₂N)₂C group is positive and pyramidal group around sulfur atom possesses the negative charge. We performed *ab initio* calculations to investigate the bonding features and reactivity of thiourea dioxide.

The optimized geometries and total energies for monomer (I) and dimer(II) of thiourea dioxide are given in Table 4.



In general, the optimized geometries are in good agreement with the experimentally determined structural data. The sum of angles around C atom is about 360° that represents the planar geometry. The fact that the N₂CS part of the molecule is essentially planar can be attributed to the strong electron withdrawing power of the SO₂ group which can be reduced to SO₂⁻ group. Various tautomeric forms of III-VII can be considered for thiourea dioxide compound.



Structure IV was suggested to be best represent the valence bond structure for thiourea dioxide in previous studies.¹³ The relatively short C-N bonds was assigned to have partially double bond character. Experimental studies of nitro-

Table 5. Calculated Mulliken Atomic Charges at 6-31G* and 3-21G*.

The values in parentheses are for 3-21G* basis sets

	Monomer	Dimer
C	0.4067 (0.5464)	0.4008 (0.5461)
S	1.1334 (1.1517)	1.2165 (1.2308)
O	-0.7718 (-0.7108)	-0.8088 (-0.7086)
N	-0.8564 (-0.9175)	-0.8525 (-0.9139)
Na	0.0018 (-0.1382)	0.0303 (-0.1028)

^aAtomic Charges with H atoms summed into N atom.

guanidine, (NH₂)₂CNNO₂, indicate that double bond of C-N is present in the solid state.⁹ However, our calculations reveal that C-N bonds have single bond character and S-O bonds in SO₂ group have a considerable amount of double bond character in terms of both bond order and atomic charge. The bond order of C-N was computed to be 1.150. This value is the range of single bond strength. Mulliken atomic charge on N atom was calculated to be -0.8564 in monomer at 6-31G* level, as shown in Table 5. The values for dimer at 3-21G* level are comparable to this value. Nitrogen atom in NH₂ group is more electronegative than that of hydrogen atom. Most of negative charge on N atom comes from hydrogen atoms. In Table 5, N atomic charges with H atoms summed up are close to neutral. On the basis of bond order and atomic charge, the roles of III and IV structures are not important. The calculated S-C bond order of 0.481 is very weak and that is consistent with the long bond distance of 1.883 Å in dimer at 6-31G* level. The S-O bond order is 1.571 and the optimized bond distance of 1.468 Å in monomer is shorter than that of sulfate S-O distance of 1.49 Å.¹⁰ The S-O bond has a partial double bond character. There are considerable charge separation on C, S, and O atoms. These are 0.4067, 1.1334, and -0.7718 for C, S, and O atoms in monomer, respectively. The possible structure of thiourea dioxide is the combination of V and VI.

The calculated O...H bond distances in dimer are 2.003 Å and 1.855 Å at 6-31G* and 3-21G* basis sets, respectively. As we have observed hydrogen bonding in crystal structural data, these distances indicate a relatively strong intermolecular hydrogen bonding.¹¹ The hydrogen bonding energy was computed to be 22.3 kcal/mol for dimer. This value also supports the strong interaction. The energies of hydrogen bonds range from 26 kcal/mol for the stronger bonds to the values around 7 kcal/mol for the weaker hydrogen bonds.¹⁰

Figure 3 shows the electron density difference map that is a whole molecule's density minus the density of the individual atoms. This plot provides a description of the spatial aspects of the charge distribution. This map is plotted in the molecular plane defined by S, C, and N atoms. The electron density is concentrated on around O and N atoms due to both the lone paired electrons and attraction from adjacent atoms. As shown in figure, the electron density around S and C atoms is shifted significantly toward the more electronegative atoms. Note that the electron density is pretty low between S and C bond. This is consistent with the long bond distance of S-C bond and large atomic charges on S and C atoms.

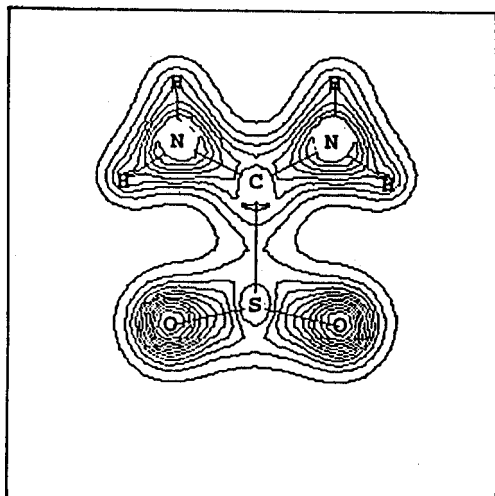


Figure 3. The electron density difference map of thiourea dioxide in the plane defined by S, C, and N atoms.

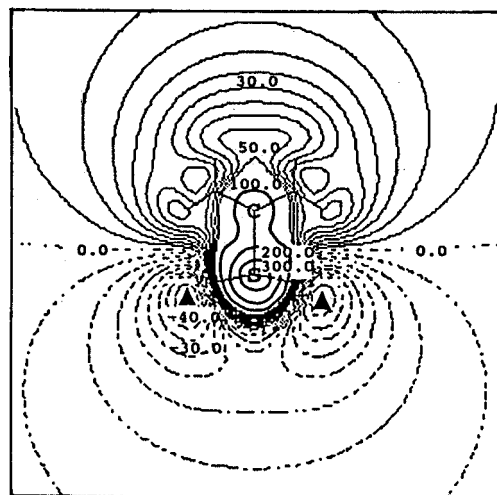


Figure 5. The calculated molecular electrostatic potential of thiourea dioxide, 1.0 Å below the molecular plane. The projections of the nuclear positions are indicated. Dashed contours correspond to negative potentials; all values are in kcal/mol·e. The positions of the most negative potentials in this plane are shown; the value is (▲) -44.7.

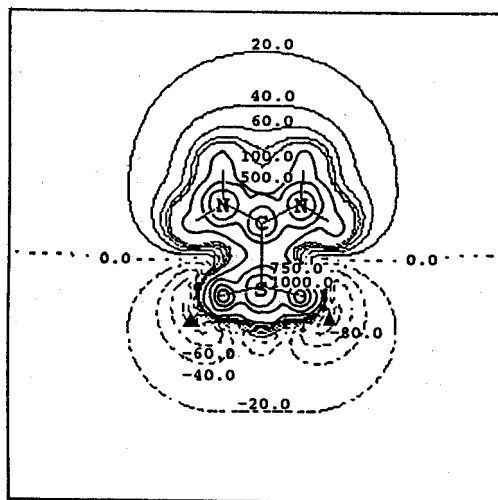


Figure 4. The calculated molecular electrostatic potential of thiourea dioxide, in kcal/mol·e, in the molecular plane. Positions of the nuclei, or their projections in this plane are indicated. Dashed contours correspond to negative potentials. The positions of the most negative potentials are indicated; the value is (▲) -87.8.

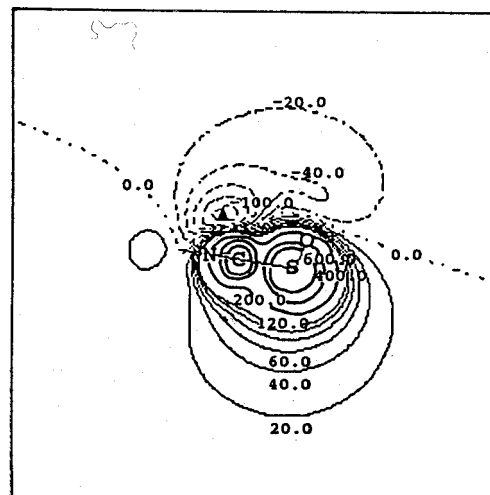


Figure 6. The calculated molecular electrostatic potential of thiourea dioxide in the plane bisecting the S-C axis. Positions of the nuclei are indicated. Dashed contours correspond to negative potentials; all values are in kcal/mol·e. The positions of the most negative potentials in this plane are shown; the value is (▲) -111.5.

The calculated molecular electrostatic potentials (MEP) are displayed in Figure 4, 5, and 6. These figures are given in the molecular plane, 1.0 Å below the molecular plane, and the plane bisecting the S-C axis, respectively. The major regions of negative electrostatic potentials in Figure 4 are associated with the lone pair electrons on oxygen atoms of the SO₂ group. One also expects to find negative potentials near nitrogen atoms due to lone pair electrons. These potentials are particularly strong when the geometry around the N atoms is pyramidal. However, it is also quite sizable for the planar geometries.¹² In thiourea dioxide compound, we have also observed the local minimum of -111.5 kcal/mol·e on the nitrogen atoms as shown in Figure 6. The local geometry around nitrogen atoms is planar. In Figure 5 displayed MEP at 1.0 Å below the molecular plane, there are still two

local minima (-44.7 kcal/mol·e) in these regions for oxygen's lone pair electrons. The most positive potential occurs around sulfur atom. And in Figure 6, the positive potentials are formed around both S and C atoms. However, the potential of sulfur atom is more positive than that of carbon atom. These results are in good agreement with a recent report¹³ indicating that the nucleophilic reaction is occurring on either S or C atoms of R₂CSO₂ depending on the substituent group.

Conclusions

The molecular structure of thiourea dioxide shows that the thiourea portion of the molecule has a planar conformation and the sulfur atom in the sulfur dioxide part is at the apex of a trigonal pyramid formed with the two oxygen atoms and the carbon atoms as the base. The bond distance of S-C is rather long. The C-N bond length is relatively short compared with that of normal C-N single bonds. The S-O bond is close to the average length for sulfate S-O bonds. These are well agreed with the bond distances calculated theoretically by *ab initio* calculations.

The valence structure of thiourea dioxide is suggested to be a combination of zwitterion forms, V and VI on the basis of bond distances, bond orders, and atomic charges. The electron density and molecular electrostatic potentials are analyzed to study the reactivity. The sites of nucleophilic reactions would be either sulfur or carbon atoms. The potentials on sulfur atom are calculated to be higher than carbon atom in thiourea dioxide compound. The possible coordination sites to the transition metal ions could be the oxygen atoms which have the high negative charge density.

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