Research Article

Synthesis, Crystal Structure, and DFT Calculations of 1,3-Diisobutyl Thiourea

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1,3-Diisobutyl thiourea was synthesized and characterized by single crystal X-ray diffraction. It gives a monoclinic ($\alpha = \gamma = 90^\circ$ and $\beta \neq 90^\circ$) structure with the space group P21/c. The unit cell dimensions are $a = 11.5131$ (4) Å, $b = 9.2355$ (3) Å, $c = 11.3093$ (5) Å, $\alpha = 90^\circ$, $\beta = 99.569^\circ$ (2), $\gamma = 90^\circ$, $V = 1185.78$ (8) Å³, and $Z = 4$. The crystal packing is stabilized by intermolecular (N–H···S) hydrogen bonding in the molecules. The optimized geometry and Mulliken's charges of the said molecule calculated with the help of DFT using B3LYP-6-311G model support the crystal structure.

1. Introduction

Thiourea derivatives are well known sulphur containing compounds acting as ligands in the field of coordination chemistry [1–3]. Such ligands are capable of affording complexes with metal ions; the resultant complexes have been reported to have imperative antimicrobial [4] and anticonvulsant [5] applications. Thiourea derivatives and their complexes have numerous catalytic applications in asymmetric organocatalysis [6–8], have been used as cocatalysts in Pauson-Khand reactions [1], Pd-catalyzed reactions [1, 9], Heck and Suzuki coupling reactions, and so forth [2, 9]. Thiourea derivatives got much more attention in the field of highly enantio- and diastereoselective catalysis [10] and have also been applied as cocatalysts in nanoparticles and a number of other types of reactions [11, 12]. The challenging task in the chemistry of thiourea is its syntheses and structural characterization. Several research groups are trying to make this versatile group of compounds easily accessible and have reported various methods [13–16].

In continuation to our previous work [17] the title compound was obtained unexpectedly. Surprisingly a comprehensive research survey does not show solid state structural data of title compound **1**. The structure of the compound was determined by X-ray diffraction and its DFT optimized geometry was determined using B3LYP-6311G model of theory [18]. Theoretical data obtained for the compound compare well with the experimental data.

2. Experimental

All chemicals, that is, carbon disulphide and isobutyl amine, are commercially available and were used without further purification. Solvents were distilled prior to use.

2.1. Synthesis of 1,3-Di(isobutyl)thiourea. Solution of carbon disulphide (498.0 mmole; 50 mL) was prepared in petroleum ether (100 mL) and was cooled to 0°C in an ice bath, following

SCHEME 1: Reaction between CS_2 and isobutylamine to afford 1,3-diisobutyl thiourea.

the literature procedure [16, 17]. An excess amount of isobutylamine (996.0 mmole; 61.42 mL) was slowly and carefully added with constant stirring. The stirring was continued overnight. The solvent and all other volatiles were removed under reduced pressure and the oily compound was dissolved in ethyl acetate. After 2 days needle-like colorless crystals appeared in the solution; they were further allowed for few days to grow well. The same reaction was repeated by mixing equimolar amounts of CS_2 and isobutylamine by adopting the same procedure but instead of the expected dithiocarbamate 2, product 1 was exclusively obtained (Scheme 1).

2.2. X-Ray Crystallography. A crystal of suitable dimensions was selected for X-ray structure analysis. The diffraction intensity data were collected on a Bruker kappa APEXII CCD diffractometer using graphite-monochromator Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at ambient temperature. For data collection ω scan and multiscan absorption correction was applied. Final refinement on F^2 was carried out by full-matrix least-squares techniques. Structure solution and refinements were accomplished with SHELXL-97 [19] and *publCIF* [20].

2.3. DFT Calculations. The geometry of title compound (1) was obtained from X-ray crystallographic data. The molecular structure of (1) ($\text{C}_9\text{H}_{20}\text{N}_2\text{S}$) in ground state is optimized by DFT method including correlation correction using B3LYP-6311G model of theory [18]. Mulliken's charges were calculated by using the same model of theory; the data so-obtained are given in Table 5 and optimized structure of the compound is given in Figure 2. All calculations were performed by using Gauss-view molecule visualizer program and GAUSSIAN-03 program [18, 21, 22].

3. Results and Discussion

The reaction of primary or secondary amines with carbon disulphide gives dithiocarbamates; the reaction is straightforward and usually proceeds without the formation of side products. We treated isobutylamine with carbon disulphide in petroleum ether and instead of dithiocarbamate derivative 2, compound 1 was exclusively obtained as solid (Scheme 1). The reaction proceeded at ambient temperature without adding a catalyst and excellent yield was achieved. The reaction probably proceeds through formation of isothiocyanate intermediate which reacts further with amine and rearranges to thiourea [16].

Single Crystal Studies. The molecular structure of compound 1 is given in Figure 1 with numbering scheme. It crystallizes in monoclinic crystal system ($\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$) with the space group P21/c; the crystal packing in unit cell is stabilized

TABLE 1: Crystal data and structure refinement.

Crystal parameter	Value
Empirical formula	$\text{C}_9\text{H}_{20}\text{N}_2\text{S}$
Formula weight	188.34
Temperature	296 K
Wavelength	$0.71073 \text{ \AA}$
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	a 11.5131(4) $\text{\AA}$
	b 9.2355(3) $\text{\AA}$
	c 11.3093(5) $\text{\AA}$
	β 99.569(2)
Volume	$1185.78(8) \text{ \AA}^3$
Mu	0.232 mm^{-1}
Z, density	4, 1.055 g cm^{-3}
$F(0, 0, 0)$	416.0
(h, k, l) min	(-13, -9, -13)
(h, k, l) max	(13, 11, 13)
Correction method	Multiscan
Theta (max)	25.250
R (reflection)	0.0716 (1637)
wR_2	0.2021 (2145)
Data completeness	1.000
Goodness of fit	1.053

FIGURE 1: Crystal structure (ORTEF plot) of 1,3-diisobutyl thiourea molecule with labeling scheme.

by intermolecular $\text{N-H} \cdots \text{S}$ bonding with an average distance of $2.819 \text{ \AA}$, which is relatively stronger than the reported one $2.87 \text{ \AA}$ [23] and is closer to $2.837 \text{ \AA}$ [24]. The data pertinent to crystal structure determination are summarized in Table 1.

The geometry around nitrogen atom is distorted and cannot be predicted on the basis of hybridization. The distortion can easily be traced out by the involvement of lone pair of electrons on nitrogen in delocalization phenomenon with the π electrons of $\text{C}=\text{S}$ moiety. The C5-N1 bond distance ($1.328 \text{ \AA}$) and C5-N2 ($1.343 \text{ \AA}$) are shorter than average C-N single bond distance ($1.499 \text{ \AA}$) and similarly that of $\text{C}=\text{S}$ bond distance ($1.698 \text{ \AA}$) is longer than the average distance ($1.599 \text{ \AA}$) reported in literature [25]. These data support partial double bond characters between $\text{N}=\text{C}$ and flow of

TABLE 2: Hydrogen bonding data for the title compound.

X	H	Y	$d(X-H)$ (Å)	$d(H-Y)$ (Å)	$d(X-Y)$ (Å)	$\angle(XHY)$ (°)
N1	H1a	S1	0.861(4)	2.683(8)	3.479(2)	154.33(3)
N2	H2a	S1	0.860(4)	2.819(3)	3.573(3)	147.37(5)

TABLE 3: Selected bond lengths (experimental and calculated) belong to compound 1.

Bonded atoms	Experimental	Calculated
S1-C5	1.698(3)	1.7375
N1-C5	1.328(4)	1.3665
N1-C4	1.452(4)	1.4664
N2-C5	1.343(4)	1.3624
N2-C6	1.455(4)	1.4683
C1-C2	1.419(7)	1.5385
C2-C4	1.378(6)	1.5444
C2-C3	1.542(6)	1.5379
C6-C7	1.488(6)	1.5420
C7-C8	1.490(7)	1.5409
C7-C9	1.536(6)	1.5417

TABLE 4: Selected bond angles and torsion angles for compound 1, a comparison between experimental and theoretical data.

Atoms	Experimental	Calculated
Bond angle		
C1-C2-C3	112.9(4)	111.391
C1-C2-C4	125.8(5)	109.523
C4-C2-C3	110.5(4)	111.876
C2-C4-N1	117.7(4)	114.192
C4-N1-C5	126.4(3)	125.221
N1-C5-S1	120.3(3)	123.101
S1-C5-N2	122.4(3)	122.101
N1-C5-N2	117.2(3)	114.798
C5-N2-C6	125.2(3)	129.550
N2-C6-C7	114.4(3)	112.036
C6-C7-C8	113.3(4)	112.558
C6-C7-C9	109.0(4)	112.701
C9-C7-C8	110.9(4)	111.702
Torsion angle		
C4-N1-C5-S1	171.91	170.09
S1-C5-N2-C6	0.22	0.91
C5-N1-C4-C2	150.89	149.07
C5-N2-C6-C7	89.97	85.70
N1-C4-C2-C1	43.49	45.76
N1-C4-C2-C3	175.10	173.75
N2-C6-C7-C8	60.57	60.73
N2-C6-C7-C9	175.35	175.26

FIGURE 2: The packing of thiourea (1) molecules showing the intermolecular H-bonding.

electron density from sulfur resulting in an elongation in S-C bond.

The elongation of C-S bond may also be explained on the basis of intermolecular hydrogen bonding (data reported in Table 2). The solid state crystal packing and intermolecular interactions are shown in Figure 2. The molecules of the title compound are organized and held together with the help of intermolecular N-H...S hydrogen bonding with an average distance 2.819 Å, which falls in the expected range, reported for analogous compounds, that is, 2.87 Å [23], 2.84 Å [26], and 2.837 Å [24]. The experimental and calculated data (for gaseous molecule), DFT (B3LYP/6-311G), are given in Table 3. The calculated and experimental data related to bond

angles around N atom are approximately 120° which support the planarity and sp^2 hybridization around nitrogen owing to delocalization of electrons in the molecule.

DFT-Studies and Vibrational Spectra Analysis. Experimental data correspond to solid phase while theoretical calculations belong to gaseous phase [22]. DFT calculations are usually performed on a single molecule in the unit cell [27]. DFT calculations for compound 1 were carried out by using the GAUSSIAN-03 program [18, 21, 22]. The geometry of the molecule was optimized by DFT/B3LYP with the 6-311G basis set [18]. The optimized geometry obtained through DFT was compared with crystal structure which supports the crystal structure. The crystallographic and optimized geometric bond lengths and bond angles of compound 1 are given in Tables 3 and 4, respectively.

Mullikan's charges distribution on atoms of compound (1) is given in Table 5. It can be noticed from the table that negative charge density of nitrogen and terminal carbon appears in the range of -0.660 and -0.508, respectively, which is considerably larger than other atoms bearing negative

TABLE 5: Calculated Mullikan's charges for B3LYP/6-311G.

Atoms	B3LYP/6-311G
C1	-0.508
H1A	0.168
H1B	0.187
H1C	0.177
C2	-0.190
H2	0.218
C3	-0.512
H3A	0.166
H3B	0.161
H3C	0.181
C4	-0.161
H4A	0.164
H4B	0.238
N1	-0.660
H1	0.314
C5	0.279
S1	-0.163
N2	-0.664
H2(N)	0.309
C6	-0.111
H6A	0.225
H6B	0.219
C7	-0.291
H7	0.194
C8	-0.486
H8A	0.186
H8B	0.157
H8C	0.188
C9	-0.492
H9A	0.180
H9B	0.183
H9C	0.155

charges, which shows that nitrogen is donor sites for traditional and terminal carbons are donor sites for nontraditional hydrogen bonding.

The experimental and calculated (B3LYP/6-311G) IR absorption frequency along with their respective intensities are given in Figure 3. The experimental bands are probably assigned comparatively with related molecules [28]. The presence of intermolecular interactions is responsible for the higher value of $\nu(\text{C}=\text{S})$ stretching at 1227 cm^{-1} . The absorption bands at 3346 and 3237 cm^{-1} are representing $\nu(\text{N}_1-\text{H})$ and $\nu(\text{N}_2-\text{H})$ stretching for title compound (**1**); their corresponding quantum chemical calculated $\nu(\text{N}-\text{H})$ stretching appeared to be shifted to higher frequency. The bands at $2954\text{--}2868\text{ cm}^{-1}$ are assigned to $\nu(\text{C}-\text{H})$ stretching similar to the calculated one. Strong IR bands in range $1600\text{--}1500\text{ cm}^{-1}$ represent $\nu(\text{N}-\text{H})$ bending [29]. In addition strong band at 1227 cm^{-1} corresponds to $\nu(\text{C}=\text{S})$ stretching. Lower value of $\nu(\text{C}=\text{S})$ up to 750 cm^{-1} is also reported [29, 30] but

FIGURE 3: Comparative infrared spectra of the title compound in the gaseous state (theoretical, calculated using B3LYP/6-311G method) and in the solid state (experimental).

intermolecular $\text{C}=\text{S} \cdots \text{H}-\text{X}$ interaction strongly affects the $\text{C}=\text{S}$ stretching [30].

4. Conclusions

Reaction of CS_2 and isobutylamine affords the corresponding thiourea instead of dithiocarbamate derivative. The compound could easily be purified with the help of crystallization. The crystal structure studies show the existence of intermolecular $\text{N}-\text{H} \cdots \text{S}$ type H-bonding. All structural parameters were also calculated (DFT) and were compared with the experimental data. Solid state and gaseous phase data (bonding and vibration energies) are in close agreement with each other.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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