

Electronic structure and conformational study of thiobiurets

V C JYOTHI BHASU, D N SATHYANARAYANA and
C C PATEL

Department of Inorganic and Physical Chemistry, Indian Institute of Science,
Bangalore 560 012

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Abstract Quantum mechanical calculations at all valence complete neglect of differential overlap (CNDO/2) and self-consistent charge extend Huckel (SCC-EH) and the Pi electron Pariser-Parr-Pople with limited configuration interaction (PPP-LCI) levels of approximation have been accomplished for monothiobiuret and dithiobiuret. From the calculated results, a discussion of the electronic structure, photoelectron and electronic spectra and the conformational stability are given. The electronic and ^1H nmr spectra are also reported. A trans-cis-CONHCS- structure is found to be the stable conformation for monothiobiuret consistent with other evidences.

Keywords. Monothiobiuret; dithiobiuret; CNDO/2; SCC-EH; PPP-LCI; electronic structure; electronic spectra; conformation.

1. Introduction

Monothiobiuret (Mtb) and 2,4-dithiobiuret (Dtb) ($\text{H}_2\text{NCSNHXCXNH}_2$, $\text{X} = \text{O}$ and $\text{X} = \text{S}$, respectively) are related to several simpler compounds and are the parent compounds of a large and interesting class of organic substances (Kurzer 1956). Further, dithiobiuret is isoelectronic with dithioacetylacetone, which is unknown as a free compound but exists as complexes with metals (Cox and Darken 1971). The skeleton $\text{H}_2\text{NCSNHN-}$ is reported to be of importance in the carcinostatic and antiviral activities of sulfur-nitrogen compounds (Ali and Livingstone 1974). In Dtb and Mtb, the interaction between two thioamide groups or between an amide and a thioamide group may impart some special features in their electronic structure and electronic spectrum. Further, Mtb is an interesting molecule from the conformational point of view. Four planar conformations (I to IV) can be written for Mtb. The x-ray structure of Mtb has not been made. However, the molecules of its oxygen and thio analogues, namely biuret (Hughes *et al* 1961) and 2,4-dithiobiuret (Spofford and Amma 1972) the structure of which are determined from the x-ray diffraction technique, are known to take a planar trans-cis -CXNHXCX- ($\text{X} = \text{O}, \text{S}$) conformation. A planar trans-cis conformation was independently suggested for Dtb from vibrational spectral

studies by Ray and Sathyanarayana (1975) from this laboratory. Similarly from zeroth order normal coordinate calculations for the different conformations of Mtb, Geetharani and Sathyanarayana (1976) have proposed a planar trans-cis-CONHCS- structure for Mtb as the most probable one. It was thus of interest to investigate the electronic structures of Mtb and Dtb, and the conformation of Mtb by the all valence CNDO/2 and SCC-EH methods. The ^1H nmr spectra of Mtb and Dtb are also recorded with this point in view.

Kurzer and Taylor (1962) have measured the electronic spectra of Mtb and Dtb but have not proposed any assignment. In order to clarify the assignments of the observed electronic spectra, the electronic structures of Mtb and Dtb have also been calculated by the PPP-LCI method.

2. Experimental

Mtb and Dtb were synthesised according to known methods and purified by recrystallization from methanol (Walter 1960; Kurzer 1955).

The electronic spectra of Mtb and Dtb were measured in aqueous solutions on a Unicam SP 700 A spectrophotometer. The ^1H nmr spectra were recorded with a Bruker WH 270 MHz spectrometer in DMSO- d_6 solvent. TMS was used as the internal reference.

3. Method of calculation

The usual CNDO/2 approximation and parameters were chosen for the present calculations (Pople and Beveridge 1970). The SCC-EH method (Hoffmann 1963; Carroll *et al* 1966) using the Wolfsberg-Helmholtz (1952) procedure for the evaluation of the off-diagonal elements has been employed. For the pi electron PPP calculations with limited configuration interaction (PPP-LCI) (Pariser and Parr 1953; Pople 1953), the sets of parametrization were identical to that given by Flurry (1968). The values of resonance integrals ($\beta_{\mu\nu}$) used were Mtb: CN (H_2) = -0.80, CN (H) = -1.00, CO = -2.50, CS = -1.60, (H)NC = -1.00 eV and (b) Dtb: CN (H_2) = -1.30, CN(H) = -1.30 and CS = -1.50 eV.

The geometry of Dtb was taken from the x-ray crystal structure analysis (Spofford and Amma 1972). The bond lengths and bond angles for Mtb which were not varied in this study were chosen on the basis of the structure data for Dtb and biuret (Hughes *et al* 1961). They are N-H 1.02, C-N 1.345, C-N (terminal) 1.395, C-O 1.25, C-S 1.713 Å and bond angles, 120° each.

The calculations were performed on an IBM 360/44 computer at the Computer Center of the Institute. For the CNDO/2 method, the standard program was used (Pople and Beveridge 1970). For the SCC-EH and PPP-LCI, programs written in Fortran IV by the authors were employed.

4. Results and discussion

4.1. Charge distribution

The charge densities on different atoms of Mtb and Dtb from both the CNDO/2 and SCC-EH calculations are shown in table 1. Figure 1 depicts the pi bond

orders (from CNDO/2) and pi overlap populations (from SCC-EH) for these molecules.

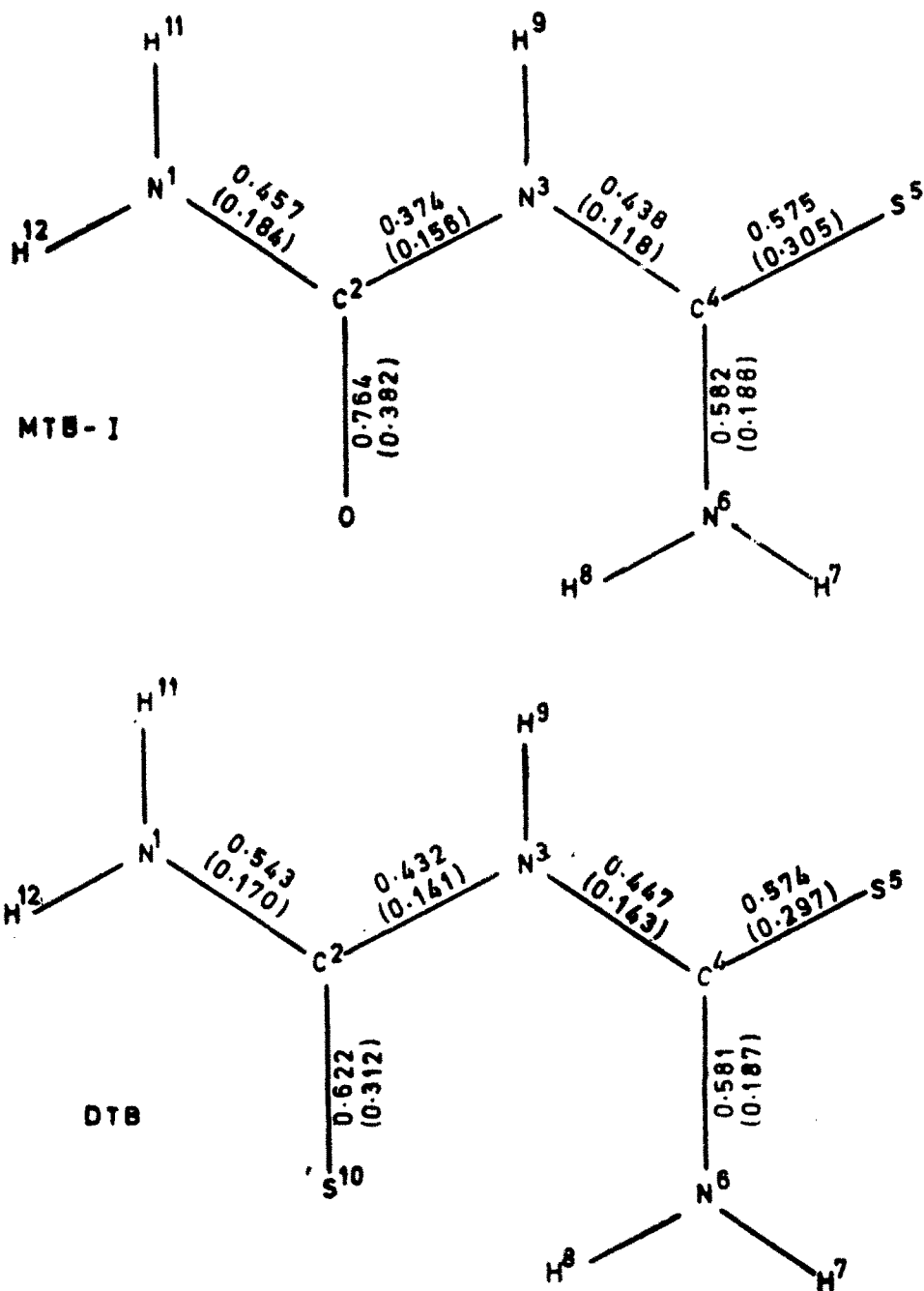


Figure 1. Bond order and pi overlap population (in paranthesis).

The charge distributions show that the terminal nitrogen atoms of Mtb are negatively charged and the charges are nearly equal in magnitude like those of Dtb (table 1). This may explain the very weak acidic nature of these molecules, the acid dissociation constant of Dtb was found to be about 4.0×10^{-9} (Usatenko and Sukhoruchkina 1963). The terminal nitrogens of Mtb and Dtb are noted to be more negatively charged than the central nitrogen atom. This may be explained as due to the fact that the terminal nitrogens are stronger pi electron donors than the central nitrogen atom. All the three nitrogen atoms of Mtb and Dtb are sigma electron acceptors and this ability overcompensates the pi donor capacity.

The sulphur atoms in these molecules are more negatively charged than the nitrogen atoms and always act as pi acceptors and sigma electron donors. In Mtb and Dtb intramolecular hydrogen bonding between the trans oxygen/sulfur and the NH_2 group may be expected (Geetharani and Sathyanarayana 1976; Spofford and Amma 1972). The existence of intramolecular hydrogen bonding may be inferred from the relatively higher positive charge on the hydrogen atom involved in hydrogen bonding.

The delocalization of the nitrogen lone pairs in these two molecules may be noted from the bond orders of the C-N and C=S groups (figure 1). This delocalization in effect decreases the double bond character of the C=S group and imparts a partial double bond character to the C-N bonds. The double bond character of the terminal C-N bonds of Mtb and Dtb is higher than the other two C-N bonds (figure 1) as is to be expected from stretching frequencies and force constants and bond distances available for Dtb (Ray and Sathyanarayana 1975; Geetharani and Sathyanarayana 1976; Spofford and Amma 1972). It is evident from the bond orders and pi overlap populations given in figure 1, that while a nearly uniform conjugation is present in Dtb, the localised double bond character of the C=O group partly changes this picture for Mtb.

4.2. Molecular orbital energies

The calculated orbital energies can be equated to the molecular ionization potentials by Koopmans' theorem (1934). Although the photoelectron spectrum (PES) of Dtb and Mtb are not reported yet, it was of interest to compare the molecular orbital energies with PES bands of simple amides and ureas and their thio analogues, which may be thought of as the constituents of Mtb and Dtb. As the SCC-EH method gives better agreement of the calculated molecular ionisation energies with the experimental PES bands (Boyd 1972), the energy levels from SCC-EH are referred to in the following discussion. However, the orbital energies and their assignments for the first few highest occupied molecular orbitals (HOMO) of Mtb and Dtb from both the SCC-EH and CNDO/2 methods are presented in table 2.

The first five HOMOs of Mtb were found to lie at -8.72 , -9.35 , -9.95 , -11.29 and -11.53 eV. The first and second HOMOs at -8.72 and -9.35 eV are found to have maximum contribution from the nonbonding orbitals of the sulphur and oxygen atoms respectively. These are comparable with the first HOMO of thioamides and amides respectively (Mines and Thompson 1975). The next HOMO at -9.95 eV is a pi type having contribution from the C=S group to which the orbital from sulfur chiefly contributes (table 2). A similar HOMO was

Table 1. Electron population and net charges for monothioureter and 2,4-dithioureter.

Method	Electron density/net charge	Atoms*											
		N ₁	C ₂	N ₃	C ₄	S ₅	N ₆	H ₇	H ₈	H ₉	O ₁₀ /S ₁₀	H ₁₁	H ₁₂
Mtb (I) CNDO/2	σ	3.426	2.789	3.466	3.021	4.737	3.482	0.854	0.811	0.857	4.885	0.872	0.848
	π	1.831	0.758	1.725	0.685	1.699	1.727				1.527		
	net	-0.257	0.453	-0.191	0.294	-0.436	-0.209	0.146	0.189	0.143	-0.412	0.128	0.152
SCC-EH	σ	3.355	2.648	3.439	2.906	4.833	3.407	0.910	0.903	0.892	5.035	0.888	0.888
	π	1.647	1.142	1.553	1.091	1.431	1.659				1.477		
	net	-0.002	0.210	0.008	0.003	-0.264	-0.066	0.090	0.097	0.108	-0.512	0.112	0.112
Dtb CNDO/2	σ	3.441	3.006	3.462	3.012	4.735	3.460	0.843	0.832	0.857	4.765	0.861	0.837
	π	1.755	0.715	1.675	0.698	1.694	1.725				1.627		
	net	-0.196	0.279	-0.137	0.290	-0.429	-0.185	0.157	0.168	0.143	-0.392	0.139	0.163
SCC-EH	σ	3.383	2.808	3.473	2.804	4.843	3.407	0.908	0.877	0.891	4.816	0.902	0.892
	π	1.681	1.096	1.564	1.099	1.458	1.656				1.445		
	net	-0.064	0.096	-0.037	0.097	-0.301	-0.063	0.092	0.123	0.109	-0.261	0.098	0.108

* The numbering of the atoms is given in Figure 1.

Table 2. First few HOMOs of monothioibiuret and 2,4-dithioibiuret.

Mtb				Dtb			
SCC-EH		CNDO/2		SCC-EH		CNDO/2	
Energy value (eV)	Assignment	Energy value (eV)	Assignment	Energy value (eV)	Assignment	Energy value (eV)	Assignment
- 8.72	$n(S)$	-10.14	$\pi(CS)$	- 8.01	$n(S)$	-10.39	$\pi(CS)$
- 9.35	$n(O)$	-10.24	$n(S)$	- 8.44	$n(S)$	-10.62	$n(S)$
- 9.95	$\pi(CS)$	-12.85	$n(O)$	- 9.44	$\pi(CS)$	-11.13	$n(S)$
-11.29	$\pi(CO)$	-14.02	$\pi(CO)$	-10.22	$\pi(CS)$	-11.40	$\pi(CS)$
-11.53	σ	-15.35	σ	-11.27	σ	-14.51	σ

noted for thioformamide (Kimura *et al* 1976). The HOMO at -11.29 eV is a pi type bonding orbital in the C=O region having contribution mainly from the oxygen atom, and amides were found to have a similar type HOMO (Sweigart and Turner 1972). Thus the general pattern of the HOMOs reveals that the molecule, Mtb, still retains the independent characteristics of a thioamide and an amide group and this feature is reflected in its electronic spectrum too.

Dtb is calculated to have the first five HOMOs at -8.01 , -8.44 , -9.44 , -10.22 and -11.27 eV. The first and second HOMOs at -8.01 and -8.44 eV comparable to the first HOMO of Mtb were found to originate mainly from the non-bonding orbitals of sulfur atoms respectively in the cis and trans positions to the NH group. The first two HOMOs of Dtb are thus similar to the first HOMO of thioamides and thioureas (Mines and Thompson 1975). The next two HOMOs at -9.44 and -10.22 eV are pi type being bonding in both the C=S regions having major contribution respectively from the sulphur atom of the cis and trans C=S moieties. Thus the HOMOs of Dtb indicate moderately interacting thioamide groups.

4.3. Electronic spectra

Table 3 contains the observed and calculated singlet transition energies (from the PPP-LCI method) and oscillator strengths for Mtb and Dtb. As seen from the figures presented in table 3, the calculated values of the transition energies are in good agreement with the experimental data.

The electronic spectrum of Mtb in aqueous solution shows two intense bands in the ultraviolet region at 256 and 206 nm. On the basis of the PPP-LCI molecular orbital calculations, the band at 256 nm may be assigned to a $\pi(C=S) \rightarrow \pi^*(C=S)$ transition and the one at 206 nm as arising from a $\pi(C=O) \rightarrow \pi^*(C=O)$ transition. Thus the observed bands of Mtb are almost localised transi-

Table 3. Electronic spectral transitions for monothioureter and 2,4-dithioureter.

Assignment	Mtb		Dtb	
	Calculated λ_{\max} (nm) f	Observed λ_{\max} (nm) f	Calculated λ_{\max} (nm) f	Observed λ_{\max} (nm) f
π (C=S) \rightarrow π^* (C=S)	257 0.216	256 0.108	π (C-S) \rightarrow π^* (C-S)	281 0.037
π (C=O) \rightarrow π^* (C=O)	219 0.323	206 0.195	π (C-S) \rightarrow π^* (NCS)	248 0.086
			π (N) \rightarrow π^* (1)	231 0.120
			π (N) \rightarrow π^* (2)	213 0.110

tions due to the C=S and C=O chromophores as in thioacetamide and acetamide respectively at 261 nm (Barrett and Deghaidy 1975) and at 200 nm (Kaya and Nagakura 1967). It may thus be noted as mentioned earlier that the interaction between the amide and thioamide groups of Mtb is weak.

The electronic spectrum of Dtb in aqueous medium exhibits four bands at 281, 248, 231 and 213 nm. The PPP-LCI calculations suggest that the 280 nm band of Dtb may be attributed to the π (C=S) \rightarrow π^* (C=S) transition. Further, according to the calculation, the observed band at 248 nm may be assigned to a combination of two transitions, one from a localised π (C=S) group to the second antibonding orbital and the other from a delocalized π (NCS) orbital to the first antibonding orbital. The third band observed at 230 nm may be attributed to a transition from a pi orbital consisting mainly of nitrogen lone pairs to the first antibonding orbital, π (N) \rightarrow π^* (1). The remaining band at 215 nm may be assigned to the π (N) \rightarrow π^* (2) transition. It is easily found that unlike Mtb, Dtb exhibits transitions besides those localised on the thioamide moieties. Thus the interaction between two thioamide groups seems to be strong in Dtb.

4.4. Conformational stability

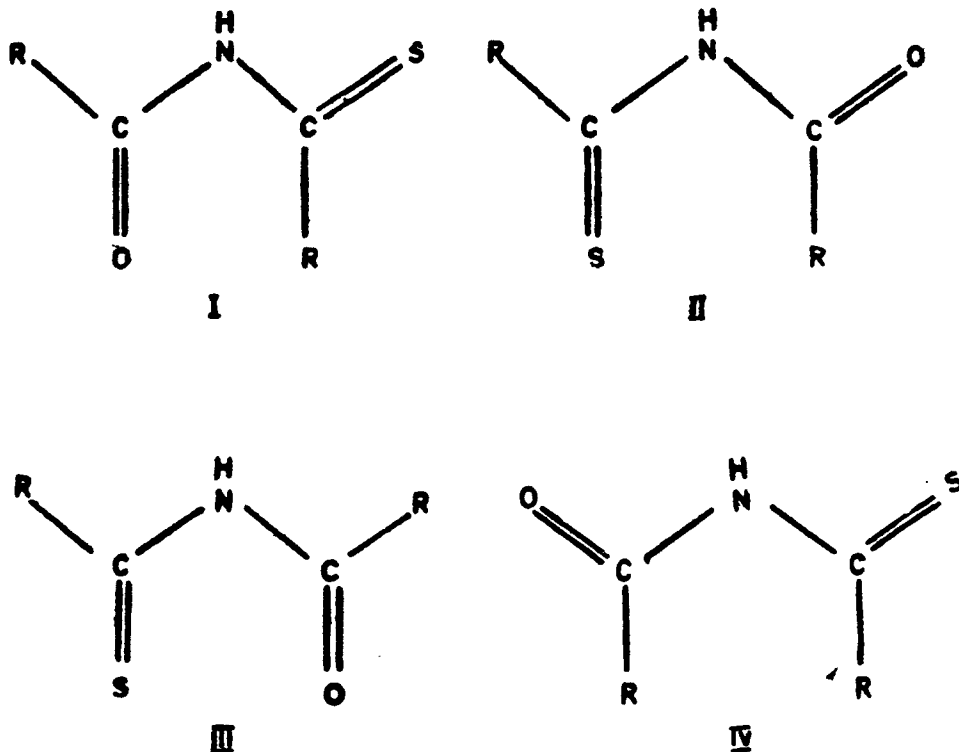
The stability of the planar trans-cis-CONHCS-form is probably mainly caused by three different effects, namely, conjugation, electrostatic interaction and hydrogen bonding.

The co-planarity of Mtb allows maximum overlap between the π -orbitals and thus result in extra stabilisation. Conjugation may thus explain the preference of the planar forms but does not account for the stability of the trans-cis or cis-trans forms over the others. The dipolar interaction effects (Marsden and Sutton 1936) may be a main factor in stabilising the trans-cis forms. The trans-cis orientation would result in the C=O and C=S bond dipoles being nearly anti-parallel minimising the dipolar interactions. Recently, Wennerstrom *et al* (1972) have suggested that the energy differences between the conformers may be interpreted as chiefly due to an electrostatic effect instead of interactions between bond dipoles. The total electrostatic energies computed following their method were -6.18 and -6.64 eV from the CNDO/2 and -1.92 and -1.75 eV from the SCC-EH methods for Mtb I and II respectively. Since the SCC-EH method yields more realistic net charges on atomic centers, the results derived from the latter method may be preferred and hence the conformation I for Mtb.

The calculated total energies for the three conformations I, II and III of Mtb by the CNDO/2 method are -82.299 , -82.252 and -79.223 au and the total orbital energies by the SCC-EH method are -361.217 , -358.010 and -353.654 eV, respectively. Both the CNDO/2 and SCC-EH treatments thus clearly suggest the trans-cis-CONHCS-form (I) of Mtb to be more stable. According to the CNDO/2 results, conformation I is more stable than the other trans-cis structure (II) by 29.1 kcal/mol.

It is known that intramolecular hydrogen bonding is strong in biuret (O...H-N) and weak in dithiobiuret (S...H-N). Further, studies on thiourea derivatives have revealed that the -NH group forms a relatively stronger intermolecular hydrogen bond with the C=S group than the -NH₂ group (Bonamico *et al* 1971) and also, thiourea derivatives exhibit greater degree of intermolecular hydrogen

bonding than urea derivatives (Aitken *et al* 1971). Judging from these considerations and also from the fact that the geometry of the molecule has a favourable O...H-N distance for intramolecular hydrogen bonding, it may be inferred that for Mtb structure I is probably more stable than structure II.



The proton NMR spectrum of Mtb consists of five signals at 9.74, 9.50, 8.92, 6.90 and 6.34 δ with equal intensities. The spectrum of Dtb, on the other hand, has only three peaks, at 10.61, 9.48 and 9.20 δ , in the intensity ratios 1 : 2 : 2. It thus appears that while there are five distinct protons in Mtb, only three different types of protons are present in Dtb. Since Dtb does not form strong S...H-N intramolecular hydrogen bonding, it is tempting to conclude that structure I of Mtb, which is favourable for strong intramolecular O...H-N hydrogen bonding, as explained earlier, may be preferred. This structure is also in accord with that previously suggested by Geetharani and Sathyanarayana (1976) on the basis of normal coordinate calculations performed for different conformations of Mtb.

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