

Notes

Conformations of Thioacetylurea & Its Sulphur Analog—A CNDO/2 Study

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The total energies of thioacetylurea and its sulphur analog calculated using CNDO/2 method reveal that the most stable conformation for both compounds is the *trans-cis* form. The electronic indices of the two compounds indicate that the charge on the ureido group becomes less on substituting sulphur.

Studies on conformations of substituted thioureas¹⁻⁵ reveal the existence of several forms, *cis-cis*, *cis-trans*, *trans-cis*, *trans-trans*, the relative proportions of which depend mainly on the substituents. The conformational preferences and electronic structure of N-acetylthiourea and its oxygen analog have been studied by us⁶. In the present work, the conformational preferences of thioacetylurea (TAU) and its sulphur analog thioacetylthiourea (TATU) have been studied using CNDO/2 procedure⁷. The computed bond orders and electron populations are employed to discuss the electronic structure. Four planar conformations may be conceived for TAU/TATU (Fig. 1). The calculations have been performed on both TAU and TATU to know the electronic effects of amide/thioamide grouping.

The calculations have been made using the CNDO/2 method⁷. For the sulphur atom the 3d-orbitals have been included in the basis set. Since the crystal structure is not known for these compounds, the structural parameters have been transferred from

Table 1—Calculated Total Molecular Energies of TAU and TATU

Conformation	TAU		TATU	
	Total energy ^a	Difference ^b	Total energy ^a	Difference ^b
<i>trans-cis</i>	-78.4804	0.0	-85.9785	0.0
<i>trans-trans</i>	-78.4748	3.51	-85.9679	6.25
<i>cis-trans</i>	-78.4635	10.61	-85.9407	23.72
<i>cis-cis</i>	-78.4577	14.24	-85.9091	43.35

^(a)Hartree; ^(b)kcal mol⁻¹

acetylurea⁸ and the C-S distance taken from thioacetamide⁹. The total molecular energy has been calculated for the four planar conformations of TAU and TATU (Fig. 1) assuming the bond lengths and bond angles to remain the same during internal rotation. The standard program of Pople and Beveridge has been employed¹⁰.

The calculated total energies (Table 1) reveal that the most stable conformation accessible to TAU is the *trans-cis* (Fig. 1). The next stable conformation is *trans-trans* which lies only some 3.51 kcal mol⁻¹ above the lowest energy conformation. The calculations indicate the same trend for TATU. The results interestingly reveal that only a small activation energy is required for the conversion of *cis-trans* to *trans-trans* form. The preference of one form or the other, can however, be affected by such factors as solvent and solid state interactions which are not taken into account in the present calculations. The calculations further indicate that *trans-cis* structure is stabilized over the other structures in the solid state. The large dipole-dipole interaction between the C=S dipoles is minimized in the *trans-cis* rotamer, so also the steric hindrance.

In Table 2, δ - and π -electron densities and the net electron population are presented for TAU and TATU. While the electron densities quoted for a single molecule may not be a good guide, comparison between related molecules by the same procedure of calculation may be more reliable.

On comparing TAU with TATU, we find less electron populations for the atoms of the thioureido group excepting for the amide X(O/S) atom, for which the reverse is true. This observation compares favourably with the results obtained for N-acetylthiourea and its oxygen analog⁶. This indicates as expected, increased delocalization in the thioureido group suggesting an increased contribution from

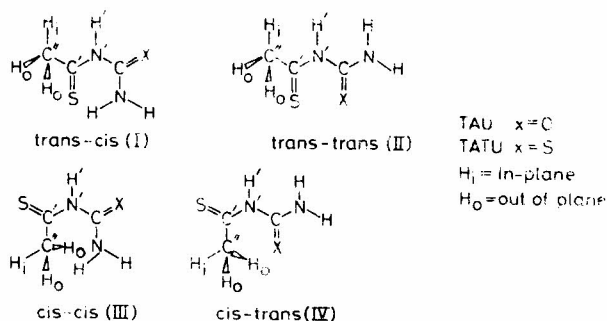


Fig. 1—Planar conformations of TAU/TATU

Table 2—Electron Populations and π -Bond Orders for TAU and TATU

Atom	Electron population						π -bond order	
	TAU			TATU			Bond TAU	TATU
	σ	π	Total	σ	π	Total		
H ₁	0.8800	—	0.8800	0.8878	—	0.8878	C—N 0.519	0.557
H ₂	0.8506	—	0.8506	0.8434	—	0.8434	C=X 0.789	0.578
N	3.4199	1.8515	5.2714	3.3477	1.7545	5.1022	C—N 0.381	0.501
C	2.7526	0.7943	3.5469	2.9334	0.7242	3.6576	C'—N 0.422	0.376
X	4.8733	1.4687	6.3420	4.7591	1.6878	6.4469	C=S 0.720	0.703
N'	3.4790	1.6441	5.1231	3.4762	1.6032	5.0794	C—C 0.261	0.263
H'	0.8926	—	0.8926	0.9014	—	0.9014		
C'	3.0788	0.7431	3.8219	3.0331	0.8023	3.8354		
S	4.8521	1.4668	6.3209	4.9304	1.3539	6.2843		
C''	3.0427	0.9978	4.0405	3.0329	1.0095	4.0424		
H _i	0.9975	—	0.9975	0.9986	—	0.9986		
H _o	0.9563	—	0.9563	0.9563	—	0.9563		

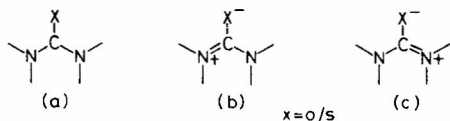


Fig. 2—Resonance structures

resonance structures (b) and (c) to the description of bonding of TATU over that in TAU (Fig. 2). This result is clearly borne out by the values of π -bond orders. Table 2 demonstrates that there is a significant decrease in the C=S (X) bond order in TATU as compared to that in TAU with consequent increase in the C-N (and C-N') bond orders. The low C-C bond orders indicate that these hardly contribute to the conjugation in TAU or TATU while C'-N' acquires slight π -bond character. These values may be useful indices for studying intermolecular and intramolecular hydrogen bonding in TATU and TAU.

In conclusion, since we are primarily interested in the ground state properties of the compounds, the CNDO procedure seems to be most promising.

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