

Ab initio STUDY OF THE CONFIGURATION AND PROTONATION OF THIOCARBAMIC ACID

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Received March 14, 1988

Accepted May 2, 1988

The *ab initio* SCF method was applied to a conformation study of thiocarbamic acid. The 3-21G calculations revealed that the *trans* isomer with the O—H···S intramolecular hydrogen bond is more stable than the *cis* isomer. The calculated rotational barrier for the rotation about the central C—N bond is very high, 125.5 kJ mol⁻¹; this value, however, decreased to 106.2 kJ . mol⁻¹ by electron correlation determined at the 2nd order Moller-Plesset perturbation level. Proton affinities for the protonation of the electronegative atoms in the acid increase in the order of the atoms N, O and S. Changes in the Mulliken gross atomic populations are examined in dependence on the configuration and protonation of the acid.

The conformation and protonation properties of and hydrogen bonds in carbamic acid and its alkyl, vinyl and aryl substituted derivatives have been studied previously¹⁻⁴ using *ab initio* SCF calculations at various levels. In this work we examine how the conformational properties of the carbamate group are affected by replacement of the oxygen atom in the carbonyl group by a sulfur atom, namely, by applying the calculations to thiocarbamic acid. The energies of protonation of the electronegative atoms in this compound are also calculated.

CALCULATIONS

The equilibrium geometries, rotational barriers and proton affinities were calculated by the *ab initio* SCF method. Similarly as previously⁴, the protonation energies were calculated for the completely optimized geometries of the two neutral as well as protonated species. Protonation perpendicular to the molecular plane was considered for the optimization of the form ionized at the nitrogen atom (dihedral angle $\Phi(S_1C_2N_3H_8) = 90^\circ$; for the atom labelling see Fig. 1). The remaining structures were optimized with the C_s symmetry preserved. The gradient optimization technique was applied using the 3-21G basis^{5,6}; during the study of the equilibrium geometry of carbamic acid², this basis gave results comparable with those obtained with the more extended 6-31G* basis. The correlation energy was calculated using the 2nd order Moller-Plesset (MP2) perturbation theory^{7,8}. The rotational barriers with respect to rotation about the C—N bond were determined as the energy

differences between the planar equilibrium geometry and the optimized orthogonal structure with the dihedral angle $\Phi(S_1C_2N_3H_4) = 90^\circ$. The calculations were performed on an EC 1045 computer using the GAUSSIAN 80 program⁹.

RESULTS AND DISCUSSION

The hydrogen atom of the hydroxy group in thiocarbamic acid can be *cis* or *trans* with respect to the nitrogen atom (Fig. 1.). The optimized geometries of the two configurations are given in Table I. The data demonstrate that the C—N and C—O bonds are longer in the *cis* form than in the *trans* form, whereas the C=S bond is somewhat (1.0 pm) shorter in the former than in the latter form. The N—H and O—H bond lengths are nearly the same in the two forms. The bond angles also differ considerably: the $N_3C_2O_6$ angle is 4.8° and the $C_2O_6H_7$ angle, 4.5° larger in the *cis* form than in the *trans* form, whereas the $N_3C_2S_1$ and $C_2N_3H_5$ angles are

TABLE I
Optimized geometries of *trans* and *cis* thiocarbamic acid (with respect to the nitrogen atom)

Bond length pm	<i>trans</i> ^a		<i>cis</i> ^b		Bond angle deg	<i>trans</i> ^a		<i>cis</i> ^b	
	$\Phi = 0^\circ$	$\Phi = 90^\circ$	$\Phi = 0^\circ$	$\Phi = 90^\circ$		$\Phi = 0^\circ$	$\Phi = 90^\circ$	$\Phi = 0^\circ$	$\Phi = 90^\circ$
C_2S_1	172.3	168.3	171.3	166.6	$N_3C_2S_1$	125.6	125.8	132.0	125.4
C_2N_3	131.3	138.2	133.0	139.9	$N_3C_2O_6$	111.8	112.8	116.6	114.5
C_2O_6	133.7	133.4	134.1	134.2	$C_2N_3H_4$	119.9	120.3	123.7	120.4
N_3H_4	99.9	99.6	99.9	99.8	$C_2N_3H_5$	120.2	120.3	118.5	120.4
N_3H_5	99.7	99.6	99.8	99.8	$C_2O_6H_7$	112.1	112.9	116.6	112.2
O_6H_7	96.7	96.8	96.8	96.9					

— E^{SCF} (a.u.): ^a *trans*, $\Phi = 0^\circ$: 563.566; *trans*, $\Phi = 90^\circ$: 563.519; ^b *cis*, $\Phi = 0^\circ$: 563.546; *cis*, $\Phi = 90^\circ$: 563.513 (1 a.u. = 2 625.50 kJ mol⁻¹).

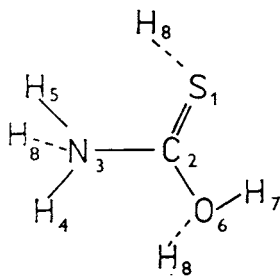


FIG. 1
Structure of and atom labelling in thiocarbamic acid

smaller in the *cis* form than in the *trans* form. The major differences are clearly due to the steric repulsion between the hydrogen atoms in the *cis* conformer.

For investigating the effect of the bond rotation on the geometry, the equilibrium geometries of the orthogonal conformers (dihedral angle $\Phi(\text{H}_4\text{N}_3\text{C}_2\text{S}_1) = 90^\circ$) of the two isomers were also calculated (Table I). The two conformers represent the transition state for the rotation about the C—N bond. The disturbed conjugation between the C—N and C=S bonds in the two orthogonal structures is associated with a C=S bond shortening and an appreciable (6.9 pm) C—N bond lengthening. The differences in the bond angles between the orthogonal conformer and the planar *trans* conformer are negligible (Table I), whereas for the *cis* form the rotation about the C—N bond is associated with considerable changes in the bond angles, whose values approach those calculated for the transition state of the *trans* form.

According to our 3-21G calculations, the *trans* form of thiocarbamic acid is more stable than the *cis* form (Table I), similarly as for carbamic acid². The energy difference in the stability of the transition states of the two forms is only 16.4 kJ mol⁻¹, whereas the differences in the energies of the planar *cis* and *trans* forms is exceedingly high, viz. 53.3 kJ mol⁻¹ (by 3-21G//3-21G calculation) or 50.1 kJ mol⁻¹ (by MP2//3-21G//3-21G calculation). Inclusion of electron correlation reduces this *cis*–*trans* energy difference by mere 3.2 kJ mol⁻¹. For carbamic acid, the energy difference between the *cis* and *trans* forms is slightly lower, viz. 44.7 kJ mol⁻¹ (3-21G//3-21G calculation). The higher stability of the *trans* form of thiocarbamic acid in comparison with the *cis* form can be ascribed to the occurrence of the O—H···S intramolecular hydrogen bond in the former ($R_{\text{S}\cdots\text{H}} = 268.7$ pm), which is stronger than the analogous O—H···O hydrogen bond in carbamic acid. A higher stability of the O—H···S intramolecular hydrogen bond as compared to the O—H···O bond has been also found by quantum chemical calculations for 1,2-benzenediol and 2-hydroxybenzenethiol¹⁰.

The energy difference between the geometries of the planar and orthogonal structures of *trans* and *cis* thiocarbamic acid, considered as the barriers of rotation about the C—N bond, are given in Table II. The data in parentheses, obtained using the rigid rotor approximation, represent the upper limits of the barrier calculated using the same bond lengths and angles for the planar and orthogonal conformers. A considerably higher rotational barrier emerges for the *trans* form (Table II). This barrier is lowered considerably, 15 to 20%, by electronic correlation at the MP2 level; however, in view of the small dimension of the basis used, this effect of the electron correlation on the rotational barrier height can be only regarded as a crude estimate. 3-21G calculation for *trans* carbamic acid² gave a value of 88.6 kJ mol⁻¹; hence, replacement of the oxygen atom in the carbonyl group by sulfur brings about stabilization of the planar conformer as compared to the orthogonal conformer. Of simpler thiocarbamates, the rotational barrier has been determined by NMR spectroscopic measurements for methyl-N,N-dimethylthiocarbamate¹¹; the barrier height values lay between 72 and 85 kJ mol⁻¹ according to the data handling procedure used.

Proton Affinities

Proton affinities for the protonation of thiocarbamic acid are given in Table III. Protonation of the C=S group can occur in both the *cis* and *trans* positions with respect to the nitrogen atom (Fig. 1). Since *ab initio* calculations for the analogous protonation of the carbonyl group oxygen in carbamic acid⁴ revealed that the *cis* form is the more stable one, protonation of the C=S group in thiocarbamic acid is studied for the *cis* form only in this work. The proton affinities *PA* for the protonation of the nitrogen, oxygen and sulfur atoms in this compound increase in order $PA(N) < PA(O) < PA(S)$. The absolute values of the gross atomic negative charges decrease in this order, viz. -0.888 , -0.701 and -0.098 e for N, O and S, respectively. Thus, protonation at a less electronegative atom leads to a more stable ion. Although the sulfur atom in the C=S group is the most suitable site for protonation of the thiocarbamate group, the absolute proton affinity value for this atom (Table III) is lower than that for the protonation of the oxygen atom of the C=O group in carbamic acid⁴ ($864.1 \text{ kJ mol}^{-1}$ by 3-21G//3-21G calculation).

Since protonation can result in appreciable changes in the geometry, particularly in the vicinity of the protonation site, the geometries of the ionized forms of thiocarbamic acid were also optimized (Table IV). The major effect of the C—X··H protonation (X = N, O, S) is a considerable lengthening of the C—X bond. The

TABLE II

Ab initio calculated rotational barriers (in kJ mol^{-1}) for the *cis* and *trans* isomers of thiocarbamic acid (with respect to the nitrogen atom)

Isomer	3-21G//3-21G ^a	MP2/3-21G//3-21G
<i>Trans</i>	125.2 (139.9)	106.2
<i>Cis</i>	88.3 (104.0)	69.2

^a Barriers calculated by using the rigid rotor approximation are given in parentheses.

TABLE III

Ab initio calculated proton affinities for the protonation of thiocarbamic acid

Protonation site (atom)	Nitrogen	Oxygen	Sulfur
Proton affinity, kJ mol^{-1}	638.8	706.3	807.2

values of the X...H length increase in order $R(\text{OH}) < R(\text{NH}) < R(\text{SH})$. The N—H and O—H bond lengths are only slightly affected by the protonation. Bond angles are subject to higher or lower changes in the various protonated species according to the protonation site.

TABLE IV

Optimized geometries of protonated thiocarbamic acid species

Bond length pm	Protonation site ^a			Bond angle deg	Protonation site ^a		
	N	O	S		N	O	S
C ₂ S ₁	163.0	164.4	179.9	N ₃ C ₂ S ₁	121.4	137.3	125.9
C ₂ N ₃	152.5	129.9	128.5	N ₃ C ₂ O ₆	104.0	108.8	115.9
C ₂ O ₆	130.7	153.2	130.1	C ₂ N ₃ H ₄	119.1	125.6	118.6
N ₃ H ₄	102.7	100.3	100.9	C ₂ N ₃ H ₅	120.0	118.2	124.3
N ₃ H ₅	102.5	100.6	100.2	C ₂ O ₆ H ₇	117.4	114.3	120.6
O ₆ H ₇	97.4	98.2	97.2	C ₂ N ₃ H ₈	91.9	—	—
N ₃ H ₈	106.3	—	—	C ₂ O ₆ H ₈	—	128.2	—
O ₆ H ₈	—	97.9	—	C ₂ S ₁ H ₈	—	—	98.3
S ₁ H ₈	—	—	134.9				

^a $-E^{\text{CSF}} = 563.810, 563.836$ and 563.874 a.u., respectively (1 a.u. = 2 625.50 kJ mol⁻¹).

TABLE V

Gross atomic charges calculated for thiocarbamic acid and its protonated species

Atom	Thiocarbamic acid		Protonated species		
	<i>trans</i> ^a	<i>cis</i> ^a	N	O	S
S1	-0.098	-0.042	0.386	0.326	0.402
C2	0.444	0.433	0.229	0.326	0.573
N3	-0.887	-0.899	-0.853	-0.904	-0.863
H4	0.388	0.361	0.485	0.425	0.458
H5	0.402	0.409	0.484	0.462	0.440
O6	-0.701	-0.667	-0.674	-0.719	-0.665
H7	0.452	0.405	0.506	0.554	0.505
H8	—	—	0.437	0.531	0.150

^a With respect to nitrogen atom.

Charge Distribution

The 3-21G gross atomic charges for *trans* and *cis* thiocarbamic acid and its ionized forms are given in Table V. The higher stability of the *trans* form with respect to the *cis* form is ascribed to the occurrence of the intramolecular hydrogen bond in the former. Since formation of hydrogen bonds is associated with changes in the Mulliken gross electronic population^{10,12,13}, changes in the atomic populations of atoms involved in the S··H—O hydrogen bond are of particular interest. The two electronegative atoms, sulfur and oxygen, possess higher negative charges in the *trans* isomer, whereas the H₇ hydrogen has a lower electron density than in the *cis* form. Such atomic redistribution being characteristic of the formation of intermolecular or intramolecular hydrogen bonds^{12,13}, the data obtained confirm the occurrence of the C=S··H—O four-membered ring intramolecular hydrogen bond in the *trans* form of thiocarbamic acid.

Protonation brings about a considerable charge redistribution in the acid (Table V). The highest change is observed at the sulfur atom, which is slightly electronegative (−0.098 e) in the nonionized acid and highly electropositive in the three protonated forms; invariably, negative charge is transferred from the acid to the proton, the charge transfer being highest in the case of protonation of sulfur.

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Translated by P. Adámek.