Preparation, NMR, Raman, and DFT/IGLO/GIAO-MP2 Study of Mono- and Diprotonated Thiourea and Theoretical Investigation of Triprotonated Thiourea[1]

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Abstract: Mono-, di-, and triprotonation of thiourea $(H_2N)_2CS$, was studied by low-temperature ^1H, ^{13}C, and ^{15}N NMR spectroscopy in superacidic systems. In FSO_3H/SO_2ClF at -80 °C, thiourea is monoprotonated exclusively at the sulfur atom giving rise to $[(H_2N)_2CSH]^+$. The addition of SbF_5 to this system increases the acidity of the solution and results in the observation of the diprotonated species $[H_3NC(SH)NH_2]^{2+}$. No NMR evidence was found for triprotonation under these conditions, although a limited equilibrium should not necessarily be detected. The dication was isolated as its AsF_6^- salt at -64 °C and decomposes at room temperature to AsF_5, HF, and $[(NH_2)_2CSH]^+AsF_6^-$. The mono- and the diprotonated AsF_6^- salts were characterized in the solid state by low-temperature Raman spectroscopy, and vibrational assignments are given for both cations. The experimental results and spectroscopic data were confirmed by density functional theory methods at the B3LYP/6-31G* level. Whereas the mono- and diprotonated ions are thermodynamically stable, the triprotonated ion is only kinetically stable. Deprotonation of triprotonated thiourea to the diprotonated species is exothermic by 76.3 kcal/mol but displays a high kinetic barrier (51.1 kcal/mol).

Introduction

Thiourea, the thiocarbonyl analogue of urea, is one of the simplest organic molecules containing a thioamide group, and its structure and properties have been studied extensively by various experimental and theoretical techniques.[2,3,4] In biochemistry, considerable interest has been focused on the role of the thioamide group, as it is a fundamental building block in the skeleton of thiopurines and thiopyrimidines.[5,6] Extensive work has been done on the protonation of thiourea in aqueous solutions. It has been known since the middle of the 19th century that thiourea forms 1:1 compounds with strong acids such as HCl and H_2SO_4.[7] There are two possible structures for monoprotonated thiourea, the sulfonium form **I** and the ammonium form **II**, and the preferred site of protonation has
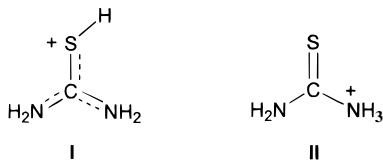
remained controversial for a long time.[8] On theoretical grounds the sulfonium structure **I** should be preferred because of its

resonance stabilization. However, on the basis of the infrared spectra of thiouronium salts in the solid state, Spinner had suggested N-protonation of thiourea.[9] On the other hand, ^1H NMR of the salts in solution indicated protonation on the sulfur atom.[10,11] In subsequent UV and IR studies of thiouronium salts, the vibrational frequencies were reassigned in favor of the sulfonium structure **I**.[12,13] Conductivity studies of thiourea in $ClSO_3H$ were also interpreted in terms of monoprotonation on the sulfur atom.[14] Semiempirical SCF calculations have been used to demonstrate that S-protonation is energetically favored over N-protonation.[15] Recently, Murgich *et al.* have used ^{14}N nuclear quadrupole resonance (NQR) spectroscopy to support S-protonation of thiourea in solution.[16] Although in the solid state the thiouronium monocation exists in the S-protonated form **I**, as shown by X-ray diffraction data,[17] the behavior of thiourea in strong acids has not been clearly established. Birchall and Gillespie studied the proton NMR spectra of thiourea in water, CF_3COOH, H_2SO_4, and FSO_3H.[11] In H_2O and CF_3COOH solutions at 25 °C, only one line due to the NH_2 group was observed. In the more acidic solvents H_2SO_4 and FSO_3H, a new resonance appeared at about δ^1H 5.0 which was attributed to the $C=SH^+$ group and the NH_2 group signal disappeared. The observations were attributed to diprotonation, with the first proton being attached to sulfur and exchanging only very slowly with the solvent and the second proton being attached to nitrogen and exchanging rather rapidly with the solvent. Cryoscopic and conductometric studies by Paul *et al.*, however, showed that

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Table 1. Measured NMR Chemical Shifts of Thiourea and Its Mono- and Diprotonated Forms

			^{1}H NMR			^{13}C NMR $\overset{\|}{\underset{\diagdown}{C}}$	^{15}N NMR	
molecule	solvent	temp	$-NH_2$	$-NH_3^+$	$-SH^+$		$-NH_2$	$-NH_3^+$
[structure: S=C(NH₂)₂]		23				183.8^a	108.3 (t)^b	
[structure: HS⁺=C(NH₂)₂]	FSO$_3$H in SO$_2$ClF	−80	6.17 (s)		3.92 (s)	168.7	106.4 (t) ($J_{N-H} = 95$)	
[structure: HS=C(NH₂)(N⁺H₃...Ha,Hb)]	FSO$_3$H:SbF$_5$ in SO$_2$ClF	−80	8.87 (d) ($J_{N-H} = 97$), 8.41 (d) ($J_{N-H} = 101$)	7.44 (d) ($J_{N-H} = 78$)	5.39 (s)	174.8	165.8 (t)^c ($J_{N-H} = 97$)	63.6 (qt) ($J_{N-H} = 76$)

^{a} In DMSO as solvent. ^{b} In pyridine as solvent (taken from Sibi, M. B. *Magn. Res. Chem.* **1991**, *29*, 401). ^{c} For an explanation of the observed apparent multiplicity, see the text.

the extent of protonation of thiourea in $H_2S_2O_7$ is only slightly higher than one,[18] and the structural aspects of diprotonated thiourea were not further investigated since then.

The formation and structure of diprotonated thiourea, a prototype sulfur containing *gitonic* onium dication, is significant in probing the nature of superelectrophilic activation. Such activation plays an important role in strong acid catalyzed electrophilic reactions. In superelectrophilic activation, non-bonded electron pairs on onium ions are able to further interact with Brönsted or Lewis acids and in the limiting case can lead to *gitonic* dications (*i.e.*, proximal as contrasted with conventional *distonic* (distant) dications). Recently, it was suggested that such activation may play an important role in enzyme catalysis of biochemical reactions.[19] Berkessel and Thauer have reported[20] a novel type of metal-free hydrogenase that catalyzes the reversible dehydrogenation of methylene(tetrahydromethano)pterin ($CH_2=H_4MPT$) to methenyl(tetrahydromethano)-pterin (CHH_4MPT^+) and H_2. It was suggested that the amidinium ion is further activated by N-protonation in the enzyme to bind a H_2 molecule with a two-electron, three-center (2e−3c) bond.

The present experimental and theoretical study of mono-, di-, and triprotonated thiourea is therefore relevant to a better understanding of protosolvolytic activations. We have previously investigated the structures of di- and triprotonated urea,[21] diprotonated carbonic acid,[22] and the protonated guanidinium dication.[23] Herein, we report the investigation of mono-, di-, and triprotonated thiourea by NMR and Raman spectroscopy by density functional theory and by DFT/GIAO-MP2/IGLO calculations.

Results and Discussion

Preparation and ^{1}H, ^{13}C, and ^{15}N NMR Spectra of Mono- and Diprotonated Thiourea in Superacids. ^{15}N-enriched thiourea was reacted with an excess of FSO$_3$H in SO$_2$ClF as the solvent at −80 °C, and the resulting mixture was investigated by ^{1}H, ^{13}C, and ^{15}N NMR spectroscopy (see Table 1). Under these conditions, only sulfur-monoprotonated thiourea (thiouronium ion **3**) was observed, which is characterized by a shielding of 8 ppm in the ^{13}C NMR spectrum ($\delta^{13}C_{exp}$ 168.7) as compared to neutral thiourea ($\delta^{13}C_{exp}$ 176.7). Although some

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of this shielding difference might be due to solvent and temperature effects, it can be rationalized by an increase in resonance stabilization in **3** upon protonation. The ^{15}N NMR spectrum of the solution consists of one triplet at $\delta^{15}N_{exp}$ 106.4 ($J_{N-H} = 95$ Hz), which is shielded by 1.9 ppm as compared to neutral thiourea ($\delta^{15}N_{exp}$ 108.3). The magnetic equivalence of both nitrogen atoms, even at −80 °C, is attributed to rapid proton exchange between FSO$_3$H and the C=SH group in the planar minimum energy structure of C_s symmetry (see Figure 1). The alternative explanation of essentially free rotation of the SH group around the C−S bond is less likely in view of its partial double-bond character.
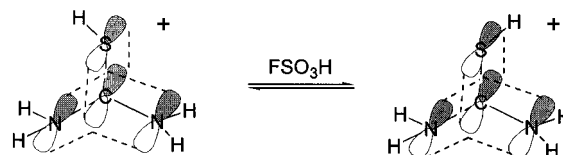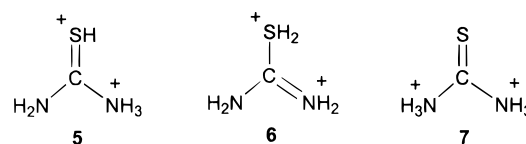

Protonation of thiourea under these conditions thus occurs on the sulfur atom resulting in a planar, resonance stabilized thiouronium ion **3** (eq 1). Our results are in contrast to the

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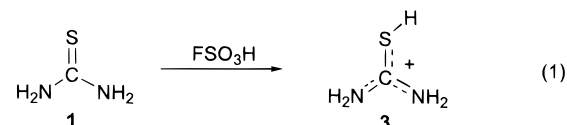
previous[11] report of Gillespie *et al.*, who, on the basis of their ^{1}H NMR studies, had suggested diprotonation of thiourea in fluorosulfuric acid FSO$_3$H.

When more acidic FSO$_3$H:SbF$_5$ ($H_0 = -22$) is used in the place of FSO$_3$H ($H_0 = -15$) at −80 °C with SO$_2$ClF as the solvent, thiourea is readily diprotonated and the resulting dication could be observed by ^{1}H, ^{13}C, and ^{15}N NMR spectroscopy. In theory, protonation of the thiouronium ion **3** can yield three different dications: the N,S-diprotonated structure **5**, the S,S-diprotonated structure **6**, or the N,N-diprotonated structure **7**.

Only the N,S-diprotonated structure **5** was observed by NMR spectroscopy (see Table 1). This dication ($\delta^{13}C_{exp}$ 174.8) is characterized by a deshielding of 6.1 ppm at the thiocarbonyl carbon with respect to thiouronium ion **3** ($\delta^{13}C_{exp}$ 168.7). This
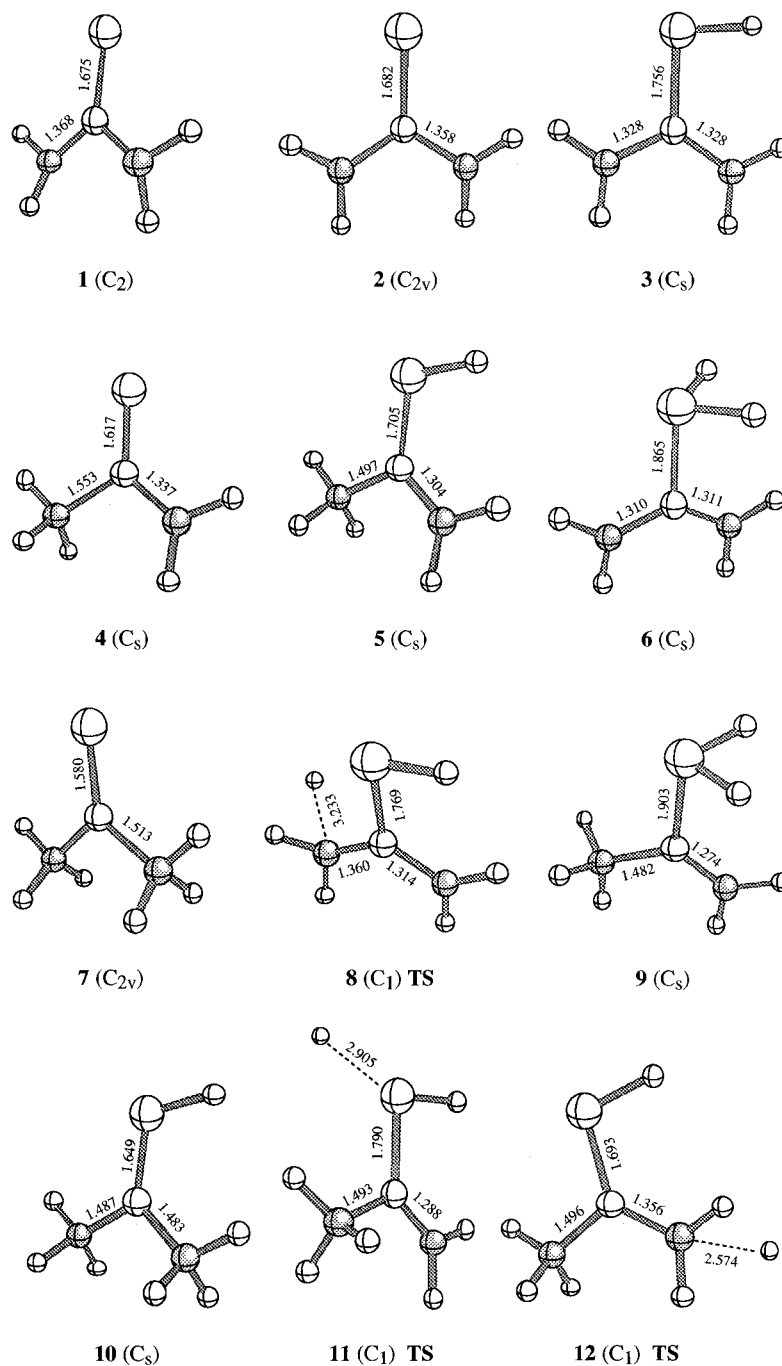
Figure 1. B3LYP/6-31G*-optimized geometries of thiourea and its mono-, di-, and triprotonated forms.

deshielding effect can be attributed to a decrease in resonance stabilization when going from the monocation to the dication, since the NH$_3$ group can no longer participate in the resonance stabilization due to the lack of a free valence electron pair on its nitrogen atom. The ^{1}H NMR spectrum of the solution showed three groups of peaks at δ^1H$_{exp}$ 8.64 (t), 7.44 (d), and 5.39 (s) of relative areas of 2:3:1 which may be assigned to the NH$_2$, NH$_3$, and SH protons, respectively. The ^{15}N NMR spectrum of the solution at -80 °C exhibits an unresolved doublet of doublets centered at δ^{15}N$_{exp}$ 165.8 ($J_{N-H} \sim 97$ Hz) which, due to the similarity of the two coupling constants involved, gives the appearance of a triplet and a quartet centered at δ^{15}N$_{exp}$ 63.6 ($J_{N-H} \sim 76$ Hz) which correspond to the NH$_2$ and NH$_3$ groups, respectively. Therefore, in FSO$_3$H:SbF$_5$ solution, thiourea undergoes diprotonation involving the sulfur and one of the nitrogen atoms (eq 2).
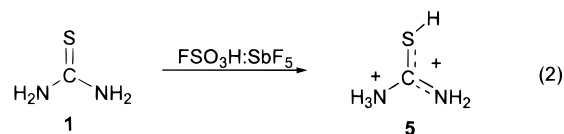
No evidence for triprotonation was observed under these conditions, even in the presence of a large excess of SbF$_5$. There could, however, be a limited equilibrium present in the system, which not necessarily would be detectable by NMR spectroscopy.

Preparation and Properties of Solid [(H$_2$N)$_2$CSH]$^+$AsF$_6^-$ and [H$_3$NC(SH)NH$_2$]$^{2+}$2AsF$_6^-$ Salts. The reaction of thiourea with a large excess of AsF$_5$ in anhydrous HF solution at -64 °C, followed by removal of the excess AsF$_5$ and HF at the same temperature, produces solid [H$_3$NC(SH)NH$_2$]$^{2+}$·2AsF$_6^-$ in quantitative yield (eq 3). The resulting white solid is stable at -64 °C and has a dissociation pressure of about 15 Torr at 21

$$(H_2N)_2CS + 2AsF_5 + 2HF \xrightarrow[-64\,°C]{HF}$$
$$[H_3NC(SH)NH_2]^{2+}\cdot2AsF_6^- \quad (3)$$
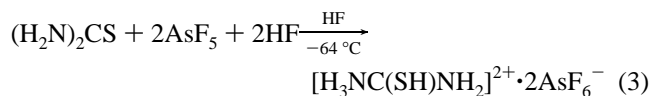
°C. At room temperature, it decomposes with the loss of 1 mol of HF and AsF_5 to give $(H_2N)_2CSH^+AsF_6^-$ (eq 4). The

$$[H_3NC(SH)NH_2]^{2+}\cdot2AsF_6^- \xrightarrow{21\,°C}$$
$$(H_2N)_2CSH^+AsF_6^- + HF + AsF_5 \quad (4)$$
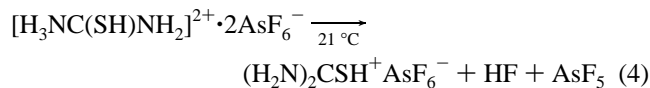
monoprotonated AsF_6^- salt is a white solid which is stable at room temperature. The structures of the di- and monoprotonated salts were confirmed by low-temperature Raman spectroscopy.

Raman Spectra of Solid [(H2N)2CSH]+AsF6− and [H3NC-(SH)NH2]2+·2AsF6−. The Raman spectra of thiourea and its mono- and diprotonated AsF_6^- salts were recorded at −110 °C. The observed frequencies and their assignments are summarized in Tables 2−4. The vibrational analysis of thiourea Table 2 is difficult due to the very small energy differences between the transoid, cissoid, and planar structures and the strong influence these structural changes can have on the lower frequency deformation modes and their intensities.[4] Furthermore, a thorough normal coordinate analysis has shown that most of the lower frequency modes are strongly mixed.[24] Also, the calculated frequencies are harmonic values for the gaseous molecule, while the observed values are anharmonic frequencies of the solid which is strongly hydrogen bridged and, as a result, exhibits an unusually long C−S bond distance of 1.746 Å.[25] These solid state effects also result in thiourea being planar in the solid phase, while the theoretical calculations for the free gaseous molecule predict a nonplanar transoid structure with the planar structure being the transition state between the minimum energy transoid and a slightly higher energy cissoid structure.[4] In view of these complications, it was not surprising that the vibrational analysis of thiourea still presented many unanswered questions. Since our study of the protonation effects on thiourea required reliable vibrational assignments, the vibrational spectrum of this molecule was reanalyzed.

The relevant literature data,[4,24] together with the Raman and DFT data from this study, are summarized in Table 2. As can be seen, the MP2 and DFT calculations for transoid thiourea, while being satisfactory for most fundamental vibrations, give poor results for ν_6, ν_7, ν_9, ν_{15}, and ν_{17} and, particularly, for the infrared intensities of ν_7 and ν_9. The previously[24] published HF/3-21G* values for the planar C_{2v} structure give the best fit with the reported[24] infrared and our revised Raman data and, therefore, will be used as the basis of our analysis. A comparison of the previously[4] reported MP2/6-31G* data with our DFT B3LYP/6-31G* data for the transoid C_2 structure also shows that the quality of our DFT calculations is comparable to the MP2 results and, therefore, our DFT calculations were used to analyze the mono- and diprotonated thiouronium cations.

The observed Raman spectra and calculated DFT frequencies exhibit the features expected for the protonated cations. In the monoprotonated cation, new bands at 2582 and 973 cm^{-1} are observed which are due to the S−H stretching and in-plane deformation modes, respectively. Furthermore, the N2CS skeletal modes show the predicted shifts, *i.e.*, the antisymmetric and the symmetric CN_2 stretching modes moved to higher frequencies and the C−S stretching mode to a lower frequency, as expected from increased C−N and decreased C−S double-

bond character in the protonated species. The frequency increase of 205 cm^{-1} for the symmetric NH_2 stretching mode in monoprotonated thiourea is not due to an intramolecular protonation effect but is attributed to decreased intermolecular hydrogen bonding in the protonated species due to the presence of the interspaced AsF_6^- anions and decreased nucleophilicity of the protonated sulfur atom. Consequently, the Raman data leave no doubt that, in solid monoprotonated thiourea, the protonation occurs exclusively on the sulfur and not on the nitrogen atom, which is in excellent agreement with previous findings.[12,17] The appearance of new strong bands in the region expected for AsF_6^- [26] confirm the presence of this anion, although the overlap of the AsF_6^- stretching modes with the C−S stretching mode adds some ambiguity to the individual assignments, and the C−S stretching mode might equally well be the 700 cm^{-1} Raman band instead of the one at 711 cm^{-1}.

For the diprotonated thiouronium ion, for which no previous vibrational data were available, the S−H stretching and deformation bands were observed at 2540 and 1000 cm^{-1}, respectively. The expected NH_3 group stretching modes were not directly observed due to weak scattering and fluorescence problems with the sample, but the symmetric NH_3 deformation mode was observed at 1534 cm^{-1}. The CN_2 stretching modes also exhibit the expected shifts. The two nitrogen atoms are no longer equivalent. One is present as an NH_3 group which, due to the lack of a free valence electron pair on the nitrogen, cannot form a partial C=N double bond through back-bonding, while the other one is present as an NH_2 group which now exhibits increased back-bonding. Therefore, the C−NH2 stretching frequency in the diprotonated cation increased by about 100 cm^{-1}, while the C−NH3 frequency decreased by about 200 cm^{-1}, relative to the averaged C−NH2 stretching frequency of 1499 cm^{-1} in the monoprotonated cation. Thus, the observation of the S−H modes and the pronounced changes in the N2CS skeletal modes, which follow closely the predicted DFT frequencies, strongly support a dication with protonation on the sulfur and one of the two nitrogen atoms. As with the singly protonated salt, the AsF_6^- modes were again observed at their characteristic frequencies,[26] with a similar ambiguity in the choice of the C−S stretching mode between the 722 and the 700 cm^{-1} bands.

Calculated Structures and Energies of Mono-, Di-, and Triprotonated Thiourea. To study the effect of protonation on the structure and energetics of thiourea, density functional theory calculations were carried out for thiourea and its mono-, di-, and triprotonated forms. Even though the calculational results pertain to the idealized gas phase, important information can be obtained on the structures and relative stabilities. Optimized geometries were obtained at the B3LYP/6-31G* level. Vibrational frequencies at the B3LYP/6-31G*//B3LYP/6-31G* level were used to characterize stationary points as minima and to evaluate zero-point vibrational energies (ZPE) which were scaled by a factor of 0.96. Unless otherwise stated, B3LYP/6-31G* structures and energies are used throughout the text. Calculated energies and relative energies are listed in Table 6. A comparison of experimental and calculated bond lengths and bond angles for thiourea and thiouronium ion is given in Table 7 and Table 8, respectively. Optimized geometries are depicted in Figure 1. An energy diagram for the di- and triprotonation of thiourea at the B3LYP/6-31G* level is given

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Table 2. Vibrational Spectra[a] of Solid Thiourea at 25 and −110 °C and Their Assignments in Point Group C_2 (Transoid Structure)

assignt		PED[b]	Raman, 25 °C	Raman, −110 °C	IR,[c] 25 °C	DFT,[d] B3LYP/6-31G*	HF,[e] 3-21G*	MP2,[f] 6-31G*
						calcd freq, (IR) [Ra] intens		
A	$\nu1$	ν_{as} NH$_2$ in phase (99)	3285 [0.2]	3275 [0.2]	3275 (vs)	3684 (14)	3695 (48) [98]	3675 (62)
	$\nu2$	ν_{sym} NH$_2$ in phase (99)	3181 [0.4]	3181 sh 3173 [0.8]	3170 (vs)	3556 (7)	3580 (29) [171]	3542 (79)
	$\nu3$	δ_{bend} NH$_2$ in phase (96)	1643 [0.1]	1634 [0.1]	(1613)	1684 (69)	1657 (86) [2]	1695 (82)
	$\nu4$	ρ NH$_2$ (37), nsym CN$_2$ (29) n CS (17), δ CN$_2$ (16)	1389 [0.9] 1374 [0.4]	1389 [1.2] 1375 [0.6]	1413 (vs)	1430 (268)	1406 (382) [9]	1476 (99)
	$\nu5$	νsym CN$_2$ (59), ρ NH$_2$ (34)	1097 [2.6]	1099 [3.3]	1083 (s)	1082 (55)	1055 (94) [18]	1114 (13)
	$\nu6$	ν CS (71), δ CN$_2$ (12), ρ NH$_2$ (10)	738 [10]	736 [10]	(728)	765 (9)	737 (34) [4]	805 (5)
	$\nu7$	ω NH$_2$ (78) τ NH$_2$ (22)	575 [0.2]	594 [0.5] 576 [0.5]		419 (296)	592 (0) [2]	553 (166)
	$\nu8$	δ CN$_2$ (79), ρ NH$_2$ (12)	480 [3.3]	478 [2.8]	463 (sh)	459 (9)	456 (3) [2]	477 (10)
	$\nu9$	τ NH$_2$ (64), ω NH$_2$ (36)	n obsd	n obsd	n obsd	369 (129)	365 (0) [0.3]	385 (161)
B	$\nu10$	ν_{as} NH$_2$ out of phase (99)	3377 [0.2]	3382 [0.1] 3350 [0.1]	3380 (vs)	3684 (65)	3693 (101) [14]	3675 (31)
	$\nu11$	ν_{sym} NH$_2$ out of phase (99)	3235 [0+]	3220 [0+]	3170 (vs)	3549 (39)	3570 (114) [15]	3549 (23)
	$\nu12$	δ NH$_2$ (89), ν_{as} CN$_2$ (10)	1617 [0+]	1618 [0.1]	1613 (vs)	1659 (204)	1622 (211) [12]	1672 (208)
	$\nu13$	ν_{as} CN$_2$ (77)	1492 [0.1] 1476 [0.1]	1495 [0.2] 1478 [0.2]	1472 (vs)	1447 (97)	1436 (210) [3]	1489 (339)
	$\nu14$	ρ NH$_2$ (87), ν_{as} CN$_2$ (13)	(1097)	1095 (sh)	1083 (s)	1089 (15)	1051 (14) [0.5]	1111 (69)
	$\nu15$	π N$_2$CS out of plane (56) ω NH$_2$ (44)	(738)	720 (sh)	728 (vs)	640 (66)	735 (501) [2]	663 (123)
	$\nu16$	τ NH$_2$ (67), ω NH$_2$ (21), π N$_2$CS (12)	622 [0.1]	629 [0+]	630 (s)	592 (142)	624 (151) [3]	611 (181)
	$\nu17$	τ NH$_2$ (42), ω NH$_2$ (32), π N$_2$CS (26)	500 (sh)	502 [1.2]	485 (vs)	533 (73)	507 (221) [2]	420 (253)
	$\nu18$	δ N$_2$CS in plane (94)	402 [0.2]	400 [0.1]	413 (wm)	400 (6)	381 (2) [3]	412 (2)

[a] Frequencies in cm^{-1}; calcd IR and Raman intensities in km/mol and Å^4/amu, respectively. [b] The given potential energy distribution is in percent and was taken from ref 10. [c] Data from ref 102. [d] Data from this work; frequencies are unscaled. [e] Data from ref 101, calculated for the plane C_{2v} structure; stretching and deformation frequencies were scaled by factors of 0.9 and 0.8, respectively. [f] Data from ref 4, calculated for the transoid C_2 structure.

Table 3. Raman Spectrum[a] of Solid $[(H_2N)_2CSH]^+AsF_6^-$

obsd freq (rel intens)	calc freq[b] (IR intens) DFT B3LYP/6-31G*	approx mode despcription[c]
	$(H_2N)_2CSH^+$ (C_s)	
	3673 (113)	ν_{as} NH$_2$ in phase
	3666 (118)	ν_{as} NH$_2$ out of phase
3378 (1)	3566 (116)	ν_{sym} NH$_2$ in phase
	3553 (233)	ν_{sym} NH$_2$ out of phase
2582 (3.0)	2712 (2)	ν SH
	1716 (392)	δ NH$_2$ out of phase
	1706 (83)	δ NH$_2$ in phase
1554 (1.4)	1596 (5)	ν_{as} CN$_2$
1443 (1.3)	1456 (155)	ν_{sym} CN$_2$
1110 (3.7)	1119 (0)	ρ NH$_2$ in phase
	1076 (3)	ρ NH$_2$
973 (1)	983 (26)	δ wag SH in plane
711 (3−7)[d]	705 (10)	ν CS
	668 (1)	π N$_2$CS out of plane
	552 (186)	τ NH$_2$, ω NH$_2$, skeletal def.
	528 (340)	δ wag CS
	474 (18)	NH$_2$ deformation
461 (1.5)	453 (10)	δ CN$_2$
	436 (2)	NH$_2$ deformation
	371 (6)	δ N$_2$CS in plane
	233 (28)	τ C−SH
	AsF$_6^-$	
700 (6)		ν_{sym}
679 (10)		ν_{sym}
368 (3)		δ_{sym}

[a] Recorded at −110 °C. [b] Unscaled frequencies calcd for the planar monocation of C_s symmetry. [c] Deduced from computer simulated motions and the analogy with the PED of planar thiourea (see Table 2). [d] The possibility that this band might belong to AsF$_6^-$ and the 700 cm^{-1} band belongs to the cation cannot be ruled out (see text).

Table 4. Raman Spectrum[a] of Solid $[H_3NC(SH)NH_2]^{2+}\cdot2AsF_6^-$

obsd freq (rel intens)	calc freq[b] (IR intens) DFT B3LYP/6-31G*	approx mode despcription[c]
	$[H_3NC(SH)NH_2]^{2+}$ (C_s)	
	3536 (204)	ν_{as} NH$_2$
	3449 (408)	ν_{sym} NH$_2$
	3355 (170)	ν_{as} NH$_3$
	3338 (239)	ν_{as} NH$_3$
	3274 (195)	ν_{sym} NH$_3$
2540 (1.0)	2664 (45)	ν SH
1695 (1.0)	1729 (200)	δ NH$_2$
	1663 (76)	δ_{as} NH$_3$
1625 (0+)	1654 (163)	δ_{sym} NH$_3$
1600 (0.8)	1602 (87)	ν C−NH$_2$
1534 (1.2)	1583 (184)	δ NH$_3$ + skeletal stretch
1326 (0.8)	1303 (63)	ν C−NH$_3$
	1118 (21)	ρ NH$_3$ out of N$_2$CS plane
1095 (1.2)	1083 (1)	ω NH$_3$ in plane
1000 (0.5)	976 (17)	δ CS−H in plane
962 (1.2)	927 (24)	ν skeleton
	759 (257)	NH$_2$ deform
700 (1)[d]	689 (8)	ν skeleton
565 (3)[d]	568 (2)	H$_2$N−C−S bend
	525 (17)	δ N$_2$CS out of plane
471 (3)	443 (4)	in plane deformation
	364 (19)	δ wag C−S in plane
	347 (40)	τ C−SH
	75 (1)	τ C−NH$_3$
	AsF$_6^-$	
722 (6)[d]		ν_{sym}
682 (10)		ν_{sym}
370 (5)		δ_{sym}

[a] Recorded at −110 °C. [b] Unscaled frequencies calcd for the planar dication of C_s symmetry. [c] Deduced from computer simulated vibrational motions. [d] The assignments of these bands to the dication and AsF$_6^-$ are somewhat tentative (see text).

in Figure 2. To verify the experimentally observed chemical shifts, we have also carried out MO calculations using the direct IGLO[27] and GIAO-MP2[28] methods. B3LYP/6-31G* geometries were used for the chemical shift calculations. Calculated NMR chemical shifts are listed in Table 5. The experimental and calculated ^{15}N NMR chemical shifts are correlated in Figure 3.

Thiourea. The optimized geometry of thiourea **1** is in agreement with previous[4] calculations at the MP2/6-31G* level

Table 5. Calculated GIAO-MP2(tzp/dz) NMR Chemical Shifts of Thiourea and Its Mono-, Di-, and Triprotonated Forms (IGLO Calculated NMR Chemical Shifts in Parantheses)

	^{13}C	^{15}N	
molecule	$-C=$	$-NH_2$	$-NH_3^+$
	Thiourea		
1 (C_2)	192.7 (213.7)	104.8 (93.3)	
2 (C_{2v})	186.0 (203.4)	101.2 (89.5)	
	Monoprotonated Thiourea		
3 (C_s)[a]	176.3 (188.5)	N^1 112.1(94.2)	
		N^2 110.7 (93.3)	
4 (C_s)	152.1 (177.3)	119.6 (105.6)	98.0 (69.9)
	Diprotonated Thiourea		
5 (C_s)	178.8 (200.8)	163.7 (153.2)	72.0 (47.6)
	Triprotonated Thiourea		
9 (C_s)	163.0 (172.8)	239.1 (232.2)	82.8 (57.8)
10 (C_s)[a]	188.1 (225.0)	N^1 85.3 (62.2)	
		N^2 9.5 (56.0)	

[a]

3   **10**
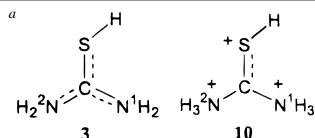
Table 6. Total Energies (-au) and Zero-Point Vibrational Energies (kcal/mol) and Relative Energies (kcal/mol) of Thiourea and Its Mono-, Di-, and Triprotonated Forms

molecule	B3LYP/6-31G*// B3LYP/6-31G*	ZPE[a]	NIMAG[b]	rel energy
	Thiourea			
1 (C_2)	548.215 63	37.12	0	0.00
2 (C_{2v})	548.214 59	35.98	2	−0.48
	Monoprotonated Thiourea			
3 (C_s)	548.565 61	42.53	0	0.00
4 (C_s)	548.537 36	44.77	0	19.97
	Diprotonated Thiourea			
5 (C_s)	548.674 55	50.81	0	0.00
6 (C_s)	548.657 70	48.55	0	8.31
7 (C_{2v})	548.659 97	52.83	0	11.17
8 (C_1)	548.502 75	43.20	1	100.19
	Triprotonated Thiourea			
9 (C_s)	548.560 19	55.36	0	0.00
10 (C_s)	548.561 63	57.33	0	1.07
11 (C_1)	548.471 78	50.99	1	51.11
12 (C_1)	548.444 70	51.25	1	68.36

[a] ZPE at the B3LYP/6-31G*//B3LYP/6-31G* level scaled by a factor of 0.96. [b] Number of imaginary frequencies at the B3LYP/6-31G*// B3LYP/6-31G* level. [c] Relative energy at the B3LYP/6-31G*//B3LYP/ 6-31G* + ZPE level.

Table 7. Experimental and Calculated Geometries of Thiourea

param	expt[a]	calc[b]
C−S	1.720	1.675
C−NH$_2$	1.340	1.368
S−C−N	120.5	122.8
N−C−N	119.0	114.4

[a] Taken from ref 2. [b] At the B3LYP/6-31G* level.

and with the reported[25a] X-ray structure of thiourea. The transoid nonplanar structure **1** (C_2) with pyramidal NH$_2$ groups was found to be the global minimum structure on the potential energy surface of thiourea at the B3LYP/6-31G* level, as confirmed by frequency calculations. Similar structures have previously been calculated for guanidine[25b] and for urea.[21] We also calculated the planar C_{2v} structure **2**. However, frequency calculations show that structure **2** is the transition state for the inversion process in **1**. Structure **2** is only 0.65 kcal/mol less stable than structure **1** at the B3LYP/6-31G* level. Interest-

Table 8. Experimental and Calculated Geometries of Thiouronium Ion

param	expt[a]	calc[b]
C−S	1.737	1.756
C−N(1)	1.317	1.328
C−N(2)	1.297	1.328
S−C−N(1)	121.3	123.0
S−C−N(2)	117.1	116.4
N−C−N	121.7	120.7

[a] In thiouronium nitrate (taken from ref 17). [b] At the B3LYP/6-31G* level.

ingly, when zero-point energy is taken into consideration, structure **2** becomes even slightly (0.48 kcal/mol) more stable than structure **1**. This small energy difference between structures **1** and **2** indicates that the molecule can easily undergo inversion. The calculated bond lengths and angles of thiourea are listed in Table 7 together with the available experimental geometries. The results show that the experimental C−S distance (1.720 Å) is longer by 0.05 Å and the C−N distance (1.340 Å) is shorter by 0.03 Å than the corresponding calculated bond distances (1.675 and 1.368 Å, respectively). This may be partly due to the strong intermolecular S−H hydrogen bonding prevalent in the solid.

We have also calculated the ^{13}C and ^{15}N NMR chemical shifts of thiourea using the IGLO and GIAO-MP2 methods (Table 5). The GIAO-MP2 calculated ^{13}C ($\delta^{13}C_{calc}$ 186.0) and ^{15}N ($\delta^{15}N_{calc}$ 101.2) chemical shifts of thiourea **2** are in good agreement with the experimental chemical shifts of $\delta^{13}C_{exp}$ 183.8 and $\delta^{15}N_{exp}$ 108.3, respectively. The IGLO-calculated ^{13}C chemical shift, however, differs somewhat from the experimental value (see Tables 1 and 5).

Monoprotonated Thiourea. Both, S-protonated thiourea **3** (C_s) and N-protonated thiourea **4** (C_s) were found to be stable minimum structures at the B3LYP/6-31G* level. In agreement with the experimental results, structure **3** was found to be 20.0 kcal/mol more stable than structure **4**. Protonation of **1** to form **3** was calculated to be exothermic by 214.2 kcal/mol. X-ray crystallographic studies[17] on thiouronium nitrate show that the acidic proton is attached to the thiocarbonyl sulfur atom of thiourea and forms a hydrogen bond to an oxygen atom of the nitrate ion. In the solid state, thiouronium ion **3** was found[17] to be planar due to the partial double-bond character of the C=S bond. A C=S bond elongation of 1% (0.02 Å) and a shortening of the neighboring C−N(NH$_2$) bond by 2.5% (0.03 Å) relative to thiourea was observed experimentally.[17] The calculated structure of thiuronium ion **3** is in reasonable agreement with the available experimental parameters. The increase in C=S bond length upon protonation, however, is somewhat larger in the calculated structure of **3** (4.8% (calcd) *vs* 1% (exptl), *vide infra*), which is likely to be due to additional hydrogen bonding present in the solid state. A comparison of experimental vs calculated bond lengths and angles in **3** is given in Table 8.

The GIAO-MP2-calculated ^{13}C ($\delta^{13}C_{calc}$ 176.3) and average ^{15}N ($\delta^{15}N_{calc}$ 111.4) NMR chemical shifts of **3** compare well with the experimental values of 168.8 and 106.4, respectively (see Tables 1 and 5). IGLO also gives similar results.

Diprotonated Thiourea. We have also calculated the three possible structures of diprotonated thiourea at the B3LYP/6-31G* level. In agreement with the experimental results, the N,S-diprotonated structure **5** (C_s) was found to be the lowest in energy, being 8.3 kcal/mol more stable than S,S-diprotonated
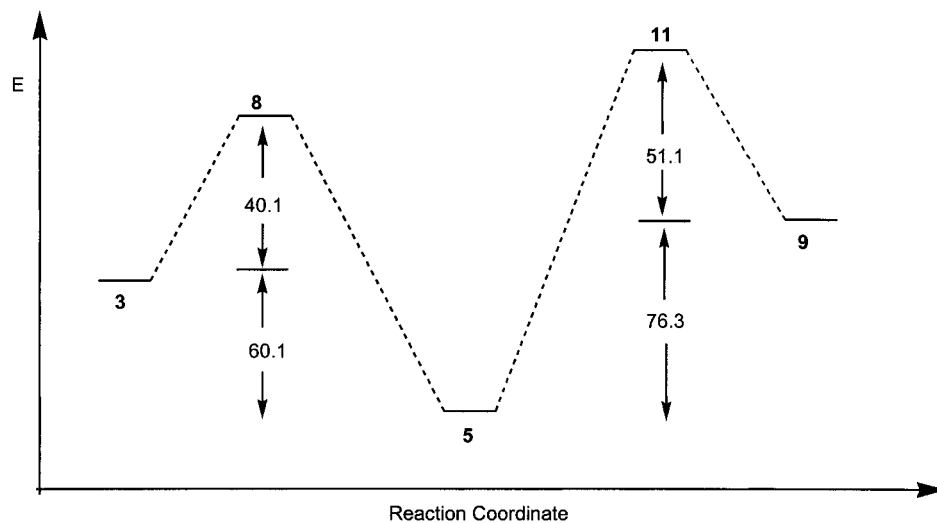
Figure 2. Energy diagram for the di- and triprotonation of thiourea (at the B3LYP/6-31G* level; energies in kcal/mol).

structure **6** (C_s). Another possible structure for diprotonated thiourea is N,N-diprotonated thiourea **7** (C_{2v}, isostructural to acetone) which was found to be 11.2 kcal/mol less stable than **5**. Protonation of **3** to form **5** is calculated to be exothermic by 60.1 kcal/mol. We have also identified the transition state **8** for protodissociation of **5** into **3**, which lies 100.2 kcal/mol above minimum structure **5**. Thus, dication **5** has a very high kinetic barrier to decomposition. Diprotonated thiourea **5** (C_s) is characterized by longer C−S and C−N(NH$_3^+$) bonds (1.705 and 1.497 Å, respectively) and a shorter C−N(NH$_2$) (1.304 Å) bond as compared to those of thiourea. This indicates that one of the positive charges in **5** is localized on nitrogen (NH$_3^+$) and the second positive charge is delocalized among S−C−N, which is also supported by the observed vibrational frequencies (*vide infra*).

The observed ^{13}C and ^{15}N NMR chemical shifts in **5** are well reproduced by both GIAO-MP2 and IGLO methods (see Tables 1 and 5). For example, the GIAO-MP2-calculated $\delta^{13}C_{calc}$ 178.8 of **5** is deshielded by 2.5 ppm compared to that of **3** ($\delta^{13}C_{calc}$ 176.3), which agrees well with the corresponding experimental deshielding of 6.1 ppm. Similarly, the two GIAO-MP2-calculated ^{15}N NMR chemical shifts of **5** at $\delta^{15}N_{calc}$ 163.7 and $\delta^{15}N_{calc}$ 72.0 compare very well with the two experimental values of $\delta^{15}N_{exp}$ 165.8 and 63.6, respectively. IGLO also correctly reproduces the direction of the shielding effects but somewhat overestimates their magnitude (see Table 5).

Triprotonated Thiourea. Further protonation of diprotonated thiourea **5** can occur either on sulfur or on nitrogen leading to structures **9** and **10**, respectively (Figure 1). We have
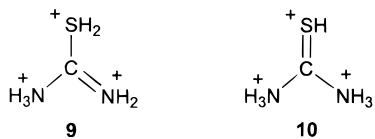
calculated N,S,S-triprotonated thiourea **9** and N,N,S-triprotonated form **10** at the B3LYP/6-31G* level. Structure **9** was found to be only 0.9 kcal/mol less stable than the N,N,S-triprotonated form **10**, and both are minima on the potential energy surface, as confirmed by frequency calculations. However, by including zero-point vibrational energy, structure **9** becomes 1.1 kcal/mol more stable than structure **10**. Thus, energetically, structures **9** and **10** are similar. The average C−N bond length of 1.485 Å and the C−S bond length of 1.649 Å in **10** underline the thiocarboxonium ion nature of this structure. On the other hand, the C−S (1.903 Å), C−N(NH$_3$) (1.482 Å),
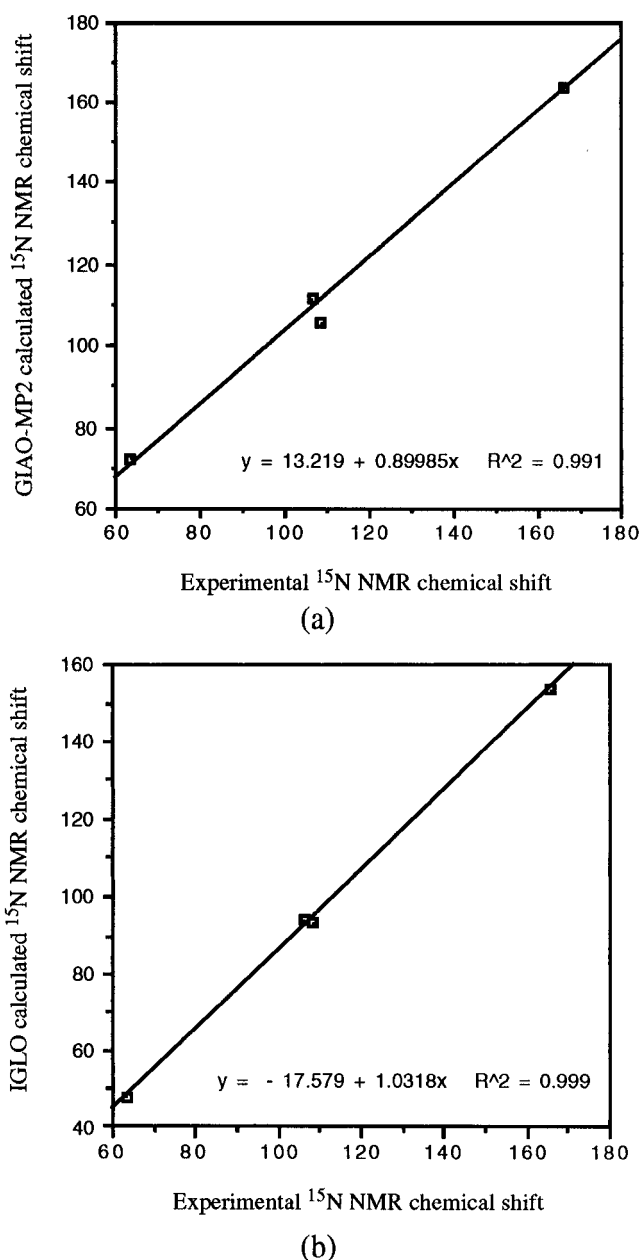

$$y = 13.219 + 0.89985x \quad R^2 = 0.991$$

Experimental ^{15}N NMR chemical shift

(a)

$$y = -17.579 + 1.0318x \quad R^2 = 0.999$$

Experimental ^{15}N NMR chemical shift

(b)

Figure 3. Plot of (a) IGLO-calculated vs experimental and (b) GIAO-MP2-calculated vs experimental ^{15}N NMR chemical shifts of protonated thioureas.

and C−N(NH$_2$) (1.274 Å) bond lengths in **9** indicate the iminium ion nature of structure **9** (see Figure 1).

The S-protonation of diprotonated thiourea **5** to form N,S,S-triprotonated thiourea **9** was found to be endothermic by 76.3 kcal/mol. We have also located the transition structure **11** (C_1) for the deprotonation of **9**. Transition state **11** lies 51.1 kcal/mol above structure **9**. Thus, N,S,S-triprotonated thiourea **9** also has a high kinetic barrier for deprotonation. On the other hand, N-protonation of diprotonated thiourea **5** to form N,N,S-triprotonated thiourea **10** was calculated to be endothermic by 77.4 kcal/mol. The transition state **12** (C_1) for the deprotonation of **10** is was found to be 67.3 kcal/mol higher in energy. Therefore, the N,N,S-triprotonated structure **10** also has a high kinetic barrier for deprotonation.

Both GIAO-MP2 and IGLO methods predict a shielding effect in the ^{13}C NMR chemical shift of triprotonated thiourea **9** (GIAO-MP2, $\delta^{13}C_{calc}$ 163.0; IGLO, $\delta^{13}C_{calc}$ 172.8) of 15.8 and 28.0 ppm, respectively, compared to the diprotonated species **5** (GIAO-MP2, $\delta^{13}C_{calc}$ 178.8; IGLO, $\delta^{13}C_{calc}$ 200.8). The ^{15}N NMR chemical shifts of **9**, on the other hand, are predicted to be further deshielded compared to **5**. For example, GIAO-MP2 calculates a deshielding of 75.4 and 10.8 ppm for the NH$_2$ ($\delta^{15}N_{calc}$ 239.1) and NH$_3^+$ ($\delta^{15}N_{calc}$ 82.8) groups in **9**, respectively, as compared to **5**. IGLO gives similar results (see Table 5).

Conclusions

The mono-, di-, and triprotonation of thiourea was investigated by ^{13}C and ^{15}N NMR spectroscopy under superacidic conditions at low temperature and by density functional theory methods. In the case of thiourea, the C_2 symmetrical structure **1** is preferred over C_{2v} **2** by only 0.5 kcal/mol. Contrary to previous[11] reports in the literature, thiourea was found to be monoprotonated in FSO$_3$H/SO$_2$ClF at −80 °C and the resulting thiouronium ion **3** was identified by ^{13}C and ^{15}N NMR spectroscopy. The preferred structure for monoprotonated thiourea is the S-protonated form **3**. Diprotonated thiourea **5** was prepared and characterized by ^{13}C and ^{15}N NMR in FSO$_3$H:SbF$_5$ superacid. In addition, **3** and **5** were isolated as stable AsF$_6^-$ salts at −64 and 21 °C, respectively, and were characterized by their material balances and Raman spectroscopy. The N,S-diprotonated form **5** was found to be the minimum energy structure. NMR chemical shifts were evaluated using the IGLO and GIAO-MP2 methods and are compared to the experimental values. Triprotonated thiourea was not observed experimentally but was calculated to be a kinetically stable species at the B3LYP/6-31G* level. The N,S,S-triprotonated form **9** was found to be the minimum energy structure, differing by only 1.1 kcal/mol in energy from the N,N,S-triprotonated structure **10**. Both GIAO-MP2- and IGLO-calculated ^{13}C and ^{15}N NMR chemical shifts of the preferred structures (even though they refer to the idealized gas phase) are in good agreement with the experimentally obtained data (see Figure 3). Thiourea plays a significant role in biological chemistry. Its basic properties, as shown in the present protonation study, can involve mono-, di-, and even tridentate interactions with electron pair acceptors.

Experimental Section

98% ^{15}N-enriched thiourea (^{15}NH$_2$)$_2$CS (Cambridge Isotope Laboratories), thiourea (Aldrich), AsF$_5$ (Ozark Mahoning), and HF (Matheson) are commercially available and were used as received. SbF$_5$ (Allied Chemical) and FSO$_3$H (3M) were doubly distilled prior to use.

SO$_2$ClF was prepared from sulfuryl chloride and ammonium fluoride as previously[29] described by Prakash *et al.* Volatile materials used in the preparation of [NH$_3$C(SH)NH2]$^{2+}$·2AsF$_6^-$ were manipulated in a well-passivated (with ClF$_3$ and HF) (Monel Teflon-FEP vacuum system.[30] Nonvolatile materials were handled in the dry nitrogen atmosphere of a glovebox.

^{1}H, ^{13}C, and ^{15}N NMR spectra were obtained on Varian Associates Model Unity 300 spectrometer equipped with a 5 mm variable-temperature broad band probe at 300, 75.4, and 30.4 MHz, respectively. ^{1}H and ^{13}C NMR spectra were obtained with respect to TMS by using an acetone-d_6 capillary as external standard. ^{15}N NMR chemical shifts were referenced to anhydrous NH$_3$. The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 488 nm excitation line of an Ar ion laser and a previously[31] described cooling device.

Density functional theory calculations were performed with the GAUSSIAN-94[32] package of programs. NMR chemical shifts have been evaluated using the direct IGLO[27] method with the II basis set. GIAO-MP2[28] chemical shift calculations using the tzp/dz basis set haven been performed with the ACES II[33] program. The calculated ^{13}C and ^{15}N NMR chemical shifts (δ values) are referenced to TMS and NH$_3$, respectively.

Protonation of Thiourea. Thiourea (∼30 mg) was dissolved in approximately 0.5 mL of SO$_2$ClF in a 5 mm NMR tube and cooled to −78 °C in a dry ice/acetone bath. Approximately 1.5 mL of 50% v/v solution of FSO$_3$H:SbF$_5$ (1:1 molar solution) or FSO$_3$H (see text) in SO$_2$ClF was added to the solution at −78 °C. The ensuing mixture was vigorously stirred (Vortex stirrer) under periodic cooling prior to transfer to a precooled NMR instrument (−80 °C).

Preparation of [NH$_3$C(SH)NH$_2$]$^{2+}$·2AsF$_6^-$ and (NH$_2$)$_2$C(SH)$^+$AsF$_6^-$. Thiourea (2.52 mmol) and anhydrous HF (4 mL of liquid) were combined at −196 °C in a Teflon-FEP ampule. Arsenic pentafluoride (11.93 mmol) was added to this mixture at −196 °C, and the contents of the ampule were allowed to warm slowly to −64 °C (CHCl$_3$/liquid nitrogen bath). During warmup, a white solid was formed which was only partially soluble in the excess of HF. Removal of all material, volatile at −64 °C in vacuo, resulted in 1.164 g of a white solid residue (weight calculated for 2.52 mmol of NH$_3$C(SH)NH$_2^{2+}$ 2 AsF$_6^-$ = 1.149 g). The residue was transferred at −196 °C into a 5 mm glass tube under the nitrogen atmosphere of a glovebox and characterized by Raman spectroscopy at −130 °C (see text). When allowed to warm to 21 °C, the salt slowly decomposed exhibiting a dissociation pressure of approximately 15 Torr. Removal of all material, volatile at 21 °C in vacuo, resulted in 0.675 g of a white solid residue (weight calculated for 2.52 mmol of (NH$_2$)$_2$CSH$^+$AsF$_6^-$ = 0.670 g). The solid was again characterized by Raman spectroscopy at −110 °C (see text).

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