^{1}H, ^{13}C, ^{15}N NMR and Theoretical Study of Protonated Carbamic Acids and Related Compounds[1]

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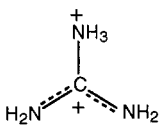
Mono-O-protonated carbamic acid, mono-O-protonated *N*-methyl carbamate, and mono-O-protonated methyl carbamate and di-O-protonated *N*,*N*-bis(carboxyl)-1,2-diaminoethane were prepared in FSO_3H/SO_2ClF and FSO_3H:SbF_5/SO_2ClF at −78 °C and were characterized by ^{1}H, ^{13}C, and ^{15}N NMR spectroscopy. Persistent diprotonated carbamic acid, diprotonated *N*-methyl carbamate, and diprotonated methyl carbamate were not observed under these conditions. The structures, energies, and ^{13}C and ^{15}N NMR chemical shifts of mono-, and diprotonated carbamic acids as well as other protonated species were also calculated by ab initio/IGLO/GIAO-MP2 method and compared with the experimental results.

Introduction

We have recently reported[2] the study of guanidine in superacids. Guanidine was found to be diprotonated in Magic Acid (FSO_3H:SbF_5; 1:1)[3] to give *N*,*N*-diprotonated guanidinium dication **1**, which was identified by ^{1}H, ^{13}C, and ^{15}N NMR spectroscopy and by ab initio/IGLO/GIAO-MP2 method. No persistent triprotonated guanidine could be observed. Previously, we have reported similar studies on urea[4] and carbonic acid.[5] Urea was also found to be diprotonated in Magic Acid to give persistent N,O-diprotonated urea **2**. On the other hand, in the case of carbonic acid only monoprotonated carbonic acid **3** was observed in Magic Acid. No persistent diprotonated carbonic acid was observed.[5]



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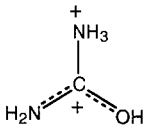

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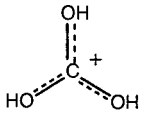

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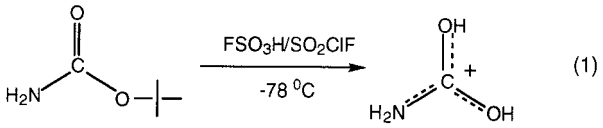
In continuation of our work we have now extended our investigations to protonated carbamic acid and related compounds by ^{1}H, ^{15}N, and ^{13}C NMR spectroscopy and ab initio/IGLO/GIAO-MP2 method as introduced by Schleyer and co-workers.[6]

Results and Discussions

Protonated Carbamic Acid. The observed NMR data of the compounds under various acid conditions are given in Table 1. The ^{15}N-labeled *tert*-butyl carbamate was prepared from ^{15}N-labeled ammonia and di-*tert*-butyl dicarbonate ($(BOC)_2O$). Protolytic ionization of *tert*-butyl carbamate in FSO_3H ($H_0 = -15$) at −78 °C with SO_2ClF as solvent resulted in the formation of mono-O-protonated carbamic acid (eq 1).



(1)

The ^{1}H NMR of mono-O-protonated carbamic acid consists of an NH_2 peak at δ^1H 6.41 (d $J_{N-H} = 96.5$ Hz). However, under this condition δ^1H of OH groups could not be obtained due to fast exchange of OH protons with the FSO_3H protons. ^{13}C NMR spectrum consists of a peak centered at δ^{13}C of 162.4 ($J_{C-N} = 28.4$ Hz) representing C^+ carbon. The peak at δ^{13}C 162.4 is 5.3 ppm deshielded compared to the carbonyl carbon (δ^{13}C 157.1) of the neutral *tert*-butyl carbamate. The ^{15}N NMR spectrum of the same solution shows a triplet centered at δ^{15}N 69.5 ($J_{C-N} = 97.1$ Hz) representing NH_2 nitrogen.

Protolytic ionization of *tert*-butyl carbamate in substantially more acidic Magic Acid (FSO_3H:SbF_5, $H_0 \approx -22$) at −78 °C with SO_2ClF as solvent also resulted in the formation of the mono-O-protonated carbamic acid. The related amides were also found to be monoprotonated on the oxygen atom in superacids at low temperature as shown by Gillespie and Birchall.[7] The ^{1}H NMR spectrum of the solution exhibited two peaks at δ^1H 6.20 (d, $J_{N-H} = 97.0$ Hz, NH_2, 2H) and at δ^1H 8.25 (s, OH, 2H) besides the peaks resulting from the acid system [FSO_3H:SbF_5 (δ^1H 10.80), H_3O^+ (δ^1H 8.60)] and $(CH_3)_3C^+$ (δ^1H 3.00). The ^{13}C NMR spectrum of the solution at −78 °C clearly showed the formation of *tert*-butyl cation $(CH_3)_3C^+$ at δ^{13}C 334.6 (s, C^+) and 46.9 (q, CH_3, $J_{C-H} = 130.0$ Hz), as well as a singlet at δ^{13}C 161.8 (d, $J_{N-C} = 28.9$ Hz) due to the mono-O-protonated carbamic acid. The ^{15}N NMR spec-

(1) Chemistry in Superacids. Part 42. Part 41, Rasul, G. A.; Prakash, G. K. S.; Olah. G. A.; *Proc. Natl. Acad. Sci.* **1998,** *95*, 7257.
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(6) Bühl, M.; Gauss, J.; Hofmann, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1993**, *115*, 12385.
(7) Gillespie, R. J.; Birchall, T.; *Can. J. Chem.* **1963**, *41*, 148.

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Table 1. Experimental ^{1}H, ^{13}C and ^{15}N NMR Chemical Shifts at −78 °C

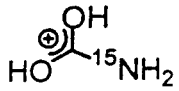
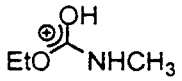
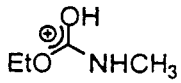
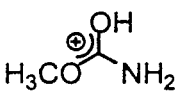
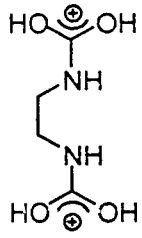
compound	Solvent	^{1}H-NMR	^{13}C-NMR (C=O)	^{15}N-NMR (30.41 MHz)
	HSO_3F in SO_2ClF	11.40 (bs, OH + HSO_3F), 6.41 (d, 96.5 Hz, 2H, NH_2)	162.4 (d, 28.4 Hz)	69.5 (t, 97.1 Hz)
	HSO_3F/SbF_5 (1:1) in SO_2ClF	8.25 (s, 2H, OH), 6.20 (d, 97.0 Hz, 2H, NH_2)	161.8 (d, 28.9 Hz)	69.6 (t, 96.6 Hz)
 Major isomer	HSO_3F in SO_2ClF	10.15 (s, 1H, OH), 6.12 (q, 4.7 Hz, 1H, NH), 3.98 (q, 7.1 Hz, 2H, EtO), 2.36 (d, 4.7 Hz, 3H, NMe), 0.95 (t, 7.1 Hz, 3H, EtO)	160.4	^{13}C-NMR 70.5 (t, 154.3 Hz, EtO), 28.0 (q, 143.3 Hz, NMe), 12.7 (q, 128.6 Hz, EtO),
	HSO_3F/SbF_5 (1:1) in SO_2ClF	8.25 (s, 1H, OH), 5.90 (bs, 1H, NH), 3.60 (q, 7.1 Hz, 2H, EtO), 2.33 (d, 4.7 Hz, 3H, NMe), 0.70 (t, 7.1 Hz, 3H, EtO)	160.4	70.1 (t, 151.5 Hz, EtO), 28.7 (q, 144.2 Hz, NMe), 12.0 (q, 128.6 Hz, EtO)
 Minor isomer	HSO_3F in SO_2ClF	9.65 (s, 1H, OH), 6.40 (q, 4.6 Hz, 1H, NH), 3.76 (q, 6.8 Hz, 2H, EtO), 2.46 (d, 4.6 Hz, 3H, NMe), 0.95 (t, 6.8 Hz, 3H, EtO)	160.7	69.9 (t, 151.1 Hz, EtO), 28.6 (q, 144.2 Hz, NMe), 12.2 (q, 129.1 Hz, EtO)
	HSO_3F/SbF_5 (1:1) in SO_2ClF	8.90 (s, 1H, OH), 5.70 (bs, 1H, NH), 3.90 (q, 2H, EtO), 2.23 (d, 3H, NMe), 0.70 (t, 3H, EtO)	159.8	71.1 (t, 153.4 Hz, EtO), 28.2 (q, 143.8 Hz, NMe), 12.5 (q, 128.7 Hz, EtO)
	HSO_3F in SO_2ClF	11.50 (bs, OH+HSO_3F), 6.40 (bs, 1H, NH_2), 3.50 (s, 3H, MeO), + methyl cleavage product (uncleaved/cleaved= 1:2)	163.0 (s)	59.3 (q, 153.8 Hz, OMe)
	HSO_3F/SbF_5 (1:1) in SO_2ClF	8.60 (bs, 1H, OH) 6.10 (s, 2H, NH_2) 3.40 (s, 3H, OMe) + minor methyl cleavage	162.7 (s)	59.5 (q, 153.4 Hz, OMe)

Table 1 (Continued)

compound	Solvent	^{1}H-NMR	^{13}C-NMR (C=O)	^{13}C-NMR
	HSO_3F in SO_2ClF	10.00 (s, 2H, OH), 6.45 (s, 2H, NH), 3.10 (s, 4H, CH_2)	161.5 (s)	40.9 (t, 143.3 Hz, CH_2)
	HSO_3F/SbF_5 (1:1) in SO_2ClF	9.90 (s, 2 H, OH), 6.05 (s, 2H, NH), 3.10 (s, 4H, CH_2)	160.8 (s)	40.7 (t, 143.8 Hz, CH_2)

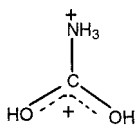
trum shows a triplet at δ^{15}N 69.6 (J_{N-H} = 96.6 Hz) representing NH_2 nitrogen.

The peak at δ^{13}C 161.9 in FSO_3H:SbF_5 solution is only 0.5 ppm shielded compared to the peak at δ^{13}C 162.4 observed in FSO_3H. This could be due to a proton exchange process occurring at the NMR time scale between the protonated carbamic acid and the acid or probably an exchange involving a small equilibrium concentration of diprotonated carbamic acid (or proto-solvated monocation) with the dication. However, the nitrogen peak at δ^{15}N 69.6 was only 0.1 ppm deshielded compared to the peak at δ^{15}N 69.5 obtained in FSO_3H.

The structures and energies of carbamic acid **1** and its protonated forms were calculated at the ab initio MP2/6-31G* level.[8] There are two possible structures for protonated carbamic acid: O-protonated **2** (C_s) and N-protonated **3** (C_s). Both were optimized at the MP2/6-31G* level (Figure 1). Structure **2** was found to be only 3.3 kcal/mol more stable than structure **3** (Table 2).

Further protonation on protonated carbamic acid **2** again can take place in two different ways. N-Protonation will lead to N,O-diprotonated carbamic acid **4**, and O-protonation will lead to O,O-diprotonated carbamic acid **5** (Figure 1). Energetically **4** was found to be 17.5 kcal/mol more stable than **5**.

The calculated structure of dication **4** is characterized by a longer C−N bond compared to protonated carbamic acid **2**. This indicates that one of the positive charge is localized on the NH_3 group, and the second positive charge is delocalized among O−C−O as indicated.



On the other hand, the calculated structure of dication **5** is characterized by a shorter C−N and a longer C−O (OH_2) bonds compared to protonated carbamic acid **2**, which indicates that one of the positive charge is localized on the OH_2 group and the second positive charge is delocalized among N−C−O (OH) as indicated.

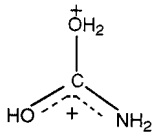


Table 2. Total Energies (-au), ZPE (kcal/mol), and Relative Energies (kcal/mol) of Protonated Guanidines

compd no.	MP2/6-31G*// MP2/6-31G* (ZPE)[a]	MP4(SDTQ)// 6-31G*//MP2/6-31G*	rel energy[b] (kcal/mol)
	Carbamic Acid, CH_3NO_2		
1	244.45755 (30.4)	244.49550	
	Monoprotonated Carbamic Acid, $CH_4NO_2^+$		
2	244.77445 (37.6)	244.81456	0.0
3	244.76923 (38.2)	244.81027	3.3
	Diprotonated Carbamic Acid, $CH_5NO_2^{2+}$		
4	244.83941 (44.5)	244.88265	0.0
5	244.81007 (43.5)	244.85312	17.5

[a] ZPE at the MP2/6-31G*//MP2/6-31G* level scaled by a factor of 0.93. [b] Based on MP4(SDTQ)/6-31G*//MP2/6-31G* + ZPE.

The ^{13}C and ^{15}N NMR chemical shifts of **2** and **3** were calculated by the IGLO[9] and GIAO-MP2[10] methods using MP2/6-31G* optimized geometries (Table 3). The GIAO-MP2-calculated δ^{13}C of **2** is 169.4, 7.0 ppm deviated from the experimental value of 162.4. The GIAO-MP2-calculated δ^{15}N of 100.7 is also substantially deviated from the experimental value of 69.5. Similarly, the IGLO-calculated δ^{13}C of 168.0 and δ^{15}N value of 81.7 are again considerably deviated from the experimental values. This is, however, in contrast with the previously reported[2] results on mono- and diprotonated guanidines where GIAO-MP2-calculated ^{13}C and ^{15}N NMR chemical shifts were found to be in excellent agreement with the experimental results.

(8) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986; p 226.

(9) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193. Kutzelnigg, W.; Fleischer, U.; Schindler, M. *NMR. Basic Principles and Progress* **1991**, *91*, 651. Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919.

(10) Gauss, J. *J. Chem. Phys. Lett.* **1992**, *191*, 614. Gauss, J. *J. Chem. Phys.* **1993**, *99*, 3629.

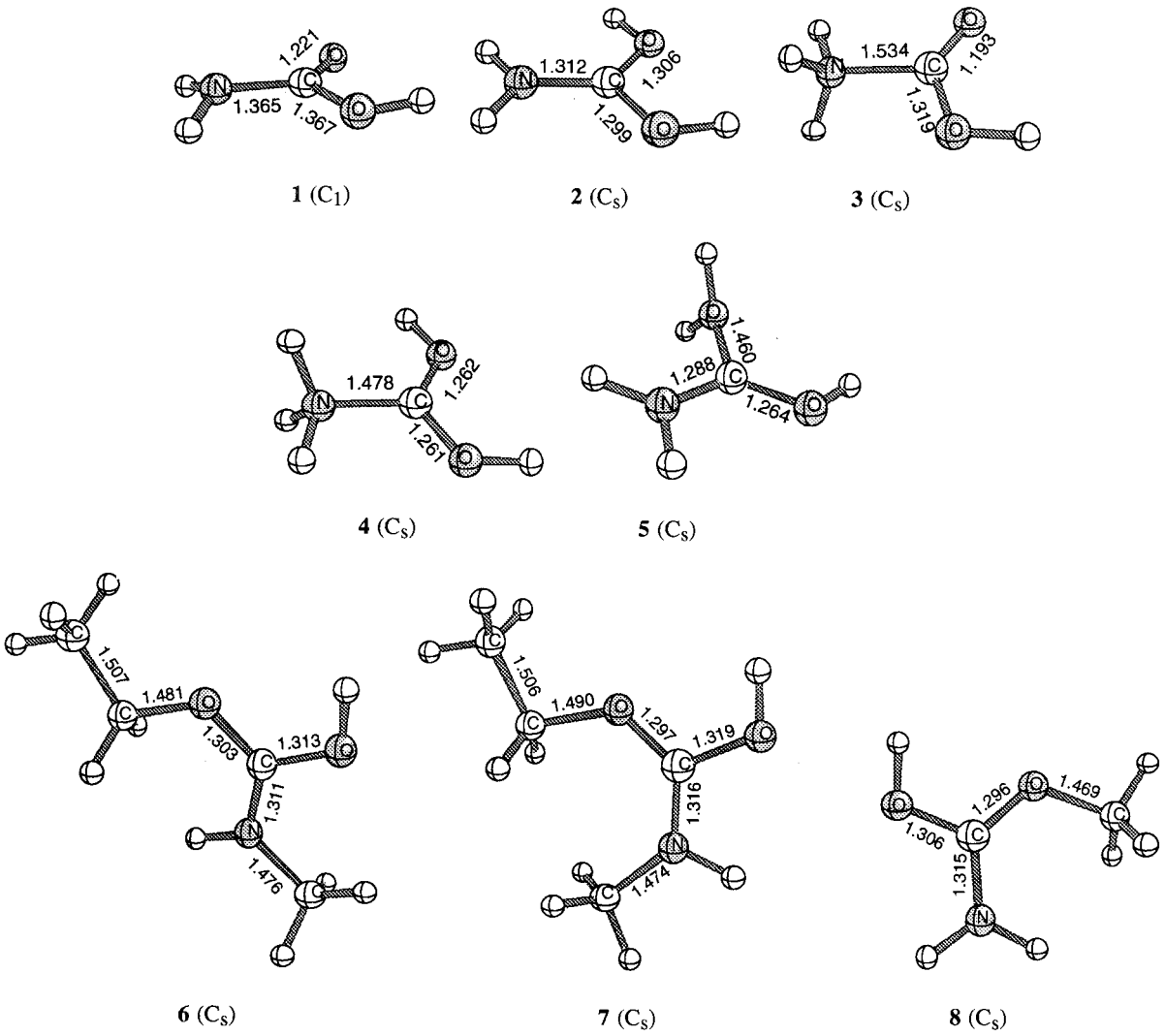
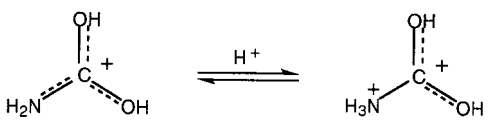


Figure 1. Selected MP2/6-31G* optimized parameters of **1**−**8**.

The ^{13}C and ^{15}N NMR chemical shifts of **4** were also calculated by the IGLO and GIAO methods. Interestingly, GIAO-MP2-calculated ^{13}C and ^{15}N NMR chemical shifts of **4** are 164.3 and 76.6, only 1.9 and 7.1 ppm, respectively, deviated from the experimental values of 162.4 and 69.5 obtained for protonated carbamic acid. Thus, the agreement between the calculated and the observed experimental data is better for diprotonated **4** than monoprotonated **2** (Tables 1 and 3). However, we found no evidence for the diprotonated species **4** under long-lived stable ion conditions.



2 **4**

Compared to guanidine[2] and urea,[4] which were found to be diprotonated in Magic Acid at low temperature to give corresponding persistent diprotonated species, carbamic acid (or carbonic acid[5]) was found to be only monoprotonated under similar conditions. This indicates that at least two nitrogen atoms may be required around a triavalent carbon to stabilize the dipositive charge. This is consistent with the fact that the nitrogen is a better electron donor than oxygen.

Protonated Ethyl *N*-Methyl Carbamate. When ethyl *N*-methyl carbamate was treated with FSO_3H in SO_2ClF at −78 °C, only the monocation, O-protonated ethyl *N*-methyl carbamate, could be observed (eq 2). Two distinct rotamers were formed in the acid solution due to the restricted rotation around C−N bond as indicated by ^1H and ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of each of the isomers consists of three peaks (Table 1).The C^+ carbon peaks at $\delta^{13}C$ 160.4 (major, assigned for trans isomer **6**) and 160.7 (minor, assigned for cis isomer **7**) are 2.0 and 1.7 ppm, respectively, shielded from that of protonated carbamic acid. Similar results were obtained when the ionization was carried out in more acidic FSO_3H:SbF_5 (1:1)/SO_2ClF medium. Again there is no indication for the formation of persistent diprotonated ethyl *N*-methyl carbamate dication.

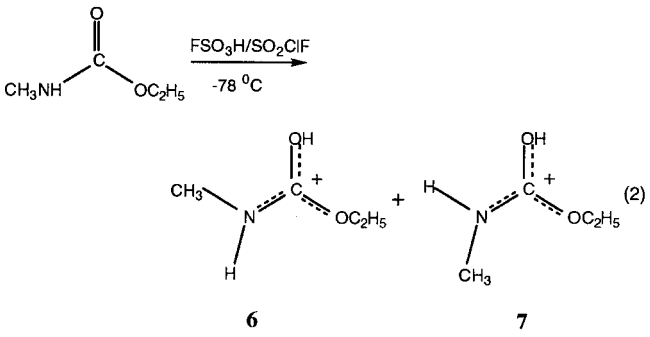
The structures of trans **6** and cis **7** isomers are fully optimized at the MP2/6-31G* level. The isomer **6** was found to be 5.4 kcal/mol more stable than the isomer **7** at the MP2/6-31G* level. The calculated geometries are given in Figure 1 and the ^{13}C and ^{15}N NMR chemical shifts are given in Table 3.

Protonated Methyl Carbamate. Ionization of methyl carbamate with FSO_3H in SO_2ClF at −78 °C gave only persistent O-protonated methyl carbamate (eq 3). The ^{13}C NMR spectrum of the ion consists of two peaks (Table

Table 3. Experimental and Calculated NMR Chemical Shifts[a]

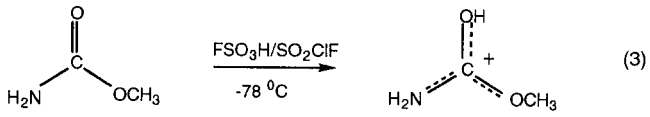
compd no.	atom	IGLO II	GIAO-MP2	expt
1	^{13}C	160.2	159.3	157.1[b]
	^{15}N	61.7	75.2	
2	^{13}C	168.0	169.4	162.4
	^{15}N	81.7	100.7	69.5
3	^{13}C	141.8	140.3	
	^{15}N	53.2	78.8	
4	^{13}C	168.0	164.3	
	^{15}N	52.1	76.6	
5	^{13}C	155.5	153.3	
	^{15}N	119.6	136.7	
6	^{13}C (C^+)	168.5		160.4
	^{13}C (CH_3NH)	28.7		28.7
	^{13}C (CH_2O)	69.3		70.1
	^{13}C (CH_3CH_2)	11.3		12.0
	^{15}N	85.8		
7	^{13}C (C^+)	168.9		160.7
	^{13}C (CH_3NH)	27.8		28.6
	^{13}C (CH_2O)	74.3		69.9
	^{13}C (CH_3CH_2)	12.6		12.2
	^{15}N	83.5		
8	^{13}C (C^+)	170.4		163.0
	^{13}C (CH_3)	58.3		59.3
	^{15}N	77.6		

[a] Calculated ^{13}C and ^{15}N NMR chemical shifts were referenced to TMS and NH_3; absolute shift, i.e., $\sigma(C) = 198.7$ and $\sigma(N) = 279.6$, respectively. [b] Experimental data is for *tert*-butyl carbamate (this work).



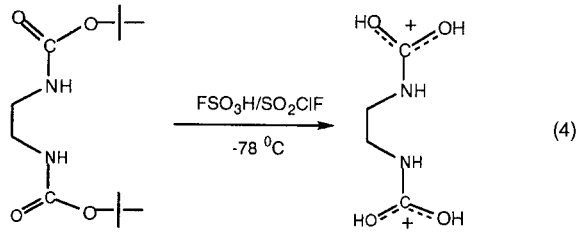
6 **7**

1). The peak at $\delta^{13}C$ 163.0 was assigned to the C^+ carbon and is only 0.6 ppm deshielded from that of protonated carbamic acid. Similar results were obtained when methyl carbamate was treated with the more acidic $FSO_3H:SbF_5$ (1:1)/SO_2ClF solution.



The structures of O-protonated methyl carbamate **8** was also optimized at the MP2/6-31G* level. The calculated geometry is displayed in Figure 1, and the ^{13}C and ^{15}N NMR chemical shifts are listed in Table 3.

Diprotonated *N,N*-Bis(*tert*-butoxycarboxyl)1,2-diaminoethane. Protolytic ionization of *N,N*-bis(*tert*-butoxycarboxyl)-1,2-diaminoethane in FSO_3H at −78 °C with SO_2ClF gave diprotonated *N,N*-bis(carboxyl)-1,2-diaminoethane dication (eq 4). The ^1H NMR spectrum of the dication consists of a NH peak at δ^1H 6.45. The ^{13}C NMR spectrum consists of two peaks centered at $\delta^{13}C$ 161.5 (s) and at $\delta^{13}C$ 40.9 (t, $J_{C-H} = 143.3$ Hz). These are consistent with formation of symmetrical dication. The peak at $\delta^{13}C$ 161.5 is assigned to the C^+ carbon and is only 0.9 ppm shielded from that of protonated carbamic acid. Similar results were also obtained when the ionization was carried out in Magic Acid ($FSO_3H:SbF_5$) at −78 °C with SO_2ClF as solvent.



Carbamic acid, urea, and guanidine and their derivatives are biologically important. They are present as substructures in the amino acids and many other biologically important molecules. The study of their protonated analogues (and their derivatives) is therefore also relevant to a better understanding of protolytic activation of the related biological systems. Recently, Thauer et al. have suggested that protosolvolytic activation may play an important role in some enzyme catalytic reactions.[11] For example, a recently discovered metal-free hydrogenase enzyme catalyzes the reversible dehyrogenation of methylenetetrahydromethaneopterin (CH_2=H_4MPT) to methenyltetrahydromethanopterin (CHH_4MPT^+) and H_2. It was suggested that the amidinium ion entity is further activated by N-protonation in the enzyme to bind a H_2 molecule via a two-electron, three-center (2e-3c) bond.[11]

Conclusions

Mono-O-protonated carbamic acid, mono-O-protonated *N*-methyl carbamate, mono-O-protonated methyl carbamate and di-O-protonated *N,N*-bis(carboxyl)-1,2-diaminoethane dication were prepared in FSO_3H/SO_2ClF and $FSO_3H:SbF_5/SO_2ClF$ at −78 °C and were characterized by ^1H, ^{13}C, and ^{15}N NMR spectroscopy. No static diprotonated carbamic acid, diprotonated *N*-methyl carbamate, and diprotonated methyl carbamate under these conditions were observed, although in highly acidic media, the exchanging system may involve the dication in some limited equilibrium. The structures of mono- and diprotonated carbamic acids as well as other protonated species were calculated at the ab initio MP2/6-31G* level. The ^{13}C and ^{15}N NMR chemical shifts of the ions were also evaluated using the IGLO and GIAO-MP2 methods and are compared with the experimental values.

Experimental Section

^{15}N-ammonia ($^{15}NH_3$) (Cambridge Isotope Laboratories), ethyl *N*-methyl carbamate, methyl carbamate, and 1,2-dicarboxylhydrazine are commercially available and were used as received. SbF_5 (Allied Chemical) and FSO_3H (3 M) were doubly distilled prior to use.

^1H, ^{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. ^1H and ^{13}C NMR spectra were obtained with respect to an acetone-d_6 capillary as external standard. ^{15}N NMR chemical shifts were referenced to anhydrous NH_3.

Preparation of ^{15}N Labeled *tert*-Butyl Carbamate. A 1.60 mL volume of a 3.3 M aqueous solution of $^{15}NH_3$ (5.25 mmol) was added dropwise to a solution of 1.091 g (5.00 mmol) $(BOC)_2O$ (di-*tert*-butyl dicarbonate) in 10 mL of methanol at

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20 °C. The reaction mixture was stirred for another 20 h and concentrated in vacuuo. The resulting wet crystals were dissolved in diethyl ether, and the solution was dried over $MgSO_4$ and filtered. Crystallization from diethyl ether resulted in analytically pure ^{15}N-labeled *tert*-butyl carbamate as white needles (502 mg, 85%). ^1H NMR: 5.6 (bs, 2H, NH_2), 1.39 (s, 9H, tBu). ^{13}C NMR: 157.1 (d, 25.7 Hz, C═O), 28.6 (s, tBu)

Study of Protonation of *tert*-butyl Carbamate. ^{15}N-Labeled *tert*-butyl carbamate (∼30 mg) was dissolved in approximately 0.5 mL of SO_2ClF 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_3H:SbF_5 (1:1 molar solution), HF:SbF_5 (1:1 molar solution), and FSO_3H in SO_2ClF 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 probe (−40 °C).

Computational Methods. Calculations were performed with the GAUSSIAN-94[12] package of programs. Geometry optimization was performed at the MP2/6-31G* level. Improved energies were obtained by single point energy calculations at the MP4(SDTQ)/6-31G*//MP2/6-31G* level. Vibrational frequencies at the MP2/6-31G*//MP2/6-31G* level were used to characterize stationary points as minima or transition state and to evaluate zero point vibrational energies (ZPE) which were scaled by a factor of 0.93.[8] Calculated energies and relative energies are listed in Table 2. IGLO calculations were performed according to the reported method[9] at IGLO II levels using MP2/6-31G* geometries. Huzinaga[13] Gaussian lobes were used as follows; Basis II: C or N: 9s 5p 1d contracted to [51111, 2111, 1], d exponent: 1.0, H: 5s 1p contracted to [311, 1], p exponent: 0.70. GIAO-MP2[10] method, which includes dynamic electron correlation in chemical shift calculations, using the tzp/dz basis set have been performed with the ACES II[14] program. The calculated ^{13}C and ^{15}N NMR chemical shifts (δ values) are referenced to tetramethylsilane (TMS) and NH_3, respectively. Calculated NMR chemical shifts are listed in Table 3. For simplicity MP2/6-31G* geometries and MP4(SDTQ)/6-31G*//MP2/6-31G* + ZPE energies will be discussed throughout.

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