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Structures and Energies of Mono-, Di-, and Triprotonated Urea: NMR/*ab Initio*/IGLO Study[1]

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The structures and NMR chemical shifts (^{13}C and ^{15}N) of urea and its mono-, di-, and triprotonated forms were calculated using high-level *ab initio* and IGLO methods, respectively. The results were compared with the experimental data obtained on mono- and diprotonated urea. Triprotonated urea was not observed experimentally.

Introduction

The structure of urea was one of the first organic structures to be determined by X-ray crystallographic methods.[2] X-ray[3] and neutron diffraction[4] studies on urea show that the hydrogen atoms are coplanar with the rest of the molecule, although unusually large amplitudes of thermal displacement were found. The H atom was found to lie closely between N and O of adjacent molecules and is expected to participate to a greater extent in hydrogen bonding.[3]

The site of protonation of urea has been the object of a series of experimental studies. The infrared spectra of uronium nitrate has been used to support O-protonation[5,6] as well as as N-protonation.[7,8] The existence of O-protonated uronium ion in the solid state was also shown by X-ray[9,10] and neutron diffraction studies.[11] Semiempirical calculations (CNDO/2) on the assumed planar uronium ion with fixed bond lengths have been used to show the effect of geometry upon protonation.[12a] Recent Raman studies[12b] led to the conclusion that the proton transfer from aqueous hydrochloric acid solutions occurred at the carbonyl oxygen and not on the nitrogen of the amide group. This conclusion is supported by theoretical calculations at the Hartree–Fock level.[12b]

The protonation of urea in strong acid has been studied by NMR spectroscopy.[13] Urea was found to be diprotonated in Magic acid (FSO_3H–SbF_5). The ^{15}N NMR spectrum of ^{15}N-enriched urea in Magic acid showed two nonequivalent nitrogens; a quartet centered at $\delta^{15}N$ 31.9 and a triplet centered at $\delta^{15}N$ 104.9, indicating the formation of O,N-diprotonated urea. At the time the structural aspects and the evaluation of the ^{15}N NMR chemical shifts were not further investigated.

Table 1. Measured NMR Chemical Shifts[a]

substrate	T/°C	acid	solvent	δ
urea	rt		DMSO	$^{13}C = 161.9$, $^{15}N = 76.2$
urea	rt	H_2SO_4		$^{13}C = 160.7$, $^{15}N = 79.3$
urea	rt	HNO_3		$^{15}N = 79.3$
urea	−80.0	FSO_3H	SO_2ClF	$^{13}C = 160.0$, $^{15}N = 79.5$
uronium nitrate	rt		DMSO	$^{13}C = 161.4$, $^{15}N = 79.9$
urea	−80.0	FSO_3H/SbF_5	SO_2ClF	$^{13}C = 156.1$, $^{15}N = 58.7$, $^{15}N = 129.9$

[a] ^{13}C and ^{15}N NMR chemical shifts are referenced to TMS and NH_3, respectively.

The formation and structure of diprotonated urea, a prototype gitonic onium dication (*vide infra*), is significant in probing the nature of superelectrophilic activation.[14] Such activation plays an important role in strong acid-catalyzed electrophilic reactions. In superelectrophilic activation, nonbonded electron pairs on onium ions are able to further interact with Bronsted or Lewis acids and in the limiting case can lead to gitonic dications i.e., proximal as contrasted with conventional distonic (distant) dications). The present experimental and theoretical study of di- and triprotonated urea is therefore relevent to our better understanding of protosolvolytic activations.[14] Furthermore, urea contains an amide linkage, and the study of protonation of amide type functionality is of importance in biological chemistry.[15,16] The structure of protonated guanidinium dication has been earlier investigated.[13] We report herein NMR/*ab initio*/IGLO calculations on the structure and energetics of mono-, di-, and triprotonated urea.

Results and Discussion

Ab initio calculations were carried out by using the SPARTAN[17] and GAUSSIAN92[18] package of programs. Restricted Hartree–Fock calculations were performed throughout. Optimized geometries were obtained with the MP2/6-31G* and MP2/6-311+G* levels. In order to obtained improved energy comparison, single point ener-

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(1) Chemistry in Superacids 16. Part 15: Rasul, G.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* Submitted.

(2) Mark, H.; Weissenberg, K. *Z. Phys.* **1923**, *16*, 1.

(3) Vaughan, P.; Donohue, J. *Acta Crystallogr.* **1952**, *5*, 530.

(4) Worksham, J. E.; Levy, H. A.; Peterson, S. W. *Acta Crystallogr.* **1957**, *10*, 319.

(5) Janssen, M. J. *Spectrochim. Acta* **1961**, *17*, 425.

(6) Kutzelnigg, W.; Mecke, R. *Spectrochim. Acta* **1961**, *17*, 530.

(7) Davies, V. M.; Hopkins, L. *Trans. Faraday Soc.* **1957**, *53*, 1563.

(8) Spinner, E. *Spectrochim. Acta* **1959**, *15*, 95.

(9) Sundera-Rao, R. V. G.; Turley, J. W.; Repinsky, R. *Acta Crystallogr.* **1957**, *10*, 435.

(10) Harkema, S.; Feil, D. *Acta Crystallogr.* **1969**, *B25*, 589.

(11) Worsham, J. E.; Busing, W. R. *Acta Crystallogr.* **1969**, *B25*, 572.

(12) (a) Harkema, S.; Feil, D. *THEOCHEM* **1972**, *12*, 465. (b) Wen, N.; Brooker, M. H. *J. Phys. Chem.* **1993**, *97*, 8608.

(13) Olah, G. A.; White, A. M. *J. Am. Chem. Soc.* **1968**, *90*, 6087.

(14) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767.

(15) Stewart, W. E.; Siddall, T. H. *Chem. Rev.* **1970**, *70*, 517.

(16) Olah, G. A.; White, A. M.; O'Brien, D. H. *Chem. Rev.* **1970**, *70*, 561.

(17) SPARTAN Version 2.0, Wavefunction, Inc., 1991, Irvine, CA.

(18) Gaussian 92, Revision B: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1992.

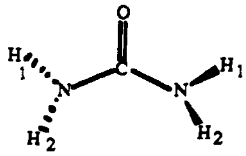
0022-3263/94/1959-2552$04.50/0

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

no.	MP2/6-31G*//MP2/6-31G* (ZPE)[a]	MP4(SDTQ)/6-31G*//MP2/6-31G*	MP2/6-311+G*//MP2/-6311+G*	MP4(SDTQ)/ 6-311+G*//MP2/ 6-311+G*	rel energy[b] (kcal/mol)
		Urea, CH_4N_2O			
1	24.607 46(38.0)	224.651 15	24.720 95	24.768 11	255.3
2	24.603 17(39.3)	224.646 08	24.716 32	24.762 56	257.4
		Monoprotonated urea, $CH_5N_2O^+$			
3	224.947 81(44.6)	224.992 65	226.048 78	226.096 87	55.6
4	224.933 45(45.1)	224.979 65	225.038 60	225.088 31	61.4
		Diprotonated urea, $CH_6N_2O^{2+}$			
5	225.047 09(52.6)	225.094 90	225.147 05	225.198 17	0.0
6	225.006 94(50.3)	225.053 08	225.109 73	225.158 99	22.3
7	225.033 67(52.5)	225.082 85	225.137 46	225.190 47	4.7
		Triprotonated urea, $CH_7N_2O^{3+}$			
8	224.891 78(57.7)	224.942 67	224.993 44	225.047 59	99.6
9	224.888 45(56.5)	224.938 09	224.990 47	225.043 37	101.0

[a] ZPE at the MP2/6-31G*//MP2/6-31G* level scaled by a factor of 0.93. [b] Based on MP4(SDTQ)/6-311+G*//MP2/6-311+G* + ZPE.

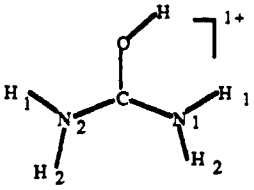
Table 3. Bond Lengths (Å) and Angles (deg) of Urea



param	expt[a,d]	expt[b,e]	expt[c,e]	MP2/ 6-31G*	MP2/ 6-311+G*
C–O	1.262(0.016)	1.243(0.006)	1.260(0.003)	1.226	1.219
C–N	1.335(0.013)	1.351(0.007)	1.352(0.002)	1.391	1.390
O–C–N	121.0(0.65)	121.5(0.25)	121.7(0.1)	123.5	123.4
$N-H_1$		0.988(0.020)	0.998(0.005)	1.013	1.009
$N-H_2$		0.995(0.007)	1.003(0.004)	1.013	1.009
$C-N-H_1$		119.8(0.8)	119.0(0.3)	11.8	112.5
$C-N-H_2$		118.1(0.9)	120.2(0.3)	116.0	116.6
$H_1-N-C-O$				13.5	12.8
$H_2-N-C-O$				145.6	147.1

[a] Reference 3. [b] Reference 4. [c] Reference 23. [d] X-ray data. [e] Neutron diffraction data.

Table 4. Bond Lengths (Å) and Angles (deg) of Uronium Ion



param	expt[a,c]	expt[b,d]	expt[c,d,f]	MP2/6-31G*	MP2/6-311+G*
C–O	1.302	1.298	1.290	1.317	1.310
$C-N_1$	1.297	1.312	1.323	1.327	1.321
$C-N_2$	1.315	1.315	1.340	1.320	1.319
$O-C-N_1$	122.0	121.7	121.9	122.7	122.7
$O-C-N_2$	116.3	116.7	118.0	114.4	114.5
O–H	0.99	1.006		0.978	0.967
N_1-H_1	0.85	1.005		1.013	1.009
N_1-H_2	1.04	1.013		1.014	1.009
$N-H_1$	0.85	1.000		1.015	1.010
N_2-H_2	1.10	1.014		1.013	1.008
H–O–C	119	113.6		114.3	115.4
H_1-N_1-C	117	123.1		122.1	122.2
H_2-N_1-C	127	119.1		121.5	121.5
H_1-N_2-C	123	119.1		118.8	118.8
H_2-N_2-C	119	120.8		122.9	123.0

[a] Reference 10. [b] Reference 11. [c] Reference 9. [d] X-ray data. [e] Neutron diffraction data. [f] Crystal structure of urea phosphate.

gies at the correlated levels of MP4(SDTQ)/6-31G*//MP2/6-31G* and MP4(SDTQ)/6-311+G*//MP2/6-311+G* were calculated. Vibrational frequencies at the MP2/6-31G*//MP2/6-31G* level were used to characterize stationary points as minima and to evaluate zero point vibrational energies (ZPE) which were scaled by a factor of 0.93.[19]

Table 5. IGLO-Calculated NMR Chemical Shifts

		IGLO II		
no.	atom	MP2/6-31G*	MP2/6-311+G*	expt
1	^{13}C	166.7	164.1	161.9
	^{15}N	66.8	64.9	76.7
2	^{13}C	157.7	156.2	
	^{15}N	61.7	60.2	
3	^{13}C	164.5	164.6	160.4
	$^{15}N_1$	70.0	68.8	
	$^{15}N_2$	73.8	74.1	
	$^{15}N_{ave}$	71.9	71.5	79.9
4	^{13}C	139.7	137.5	
	$^{15}N_1$	71.7	69.3	
	$^{15}N_2$	56.0	54.2	
5	^{13}C	162.9	161.0	156.1
	$^{15}N_1$	125.0	122.6	129.9
	$^{15}N_2$	47.1	45.8	58.7
6	^{13}C	157.3	156.4	
	^{15}N	92.6	91.4	
7	^{13}C	130.0	126.4	
	^{15}N	55.7	54.2	
8	^{13}C	183.5	180.1	
	$^{15}N_1$	60.9	59.2	
	$^{15}N_2$	65.7	64.3	
9	^{13}C	159.3	158.1	
	$^{15}N_1$	213.9	218.1	
	$^{15}N_2$	49.8	48.8	

The NMR data of urea, uronium ion and diprotonated urea under various conditions are tabulated in Table 1. Comparison of experimental and calculated bond length and bond angle parameters for urea and uronium ion are made in Table 3 and 4. Calculated energies and relative energies are listed in Table 2. IGLO calculations were performed according to the reported method[20] at IGLO II levels using MP2/6-31G* and MP2/6-311+G* geometries. Huzinaga[21] Gaussian lobes were used as follows. Basis II: C or O, 9s 5p 1d contracted to [51111, 2111, 1]; d exponent, 1.0; H, 5s 1p contracted to [311, 1]; p exponent, 0.70. Calculated NMR chemical shifts are listed in Table 5. For simplicity MP2/6-311+G* geometries and MP4(SDTQ)/6-311+G*//MP2/6-311+G* + ZPE energies will be discussed throughout the text unless otherwise stated.

Initially we have optimized the structures 1 and 2 of urea itself at the MP2/6-31G* and MP2/6-311+G* levels

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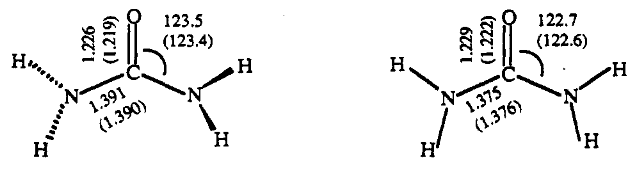
(19) Here, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, 1986; p 226.

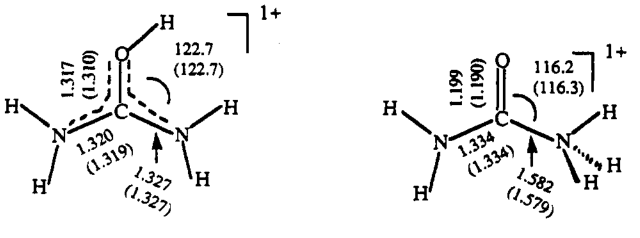
(20) Schindler, M. *J. Am. Chem. Soc.* 1987, *109*, 5950.

(21) Hazinaga, S. *Approximate Atomic Wave Function*; University of Alberta: Edmonton, Alberta, 1971.



1 (C2) 2 (C2v)

Figure 1. Selected MP2/6-31G*-optimized parameters (MP2/6-311+G*) of urea.



3 (C1) 4 (Cs)

Figure 2. Selected MP2/6-31G*-optimized parameters (MP2/6-311+G*) of monoprotonated urea.

(Figure 1). At our highest level nonplanar structure **1** is found to be only 2.1 kcal/mol more stable than the planar structure **2**. However, the structure **2** is a transition state for the inversion process in urea **1** as shown by frequency calculations at the MP2/6-31G*//MP1/6-31G* level as it contains two imaginary frequencies. The small energy differences (2.1 kcal/mol) between structures **1** and **2** indicates that the molecules can easily undergo inversion. Energy barrier for similar inversion processes for NH_3 and H_2NCN are 5.8 and 1.9 kcal/mol, respectively.[22]

The MP2/6-31G* and MP2/6-311+G* optimized geometries for urea are listed with the available experimental geometries in Table 3. The results show[3,4] that the C–O distance is longer (0.03 Å) and the C–N distance is shorter (0.04 Å) than the corresponding calculated bond distances. This could be due to the prevalence of a large number of hydrogen bonds (up to four) to the oxygen atom in urea in the solid state.[3]

We have also calculated ^{13}C and ^{15}N NMR chemical shifts of the structures **1** and **2** using the IGLO method (Table 5). Actually, both structures show considerable deviation from the experimental data. However, structure **1** seems to correlate better with the experimental data (*vide infra*, see Figure 3).

Monoprotonated Urea. There are two possible structures for protonated urea (uronium ion): O-protonated **3** and N-protonated **4**. O-protonated urea **3** is found to be 5.8 kcal/mol more stable than the N-protonated urea **4** which is consistent with the reported[12b] results at the Hartree–Fock level (HF/6-31G**). Table 4 shows the calculated geometry together with experimental geometries (also see Figure 2). X-ray studies on uronium nitrate show that the acidic proton is attached to the carbonyl oxygen atom of urea and forms a hydrogen bond to an oxygen atom of the nitrate ion.[11] The uronium ion in solid state is found to be planar.[9-11] The available experimental parameters of uronium ion agree well with the calculated structure of **3** (Table 4).

We have measured the ^{13}C and ^{15}N NMR chemical shifts of ^{15}N-labeled urea in H_2SO_4 and HNO_3 at room temperature as well as in FSO_3H/SO_2ClF at −80 °C. Each of the solutions consists of a single peak at around $\delta^{13}C$ 160 in its ^{13}C NMR spectrum and a single peak at around $\delta^{15}N$ 79 in its ^{15}N NMR spectrum (Table 1). The equivalence of the ^{15}N NMR peak (even at −80 °C) indicates that O-protonated or N-protonated uronium ion forms undergo rapid proton exchange at these acidities. To confirm this phenomenon we prepared ^{15}N-labeled uronium nitrate by crystallization at 0 °C from an aqueous solution containing equimolar amounts of ^{15}N-labeled urea and nitric acid. Pure ^{15}N-labeled uronium nitrate crystals were then obtained by recrystallization from methanol solution. The ^{13}C and ^{15}N NMR spectrum of ^{15}N-labeled uronium nitrate in DMSO at room temperature shows similar patterns as those obtained in other acid solutions (Table 1). However, we were not able to observe the proton on oxygen (or on nitrogen) by ^1H NMR spectroscopy because of rapid exchange and the quadruple broadening caused by the nitrogen atoms.

Compared to those in parent urea, $\delta^{13}C$ 160.4 of uronium ion is 1.5 ppm shielded and $\delta^{15}N$ 79.9 of uronium ion **3** is 3.2 ppm deshielded. The magnitude and direction of these shielding and deshielding effects compare very well with the IGLO calculated chemical shifts (Table 5). For example, the IGLO (II//MP2/6-311+G*) calculated $\delta^{13}C$ of uronium ion **3** is in fact 0.7 ppm shielded with respect to that of urea **1**. Similarly, calculated average $\delta^{15}N$ 70.3 of uronium ion **3** is 5.4 ppm deshielded compared to $\delta^{15}N$ 64.9 of urea **1**. The correlations between experiment and calculated chemical shifts are shown in Figure 3. The correlation is excellent.

Diprotonated Urea. Protonation on uronium ion **3** again can take place in two different ways. N-Protonation will lead to N,O-diprotonated urea **5** and O-protonation will lead to O,O-diprotonated urea **6** (Figure 4). Energetically, **5** was found to be 22.3 kcal/mol more stable than **6** at our highest level. Another possible structure for diprotonated urea is N,N-diprotonated urea **7** (isostructural to acetone), which is found to be only 4.7 kcal/mol less stable than **5**.

Diprotonated urea **5** is characterized by a longer C–O, a longer C–N (NH_3), and a shorter C–N (NH_2) bond compared to urea. This clearly indicates that one of the positive charges on nitrogen (NH_3^+) is localized and the second positive charge is delocalized among O–C–N (as in **5**) as described decades ago by Olah et al.[13] Olah et al. were able to obtain[13] the ^1H and ^{15}N NMR spectrum of ion **5** in $FSO_3H/SbF_5/SO_2$ at −80 °C. However, no ^{13}C NMR spectrum was reported at that time and no explanation was offered to the observed magnitude and direction of the ^{15}N NMR chemical shifts.

Now we report the ^{13}C and ^{15}N NMR spectrum of **5** prepared by dissolving ^{15}N laveled urea in $FSO_3H/SbF_5/SO_2ClF$ at −80 °C. The ^{13}C NMR spectrum consists of a triplet (J_{CN} = 21.6 Hz) centered at $\delta^{13}C$ 156.1. The $\delta^{13}C$ shift of **5** is shielded by 4.3 ppm from that of the uronium ion **3**. The ^{15}N NMR spectrum of the same solution shows a quartet centered at $\delta^{15}N$ 58.7 and a triplet centered at $\delta^{15}N$ 129.9 representing $-NH_3^+$ and $-NH_2$ nitrogens, respectively. Previously reported[13] corresponding NMR chemical shifts of **5** in $FSO_3H/SbF_5/SO_2$ at −80 °C were $\delta^{15}N$ 52.6 and $\delta^{15}N$ 125.6.

IGLO-calculated NMR chemical shifts of **5** are in the right direction. Calculated $\delta^{13}C$ 161.0 of **5** is 2.4 ppm shielded compared to that of **3**, and this agrees very well

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[22] Lehn, J. M. *Fort. Chem. Forsch.* **1970**, *15*, 311.

[23] Pryor, A. W.; Sanger, P. L. *Acta Crystallogr.* **1970**, *A26*, 543.

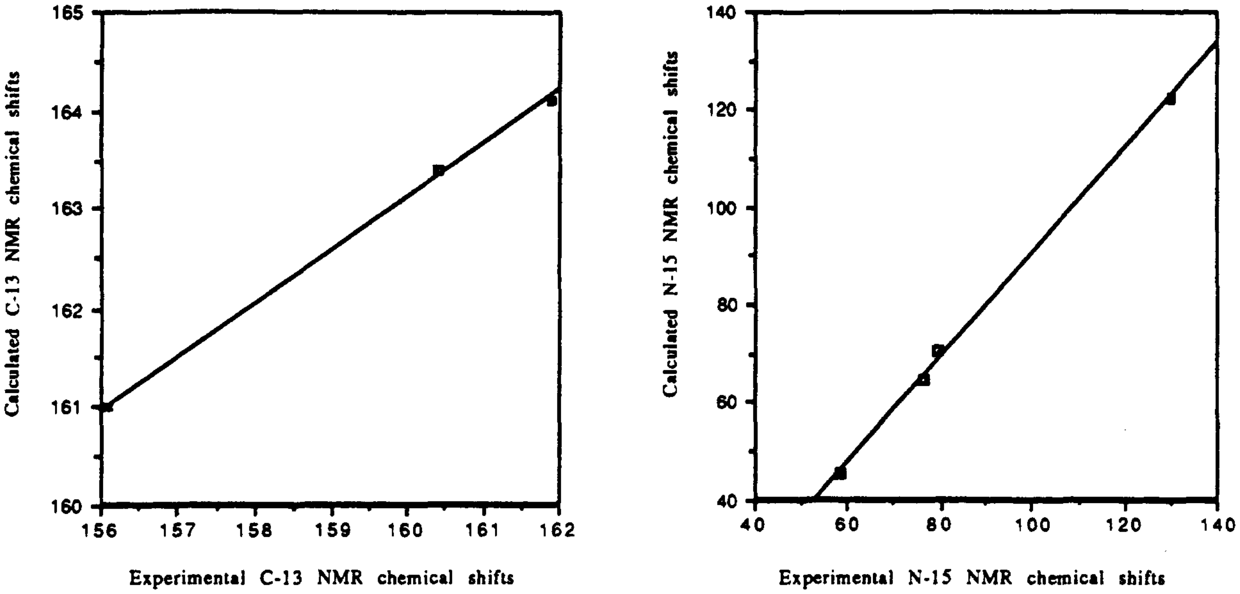
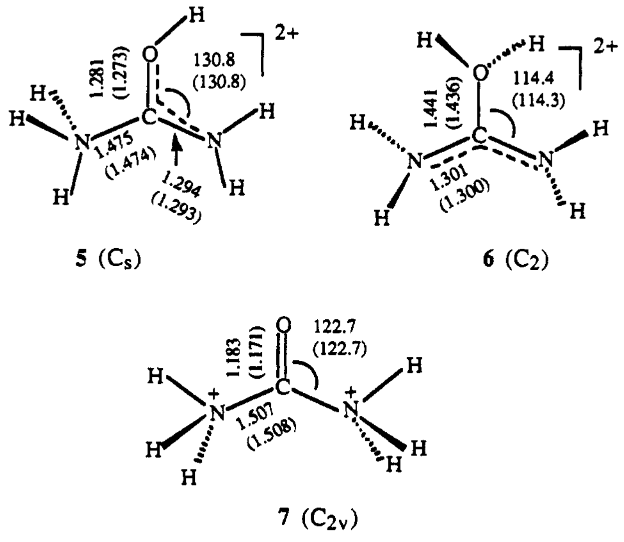
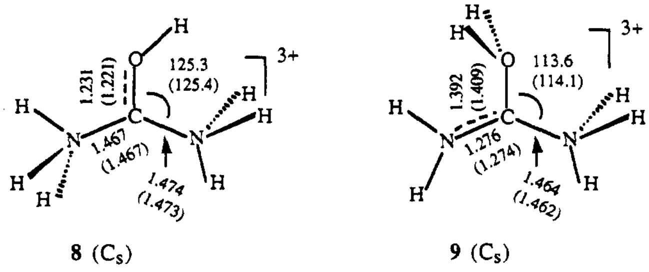


Figure 3. Calculated (II//MP2/6-311+G*) vs experimental chemical shifts of urea 1, monoprotonated urea 3, and diprotonated urea 5.



5 (Cs) 6 (C2) 7 (C2v)

Figure 4. Selected MP2/6-31G*-optimized parameters (MP2/6-311+G*) of diprotonated urea.



8 (Cs) 9 (Cs)

Figure 5. Selected MP2/6-31G*-optimized parameters (MP2/6-311+G*) of triprotonated urea.

with the corresponding experimental difference of 5.8 ppm (Table 5). Similarly, the two calculated ^{15}N NMR shifts of 5 at δ^{15}N 45.8 and δ^{15}N 122.6 compare very well with the two experimental values of δ^{15}N 58.7 and δ^{15}N 129.9, respectively (see Figure 3 for an excellent correlation).

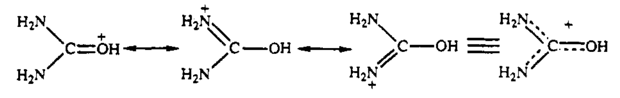
Tiprotonated Urea. Further protonation of diprotonated urea 5 can occur either on oxygen or on nitrogen leading to structures 8 and 9, respectively (Figure 5). Structure 8 was found to be only 1.8 kcal/mol more stable than the structure 9, although both are minima on the potential energy surface. The C–N bond lengths (1.45 Å) of 8 show single bond character, and the C–O bond length shows double bond character (1.23 Å). On the other hand in structure 9 C–O and C–N(H$_3$) bonds show single-bond character and the C–N(H$_2$) show double-bond character (Figure 5).

Whereas in urea, monoprotonated urea, and diprotonated urea ^{13}C NMR chemical shifts are progressively shielded (Table 5), in triprotonated urea 8 the ^{13}C NMR chemical shift is calculated to be considerably deshielded (δ^{13}C 180.1). The highly charged triprotonated species, however, could not be observed experimentally, although protosolvation of diprotonated urea is possible to a small extent. The calculated ^{15}N NMR chemical shifts of 8 and 9 are shown in Table 5.

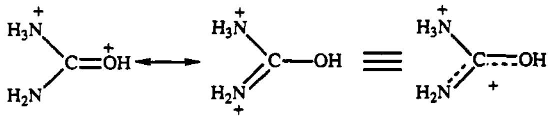
Conclusions

NMR/*ab initio*/IGLO investigation of urea, monoprotonated urea, diprotonated urea, and triprotonated urea gives substantial insight into their structure and energies. In the case of urea, the C_2 symmetry structure 1 is preferred over C_{2v} 2 by 2.1 kcal/mol. The preferred structure for monoprotonated urea is the O-protonated form 3. In the case of diprotonated urea the N,O-diprotonated form 5 was found to be the minimum energy structure. However, in the case of triprotonated urea the N,N,O-triprotonated 8 is only 1.8 kcal/mol more stable than the structure 9. The IGLO-calculated ^{13}C and ^{15}N NMR chemical shifts of the preferred structures agree very well with the experimentally obtained data (Figure 5).

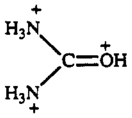
Protonated urea is a resonance stabilized cation, not unlike the guanidinium ion[13]



As two heteroatoms are sufficient to delocalize charge, diprotonated urea is also a remarkably stable dication



In the case of trprotonation only one heteroatom is available to assist in delocalization of excess charge. However, we have not been able to observe this species experimentally, although protosolvation of the diprotonated area is possible to a small extent.



Urea plays a significant role in biological chemistry. Its basic property, as shown in the present study of protonation, can involve mono-, di-, and even tridentate interactions with electron-pair acceptors.

Experimental Section

98% ^{15}N-enriched urea ($H_2{}^{15}NCO^{15}NH_2$) was obtained from Aldrich Chemical Co. The superacids $HSO_3F{:}SbF_5$ were prepared from freshly distilled HSO_3F and SbF_5. All manipulations using $HSO_3F{:}SbF_5$ were carried out in 5-mm Pyrex NMR tubes. ^{13}C and ^{15}N NMR spectra were obtained on Varian Associates Model VXR-200 NMR spectrometer equipped with a 5-mm variable-temperature broad-band probe. The ^{13}C NMR chemical shifts were referenced to external capillary tetramethylsilane signal. The ^{15}N NMR chemical shifts were referenced to anhydrous NH_3 signal.

Solutions of $H_2{}^{15}NCO^{15}NH_2$ in $FSO_3H{:}SbF_5$. ^{15}N-enriched urea was prepared by mixing 30 mg of 98% $H_2{}^{15}NCO^{15}NH_2$ with 0.5 mL of freshly prepared $HSO_3F{:}SbF_5$ solution at −80 °C in a 5-mm Pyrex NMR tube by rapid vortex stirring.

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Supplementary Material Available: Cartesian coordinates of 1–9 optimized at the MP2/6-311+G* level and calculated unscaled frequencies of 1–9 at the MP2/6-31G*//MP2/6-31G* level (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.