cations: we have observed the addition of up to six molecules of 1,3-butadiene to C_{60}^{2+} [23] (although in this reaction also, the proposed mechanism involves direct attachment of only two C_4H_6 molecules to the fullerene surface itself) and addition of several $H^{\bullet}$ atoms to both $C_{60}^{\bullet+}$ and C_{60}^{2+}.

The reaction mechanisms discussed here for reactions of fullerene cations with various neutrals are unlikely to correspond closely to those operating in the liquid or solid phase, since C_{60} is more likely to exist as an anion than as a cation under most circumstances in solution.

Conclusion

Kinetic data for the addition of a wide variety of polar neutrals to the fullerene dication C_{60}^{2+} in the gas phase are consistent with a model of nucleophilic addition involving the formation of "double-handled" secondary adducts by electron-pair donation to the charge sites upon the fullerene surface. The strongest support for this model is seen in the reactions of C_{60}^{2+} with various nitriles: in these reactions no other channels are observed to compete with association, and the rate coefficient for the tertiary addition step is invariably substantially lower than the rate coefficients for primary and secondary adduct formation.

Results for adduct formation involving $C_{60}^{\bullet+}$, and initial results for the reactivity of $C_{60}^{\bullet 3+}$, provide additional support for our model of nucleophilic addition. It appears possible, by gas-phase ion-molecule reactions, to add one "handle" to $C_{60}^{\bullet+}$, two to C_{60}^{2+}, and three to $C_{60}^{\bullet 3+}$. Neutralization of these cationic adduct species, perhaps by repeated proton transfer to an appropriate base, is capable of generating an array of novel derivatized neutral fullerenes. We have already suggested elsewhere[24] the notion that the polycationic fullerene adducts may form a useful model for polyprotonated proteins and other large molecules which have recently become accessible through the technique of electrospray ionization.[43]

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The Intrinsic Basicity of 4(5)-2′-Aminoethylimidazole (Histamine)†

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Abstract: The gas-phase basicity (GB) of histamine (**1**) relative to ammonia (defined as the standard Gibbs energy change for reaction 1) has been measured by means of Fourier transform ion cyclotron resonance spectroscopy (FT-ICR): $\mathbf{1H^+}(g) + NH_3(g) \rightleftharpoons \mathbf{1}(g) + NH_4^+(g)$. The various tautomer/conformers of $\mathbf{1H^+}(g)$ were studied by means of ab initio SCF-LCAO-MO calculations at the 6-31G//6-31G level. The calculated proton affinity agrees well with that estimated from FT-ICR results. Ring protonation is slightly preferred over side-chain protonation. Chelation provides a major contribution to the stability of $\mathbf{1H^+}(g)$. Comparison of these results with aqueous solution data reveals dramatic differences due to solvation.

1. Introduction

The title compound (**1**)[1], Figure 1, is a key molecule occurring in animal as well as in plant tissues. Free histamine produces in the organism diverse biological effects by interacting with three different biological receptors, namely, H_1, H_2, and H_3. When histamine interacts with H_2 receptors, gastric secretion is stimulated, resulting in serious clinical consequences.

The acid-base properties of the *N*-amino and *N*-imidazolyl groups and the conformational properties of the monocation are involved in all models of H_2 receptors.[2-4] Furthermore, the protonation of the imidazole group is essential for the storage of histamine in the granules of the mast cell.[5] On purely chemical grounds, it is an interesting bifunctional base. In the solid state, histamine monocation is found as the N_3-H tautomer,[6a] and histamine free base as the N_1-H one.[6b] In the monocation form, histamine forms dimers in a configuration with an intermolecular hydrogen bond between one of the hydrogen atoms of the ammonium terminal group and the N_1 atom of the imidazole ring of the nearest protonated molecule. At variance with this, in the neutral form, histamine molecules appear linked in chains through hydrogen bonds between the nitrogen atom of the amine terminal groups and the hydrogen atom bonded to the N_3 atoms. Intermolecular hydrogen bonds thus determine the crystalline structure of this compound under both the neutral and the protonated forms.

† Dedicated to Professor Robert W. Taft on his 70th birthday.
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(1) As pointed out by Vogelsanger, Godfrey, and Brown,[7] the standard nomenclature for histamine is 1*H*-imidazole-4(5)-ethanamine, but the name (2-aminoethyl)imidazole and β-(4-imidazolyl)ethylamine (following Ganellin[2]) are widely used in theoretical and biological studies.

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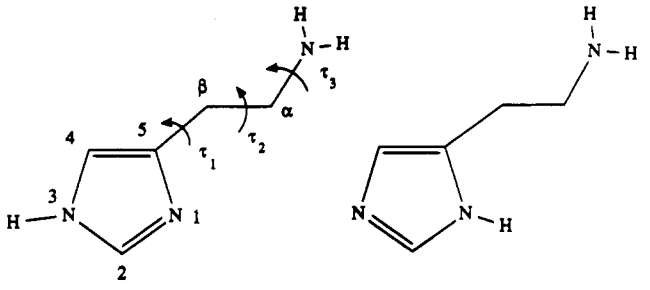

Figure 1. Notations used in the structural study of **1**(g) and **1**H$^+$(g).

Table I. Experimental Data Pertaining to the Determination of $\Delta GB(\mathbf{1})^a$

B_{ref}	$\Delta GB(B_{ref})^{a,b}$	$\delta\Delta G_{H^+}(g)^a$
$(n\text{-}C_3H_7)_3N$	35.2	1.5 ± 0.1
$(n\text{-}C_4H_9)_3N$	36.8	−0.2 ± 0.1
4-dimethylaminopyridine	37.4	−1.2 ± 0.2

[a] Values in kcal mol^{-1}. [b] Reference 14.

It is well known that, in solution at physiological pH, histamine exists as a monocation protonated in the amino group with approximately the same concentration of the cis and trans conformers of the $N_{(3)}$–H tautomer.[2] Important studies on its gas-phase structure[7] and microscopic basicity constants[8] (in aqueous solution) have appeared recently. This (and our long-standing interest in this compound[9]) has prompted us to determine its intrinsic (gas-phase) basicity. More precisely, we have measured its gas-phase basicity relative to ammonia, $\Delta GB(\mathbf{1})$, defined as the standard Gibbs energy change for the reaction:

$$\mathbf{1}H^+(g) + NH_3(g) \rightleftharpoons NH_4^+(g) + \mathbf{1}(g) \qquad (1)$$

The combination of gas-phase thermodynamic data with ab initio quantum-mechanical calculations[10] is proving to be a powerful tool for the understanding of the structure and reactivity of molecules and ions.[11] Thus, parallel to the experimental work, neutral and monoprotonated histamine were studied at the 6-31G//6-31G level.[12]

2. Experimental Results and Computational Technique

$\Delta GB(\mathbf{1})$ was determined by means of Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS).[13]

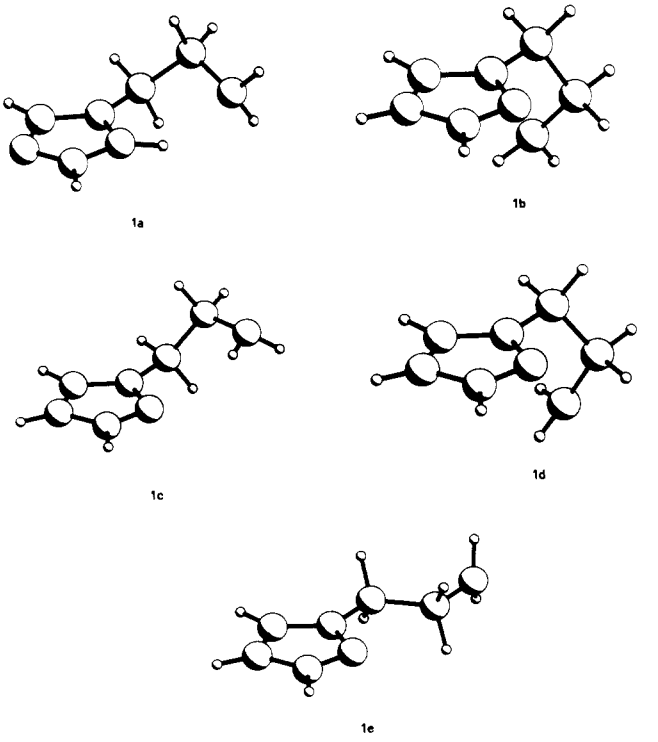

Figure 2. Selected tautomers/conformers of **1**(g).

In these experiments, the standard Gibbs energy changes $\delta\Delta G_{H^+}(g)$ pertaining to the proton-exchange reaction between **1** and the three reference bases, B_{ref} (reaction 2), were measured:

$$\mathbf{1}H^+(g) + B_{ref}(g) \rightleftharpoons \mathbf{1}(g) + B_{ref}H^+(g) \qquad (2)$$

In every case, $\Delta GB(\mathbf{1})$ was calculated as:

$$\Delta GB(\mathbf{1}) = \Delta GB(B_{ref}) + \delta\Delta G_{H^+}(g)$$

The experimental results are summarized in Table I.

From these data we deduce the average value, $\Delta GB(\mathbf{1}) = 36.5 \pm 0.2$ kcal/mol at 343 K. The proton affinity of **1** relative to ammonia, $\Delta PA(\mathbf{1})$, that is, the standard enthalpy change for reaction 1, cannot be obtained directly from FT-ICR data, but a reasonable estimate of the entropy change for this reaction, $\Delta S(\mathbf{1})$, can be made: it involves a negative contribution amounting to $-R$ ln 4 (2.75 cal/mol·K) and originating in the ratio of symmetry numbers of NH_4^+ (12) and NH_3 (3) and a positive one, associated with the cyclization entropy of $\mathbf{1}H^+$ (see below) of ca. 6 cal/mol·K.[15] At 343 K the $T\Delta S$ term thus amounts to ca. 1.1 kcal/mol. $\Delta PA(\mathbf{1})$ can then be estimated at 37.6 kcal/mol.

The ab initio calculations were performed with the MONSTERGAUSS program at the 6-31G level.[17a] The minima of the

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(10) See, e.g.: Hehre, W. J.; Random, L.; Schleyer, P. v. R., Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley: New York, 1986.

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(14) The $\Delta G(B_{ref})$ values are all taken from the same reference source: the 1988 basicity "ladder" by Professor R. W. Taft and Dr. F. Anvia. These values have been published: Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1. A correction factor of 1.125 (360/320) has been applied to account for the difference between the nominal temperature of the Taft-Anvia data (320 K) and the actual temperature (360 K) computed from recent high-pressure mass spectrometric studies: Meot-Ner (Mautner), M.; Sieck, L. W. *J. Am. Chem. Soc.* **1991**, *113*, 4448–4460. See, e.g., refs 11b and 11c.

(15) This is the value given in ref 16a for the entropy loss associated to the cyclization of protonated $H_2N\text{-}(CH_2)_2\text{-}NH_2$. This value is preferred to that for the cyclization of protonated $H_2N\text{-}(CH_2)_3\text{-}NH_2$ because, in the case of **1**, the rigidity of the imidazole ring entails a smaller loss of entropy even though $\mathbf{1}H^+$ leads to six-membered chelated structures (see text).

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Table II. Relevant Geometrical Parameters[a] (6-31G//6-31G) for the Five Significant Conformer/Tautomers for Histamine

parameter	1a	1b	1c	1d	1e
$C_{(\beta)}C_{(5)}$	1.494	1.494	1.494	1.492	1.500
$C_{(\alpha)}C_{(\beta)}$	1.533	1.532	1.544	1.542	1.538
$NC_{(\alpha)}$	1.466	1.456	1.452	1.450	1.453
HN	0.999	0.995	0.997	0.994	0.994
H'N	0.997	0.996	0.996	0.995	0.994
$HN_{(1)}$	0.994				
$HN_{(3)}$		0.989	0.989	0.989	0.989
$C_{(\beta)}C_{(5)}N_{(1)}$	122.7	121.4	122.1	121.1	122.0
$C_{(\alpha)}C_{(\beta)}C_{(5)}$	113.9	113.2	113.6	113.0	113.8
$NC_{(\alpha)}C_{(\beta)}$	111.0	110.9	115.4	115.4	113.7
$HNC_{(\alpha)}$	114.5	108.6	114.2	116.4	117.2
$H'NC_{(\alpha)}$	114.8	108.7	115.0	116.7	117.1
τ_1	316.4	68.8	301.3	62.7	0.1
τ_2	67.4	65.4	69.4	62.6	180.3
τ_3	66.5	164.1	77.4	288.3	290.4
total energy[b]	-357.755 37	-357.750 97	-357.751 36	-357.750 85	-357.747 64

[a] Bond distances in Å, and bond angles in deg. [b] Energies in atomic units.

potential energy hypersurfaces (PEH) were located by means of analytical gradients of the RHF wave functions. Davidon's optimally conditioned method was used to find out the minimal structures.[17b] The calculations were carried out up to average gradients lesser or equal to 5×10^{-4} mdyn or mdyn·Å/radian. No geometrical restrictions whatsoever were imposed in the optimization procedure.

3. Discussion

The analysis of ΔGB(**1**) requires the quantitative treatment of tautomeric and conformational equilibria in **1**(g) and $\mathbf{1H^+}$(g). Figure 1 portrays the two possible tautomeric forms for **1** as well as the three torsional angles τ_1, τ_2, and τ_3 defining the conformation with respect to the ethane skeleton. The three conformational angles τ_1, τ_2, and τ_3 are defined in such a way that the origin is on the syn arrangement. Notice that τ_1 is measured with respect to the syn configuration with respect to $N_{(1)}$ (in ref 9 this angle is defined with a phase factor of 180° relative to the present definition). Notations are thus the same as those used by Brown and co-workers.[5] These authors have recently published a careful experimental (free-expansion jet microwave spectrometer) and theoretical (ab initio, 3-21G//3-21G for all the minima of the potential energy surface and 6-31G//6-31G for some special minima) study on the structure of **1** in the gas phase. In particular, they were able to identify the four most stable tautomers/conformers (T/C) present in a gaseous sample of **1**. They are represented in Figure 2.

Our 6-31G//6-31G calculations confirm the fact that the more stable T/C is **1a**. Relevant structural data (shown in this paper for the sake of completeness) and total energies for these species are given in Table II. This table also presents data for the unchelated T/C **1e**, a useful reference structure. The molecular geometry and relative energies are very close to those reported by Brown and co-workers.[18] Inspection of Figure 2 and Table II shows that all four T/Cs present a gauche structure (τ_2 close to 60°) and an internal hydrogen bond. In this respect, the $N_{(1)}$–H distance in **1a** is some 0.005 Å larger than the $N_{(3)}$–H bond length in **1b**–**1d**. In the latter structures the NH bond lengths are found very close to that in unchelated structures such as **1e** (0.994 Å), thus indicating extremely weak hydrogen-bonding interactions. These hydrogen bonds are bent; the $N_{(1)}$–H···N angle in **1a** and the the $N_{(1)}$···H–N angle in **1c** are 122.6° and 123.8°, respectively. Chelation in **1b** and **1d** seems to involve the interaction between NH and the π-electron system of the imidazole ring.[7]

Brown's data were not obtained under strict conditions of thermal equilibrium. However, because of the very fast expansion and high dilution of histamine vapor, it can be reasonably accepted that the percentual distribution of T/Cs is not significantly different from that prevailing in the sample compartment at 403 K.

(18) There are some minor differences between our results and those given in ref 7. They likely originate in the different gradient conditions used in both studies.

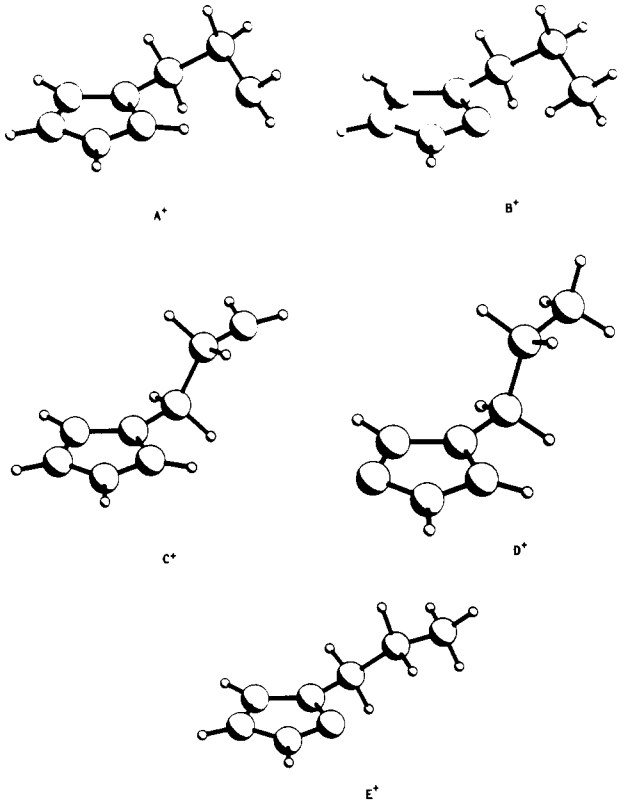

Figure 3. Selected tautomers/conformers of $\mathbf{1H^+}$(g).

Then, the standard Gibbs energy differences between the various T/Cs present in **1**(g) can be estimated at 1 kcal/mol at the most. This and the fact that the computed energy differences in **1a**–**d** are small indicate that the actual percentual distribution of these T/Cs in the gas phase is heavily dependent on even minor differential entropy contributions.

In previous papers, we studied the conformations of $\mathbf{1H^+}$(g)[9] and some of its 4-substituted derivatives,[9c,e] the stationary points in the PEH for the conformational/tautomeric manifold of $\mathbf{1E^+}$(g),[9d] and their possible relationship with biological activity.[9e] Although the ab initio calculations on $\mathbf{1H^+}$(g)[9c-e] were carried out at the STO-4G//STO-4G level, they showed in a fairly conclusive way that $N_{(1)}$ is intrinsically more basic than N and that chelation in $\mathbf{1H^+}$ (structure A^+, Figure 3) is strong.[9d] Indeed, it is well known that, in solution, **1** chelates metal ions.[2,19,20] The

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Table III. Significant Geometrical Parameters[a] (6-31G//6-31G) for Five Relevant Conformer/Tautomers of Histamine Monocation

parameter	$N_{(1)(3)}$-H^+ (A^+)	$N_{(3)}$-H (B^+)	$N_{(1)(3)}$-H^+ (C^+)	$N_{(1)}$-H (D^+)	$N_{(3)}$-H (E^+)
$C_{(\beta)}C_{(5)}$	1.498	1.498	1.495	1.494	1.494
$C_{(\alpha)}C_{(\beta)}$	1.536	1.531	1.547	1.532	1.527
$NC_{(\alpha)}$	1.473	1.520	1.439	1.539	1.538
HN	1.001	1.007	0.993	1.009	1.009
H'N	1.000	1.006	0.992	1.009	1.009
H^+N	1.967	1.048		1.010	1.009
$HN_{(1)}$	1.012	1.719	0.995	0.991	
$HN_{(3)}$	0.994	0.992	0.995		0.991
$C_{(\beta)}C_{(5)}N_{(1)}$	121.1	119.7	122.6	123.9	119.3
$C_{(\alpha)}C_{(\beta)}C_{(5)}$	113.0	112.1	113.8	110.6	108.8
$NC_{(\alpha)}C_{(\beta)}$	110.7	109.6	110.0	110.6	110.5
$HNC_{(\alpha)}$	113.6	111.6	118.3	110.7	111.2
$H'NC_{(\alpha)}$	113.4	112.0	118.5	111.1	110.9
$H^+NC_{(\alpha)}$	99.0	105.7		110.0	110.5
τ_1	322.0	322.4	284.2	272.1	315.2
τ_2	61.0	59.8	179.3	182.2	168.6
τ_3	315.9	312.4	85.0	60.4	60.0
total energy[b]	−358.169 07	−358.159 86	−358.151 04	−358.113 49	−358.134 52

[a] Bond distances in Å, and bond angles in deg. [b] Energies in atomic units.

Table IV. Selected Geometrical Parameter[a] (6-31G//6-31G) and Total Energies for Ethylamine, Imidazole, and Their Protonated Forms

parameter	**2**	$2H^+$	**3**	$3H^+$
$C_{(\alpha)}C_{(\beta)}$			1.532	1.519
$NC_{(\alpha)}$			1.453	1.537
HN			0.995	1.009
H'N			0.995	1.009
H^+N				1.009
$NC_{(\alpha)}C_{(\beta)}$			115.0	110.3
$HNC_{(\alpha)}$			116.5	110.7
$H'NC_{(\alpha)}$			116.5	110.7
$H^+NC_{(\alpha)}$				111.3
τ_1[c]			60.0	60.0
τ_2[c]			68.9	59.8
$HN_{(1)}$		0.996		
$HN_{(3)}$	0.989	0.996		
total energy[b]	−224.709 75	−225.103 44	−134.192 79	−134.565 76

[a] Bond distances in Å, and bond angles in deg. [b] Energies in atomic units. [c] τ_1 = 0 hydrogen of the methyl group in syn position with respect to $C_\alpha N$. τ_2 = 0 hydrogen of the amino or ammonium group in syn position with respect to $C_\beta C_\alpha$.

study of the whole PEH at the split-valence basis set level is now in progress.[21]

Upon protonation, the number of significant T/Cs is only two: A^+ and B^+ (Figure 3 and Table III). This important reduction originates in the strong stabilization provided by chelation, the species containing the $(N_{(1)}$-H···N$)^+$ and $(N_{(1)}$···H-N$)^+$ bonds being by far the most stable (see below). Chelation effects on N-H bond lengths can be estimated by comparing the appropriate N-H distances in the chelated structures A^+ and B^+ with those computed for the unchelated structures C^+, D^+, and E^+. It can be seen that $N_{(1)}$-H^+ and N-H^+ bonds are stretched by 0.018 and 0.041 Å, respectively. This suggests an appreciably stronger hydrogen bond in B^+ than in A^+. In these cations the hydrogen bonds are also bent, 130.5° and 143.2° for A^+ and B^+, respectively. Note that, in gas phase, the more stable T/C of the protonated molecule corresponds to the imidazolium structure (A^+). On the other hand, in solution the $N_{(3)}$-H tautomer is more stable. The chelated structures are closely related to the "scorpio" structure described in ref 9d. Analogously, we find that in the open T/Cs, C^+ is more stable than E^+.

The total energies of neutral and protonated imidazole **2** and ethylamine **3** were calculated with full geometry optimization at the same level than those for **1** and $1H^+$. Results are summarized in Table IV.

(20) The bidentate behavior of **1** is a key concept in recent models of histamine H_2 receptors: ref 4.

(21) Hernández-Laguna, A.; Smeyers, Y. G.; Arteca, G. A.; Abboud, J.-L. M.; Tapia, O. To be published.

Table V. Calculated (6-31G//6-31G) Energy Changes for Isodesmic Reactions 3–10

eq no.	reaction	ΔE[a,b]
(3)	**1a** → **1b**	2.76
(4)	**1a** → **1c**	2.51
(5)	**1a** → **1d**	2.84
(6)	A^+ + **2** → **1a** $2H^+$	12.56
(7)	B^+ + **3** → **1b** $3H^+$	22.54
(8)	**1a** + $2H^+$ → C^+ + **2**	−1.24
(9)	**1a** + $3H^+$ → D^+ + **3**	9.31
(10)	**1a** + $3H^+$ → E^+ + **3**	−3.87

[a] This work. [b] All values in kcal/mol.

Using the information given in Tables II, III, and IV, the energy changes ΔE pertaining to several relevant isodesmic reactions can be calculated. They are summarized in Table V.

The proton affinity differences relative to ammonia of **2** and **3** are known:[14] 22.0 and 13.9 kcal/mol, respectively. They can be used, together with the data from Table IV, to obtain the energy (or enthalpy) changes pertaining to the deprotonation of A^+ and B^+ to yield the most stable T/Cs of **1**(g). These ΔE values are summarized in Table V.

The experimental value of ΔPA(**1**) is the weighted average of the reactive PAs of the various T/Cs present in **1**(g). From Brown's experimental data, the relative populations are: **1a**, 37%; **1b**, 37%; **1c**, 14.8%; and **1d**, 11.1%. The averaged energy changes for reactions 11 and 12 can thus be estimated at $\Delta E(11)$ = 36.2 and $\Delta E(12)$ = 35.4 kcal/mol, respectively:

$$A^+(g) + NH_3(g) \rightarrow NH_4^+(g) + \mathbf{1}(g) \quad (11)$$

$$B^+(g) + NH_3(g) \rightarrow NH_4^+(g) + \mathbf{1}(g) \quad (12)$$

Relevant conclusions derived from these results are as follows.

1. From the above reactions and the 6-31G//6-31G level calculations, the stabilities of A^+ and B^+ are seen to be very close, the former being slightly preferred. This suggests the coexistence of both forms in the gas phase as well as the possibility of proton transfer between the two basic centers of $\mathbf{1}H^+$(g).

2. The agreement between the value of ΔPA(**1**) [obtained from the experimental ΔGB(**1**)] and $\Delta E(11)$ and $\Delta E(12)$ is excellent, especially considering that polarization orbitals were not used in these calculations. This strongly militates in favor of the 6-31G//6-31G basis set calculations used here and in Brown's work.[7]

3. The importance of chelation in determining both the absolute and the relative stabilities of A^+ and B^+ is best seen by considering the hypothetical reactions between **1a**(g) and imidazolium ($2H^+$) and ethylammonium ($3H^+$) cations to yield the un-chelated species C^+, D^+, and E^+ (see Figure 3 and Table II). At the 6-31G//6-31G level, ΔE values for reactions 8, 9, and 10 (see Table V) amount respectively to −1.24, 9.31, and −3.87 kcal/mol. From these values we deduce standard enthalpy (or energy) changes

for reactions 13, 14, and 15 of 23.2, 4.6, and 17.8 kcal/mol:

$$C^+(g) + NH_3(g) \rightarrow \mathbf{1a}(g) + NH_4^+(g) \quad (13)$$

$$D^+(g) + NH_3(g) \rightarrow \mathbf{1a}(g) + NH_4^+(g) \quad (14)$$

$$E^+(g) + NH_3(g) \rightarrow \mathbf{1a}(g) + NH_4^+(g) \quad (15)$$

Thus, in the absence of chelation, ring protonation would be vastly preferred and **1** would behave as a much weaker base. These remarkable base strengthening and leveling effects originate in the mutual "solvation"[16] of both moieties of $\mathbf{1H}^+(g)$. Furthermore, this approximately equal basicity of $N_{(1)}$ and N seems to explain the known ability of histamine to form bidentate chelates with metal ions and likely supports Kimura et al.'s model of histamine's H_2 receptor.[4]

4. Based on the ratio of protonation microconstants in D_2O solutions,[8] N protonation is seen to be favored over ring protonation by 3.97 kcal/mol[22] (in Gibbs energy) at 298 K. Clearly, this reversal of the relative basicities of both sites originates in solvation effects, the tremendous influence of water solvent on acid-base equilibria being well documented.[23] It thus seems possible that in a medium less efficient at charge dispersal (through hydrogen bonding) than water, such a stability gap could be strongly reduced. This would favor the prototopic exchange between both moieties of $\mathbf{1H}^+$. This contention is supported by the fact that recent theoretical calculations suggest that $\mathbf{1H}^+$ remains chelated even in aqueous solution.[24]

4. Experimental Section

FT-ICR studies were performed on a modified Brucker CMS-47 mass spectrometer under conditions similar to those used in previous works.[8] In every case, the attainment of equilibrium was established by means of double resonance experiments.

A sample of histamine (Aldrich) was twice sublimed and immediately introduced into the high-vacuum section of the mass spectrometer by means of a direct insertion probe. The nominal cell temperature was 343 K.

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(22) From the effect of temperature on this ratio, it can be deduced that, in D_2O solution at 313-333 K, chain protonation is 1.9 kcal mol^{-1} more exothermal than ring protonation.

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Matrix Isolation of Tricyclo[3.3.1.$0^{3,7}$]non-3(7)-ene, a Doubly Pyramidalized Alkene Predicted To Have a Nearly Tetrahedral Geometry at the Olefinic Carbons

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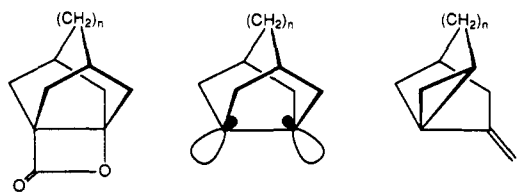
Abstract: The title alkene, which is calculated to have an approximately tetrahedral geometry at each of the doubly bonded carbons, has been generated by dehalogenation of 3,7-diiodotricyclo[3.3.1.$0^{3,7}$]nonane in the gas phase, using both potassium and cesium vapor, and has been isolated in an argon matrix at 10 K. The IR bands belonging to the alkene have been identified by photobleaching the matrix-isolated material and recording the difference spectrum. A weak band at 1496 cm^{-1} in the IR spectrum is assigned to the double-bond stretch on the basis of both semiempirical and ab initio electronic structure calculations.

As part of a systematic study of the spectroscopic and chemical effects of enforcing pyramidalized geometries on doubly bonded carbons,[2] we have reported the IR, Raman, and UV spectra of tricyclo[3.3.2.$0^{3,7}$]dec-3(7)-ene (**2b**) in matrix isolation.[3] Matrix isolation of **2b** was made possible by the availability of β-lactone **1b**[4] as a precursor, from which **2b** was generated by gas-phase pyrolysis. More recently, gas-phase pyrolysis of **1b** has allowed the photoelectron spectrum of **2b** to be obtained.[5]



1a, n = 1 **1b**, n = 2 **2a**, n = 1 **2b**, n = 2 **3a**, n = 1 **3b**, n = 2

β-Lactone **1a** has been synthesized as a possible precursor of **2a**.[4] The spectra of alkene **2a** are of even greater interest than those of its homologue (**2b**), since MM2, MNDO, and RHF/3-21G calculations[6] all predict a nearly tetrahedral geometry at each of the doubly bonded carbons of **2a**. Unfortunately, pyrolysis of **1a** did not prove to be a satisfactory method for generating **2a**.[7,8]

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