J. Am. Chem. Soc. 1981, 103, 6137-6142

Proton Affinities and Ionization Energies of Bicyclic Amines and Diamines. The Effects of Ring Strain and of 3-Electron σ Bonding

Roger W. Alder,*[†] Richard J. Arrowsmith,[†] Alan Casson,[†] Richard B. Sessions,[†] Edgar Heilbronner,[‡] Branka Kovač,[‡] Hanspeter Huber,[‡] and Mare Taagepera[§]

Contribution from the School of Chemistry, University of Bristol, Bristol BS8 1TS, England, Physikalische-Chemisches Institut, Universität Basel, 4056 Basel, Switzerland, and Department of Chemistry, University of California, Irvine, California 92717.

Received January 2, 1980. Revised Manuscript Received February 18, 1981

Abstract: Ionization energies and proton affinities of a series of medium-ring bicyclic amines and diamines with bridgehead nitrogens are reported. The photoelectron spectrum of *out*-6*H*-1-azabicyclo[4.4.4]tetradecane (**3**) is similar to n-Bu_3N and unlike that of 1-azabicyclo[3.3.3]undecane (manxine) (**2**), suggesting that the nitrogen in **3** is pyramidal. However the proton affinity of **3** is 20 kcal mol^{-1} lower than that of n-Bu_3N; it is proposed that **3** is inwardly pyramidalized and that (outside) protonation causes a large increase in strain energy in agreement with force-field calculations. The photoelectron spectra of diamines **6**–**9** show two bands due to lone-pair ionizations, the first ionization energy being exceptionally low (<7 eV). The interplay of flattening at nitrogen, and of through-space and through-bond coupling in these diamines, is discussed with the aid of force-field calculations. 1,6-Diazabicyclo[4.4.4]tetradecane (**9**) is a weaker base than 1,5-diazabicyclo[3.3.3]undecane, but it is stronger than **3**. $D(N^+–H)$ bond dissociation energies give evidence of substantial stabilization (>11 kcal mol^{-1}) of $\mathbf{6}^{+\cdot}$ and $\mathbf{9}^{+\cdot}$ by 3-electron σ bonding.

There has been much interest in recent years in the energetics for gas-phase ionization and protonation of amines.[1] Molecules with bridgehead nitrogen are particularly interesting because of the effects of geometrical constraints. The photoelectron spectra of 1-azabicyclo[2.2.2]octane (quinuclidine) (**1**) and 1-azabicyclo[3.3.3]undecane (manxine) (**2**) are quite different and this is ascribed[2] to flattening at nitrogen in **2**. The proton affinities of **1** and **2** are similar, however, and this was explained as due to the compensating effects of nitrogen flattening on the ionization energy and on the bond dissociation energy, $D(N^+–H)$, these being related to the proton affinity by the thermochemical cycle (1). We report here on the ionization and protonation of *out*-6*H*-1-azabicyclo[4.4.4]tetradecane (**3**).[3]

$$\begin{tikzcd}
R_3N\colon + H^+ \arrow[r, "\text{proton affinity (PA)}"] \arrow[d, "I_1^\circ(R_3N\colon)"'] & R_3N^+{-}H \arrow[d, "D(N^+\text{-}H)"] \\
R_3N^{+\cdot} + H^+ & R_3N^{+\cdot} + H^\cdot \arrow[l, "I^\circ(H^\cdot) = 313.6\ \text{kcal mol}^{-1}"']
\end{tikzcd} \qquad (1)$$

In diamines the nitrogen lone pairs can interact both directly through space and by mixing with other σ or π bonds in the molecule (through-bond interactions). 1,4-Diazabicyclo[2.2.2]octane (Dabco) (**4**) forms an unusually persistent radical cation in solution ($t_{1/2} \sim 1$ s in CH_3CN at 25 °C)[4] and shows two bands at 7.52 and 9.65 eV in its photoelectron spectrum.[5] Hoffmann[6] argued that in this case the through-bond interaction swamped that through space making n_+ the HOMO. In accord with this prediction Heilbronner and Muszkat[7] showed that the first ionization of Dabco corresponded to removal of an electron from an orbital of a_1 symmetry, through analysis of the vibrational fine structure of the photoelectron spectrum. From the proton affinities of quinuclidine (**1**) and Dabco (**4**) and use of the thermochemical cycle (1), Staley and Beauchamp[8] showed that $D(N^+–H)$ for protonated Dabco was less than that for protonated quinuclidine by 14 kcal mol^{-1}. They suggested that this difference in $D(N^+–H)$ values was a direct measure of the resonance stabilization of the ground-state Dabco radical cation. We now report the photoelectron spectra of diamines **5**–**9** (see Table I), the proton affinities of **6** and **9**, and an estimate, via $D(N^+–H)$ values, of the stabilization of the radical cations of **6** and **9**. These radical cations have been shown to be exceptionally persistent in solution ($t_{1/2} \sim 1$ day and 1 year, respectively, in CH_3CN at 25 °C),[9,10] and it will be argued that this stabilization is largely due to direct through-space interaction of the nitrogen orbitals (3-electron σ bond).

Experimental Section

The preparations of **3**,[3] **5**,[11] **6**,[9,11] **7**,[9,11] **8**,[11] and **9**[10,11] have been described.

Photoelectron spectra were obtained at Basel with a $\pi/2$ (5-cm radius) Turner type[12] spectrometer, using He (1α) photon excitation.

The proton affinities were determined at Irvine as described in detail previously.[13] Compounds **3**, **6**, and **9** were run with a heated inlet system at 80 °C.

Results

The photoelectron spectra of **2**, **3**, **5**, **6**, **8**, and **9** are shown in Figure 1. The spectra of **2** and **6** are closely simlar to those reported earlier.[2,9] There are two features of these spectra which we draw attention to here but do not comment on again: (i) the unusually low energy onset (~9.4 eV) of σ ionization bands in

---

[†] University of Bristol.
[‡] Univeritãt Basel.
[§] University of California.

[1] (a) Aue, D. H.; Bowers, M. T. In "Gas Phase Ion Chemistry", Bowers, M. T., Ed.; Academic Press; New York, 1979; Vol. 2, p 1. (b) Taft, R. W. In "Proton Transfer Reactions", Caldin, E. F., Gold, V., Eds.; Chapman and Hall: London, 1975; p 31.

[2] Aue, D. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1975**, *97*, 4136.

[3] Alder, R. W.; Arrowsmith, R. J. *J. Chem. Res., Synop.* **1980**, 163; *J. Chem. Res., Miniprint* **1980**, 2301.

[4] McKinney, T. M.; Geske, D. H. *J. Am. Chem. Soc.* **1965**, *87*, 3013.

[5] Bischof, P.; Hashmall, J. A.; Heilbronner, E.; Hornung, V. *Tetrahedron Lett.* 1969, 4025.

[6] Hoffmann, R.; Imamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499. Hoffmann, R. *Acc. Chem. Res.* 1971, *4*, 1.

[7] Heilbronner, E.; Muszkat, K. A. *J. Am. Chem. Soc.* **1970**, *92*, 3818.

[8] Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 1604.

[9] Alder, R. W.; Sessions, R. B.; Mellor, J. M.; Rawlins, M. F. *J. Chem. Soc., Chem. Commun.* 1977, 747.

[10] Alder, R. W.; Sessions, R. B. *J. Am. Chem. Soc.* **1979**, *101*, 3651.

[11] Alder, R. W.; Sessions, R. B.; Bennet, A. J.; Moss, R. E. *J. Chem. Soc., Perkin Trans. 1*, in press.

[12] Turner, D. W. *Proc. R. Soc. London, Ser. A* **1968**, *307*, 15.

[13] Wolf, J. F.; Staley, R. H.; Koppel, I.; Taagapera, M.; McIver, R. T., Jr.; Beauchamp, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 5417.

0002-7863/81/1503-6137$01.25/0

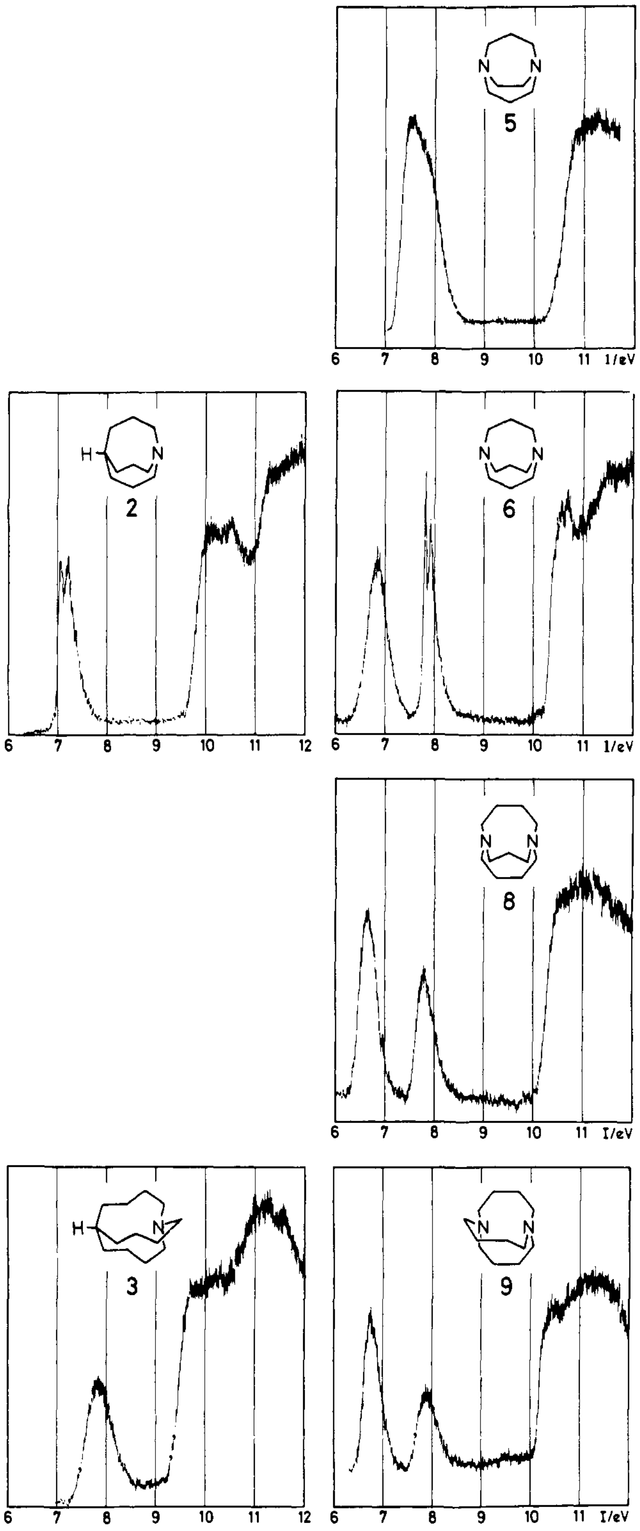


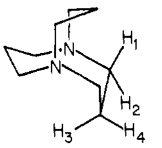
Figure 1. He(1α) photoelectron spectra of bicyclic amines.

3, perhaps due to the strain in that molecule,[3] and (ii) the changing relative intensities of the first two ionization bands in the series 6–9. The relative band areas are 1.1:1 for 6, 1.2:1 for 7, 1.5:1 for 8, and 1.8:1 for 9.

An overlap chart for the proton affinity determinations is in Table I. Several attempts were made to obtain corroboration of the equilibria involving 3 by double resonance techniques, but these remained ambiguous. With equilibria involving 3, reaction times were very long (~3 s) and it may be that reaction involves proton transfer to a low equilibrium concentration of outside pyramidalized 3. Ionization energies, proton affinities, and the deduced values of $D(N^+–H)$ for 1–9 together with some acyclic model compounds are collected in Table II.

In order to provide some guidance on the expected effects of flattening at nitrogen on I^V, PA, and $D(N^+–H)$, calculations were performed on NH_3 and NH_4^+ by the FOGO ab initio method.[14] The results are tabulated in Table III. Essentially similar results emerged from a MINDO/3 study.

Force-field calculations using Allinger's MM1 program (QCPE No. 318)[15] were performed on **2**, **3**, **6**, and **9** in order to gain some insight into conformational preferences in these molecules. Force-field calculations on amines are still in a relatively primitive state,[16] in particular, the lone pair is introduced as a pseudo-atom which must be placed on one side or other of the nitrogen so that planar amino nitrogen cannot be incorporated. For manxine (**2**), the calculations show a preference for outside vs. inside pyramidalized nitrogen (ΔH_f +2.27 vs. +6.02 kcal mol^{-1}), but the small energy difference, together with the flattening at nitrogen observed in the calculations, suggests that the true structure is probably nearly planar, in agreement with the earlier suggestion.[2] Both calculated minimum energy structures have C_3 symmetry (manxane geometry[17]). Similar conformations are found for the hydrocarbon bridges in **6**; the structure of **6** was calculated with out,out; in, out; and in,in lone pairs. The results are in Table IV. Diamine **6** shows temperature-dependent ^{1}H NMR spectra;[9] the coalescence temperature is −120 °C, giving $\Delta G^{\ddagger} = 7$ kcal mol^{-1}. The slow exchange spectrum at −160 °C in vinyl chloride can be accurately simulated with the following parameters: H_1 δ 2.74, H_2 2.90, H_3 1.86, H_4 1.01, $J_{12} = 14.0$, $J_{13} = 13.0$, $J_{23} = 5.0$, $J_{14} = 2.5$, $J_{24} = 2.0$, $J_{34} = 15.0$ Hz. Appropriately averaged parameters derived from these provide an equally satisfactory simulation of the room-temperature spectrum. These coupling constants give an R value[18] of 2.0 which translates into a dihedral angle of 57°. Models indicate that this is only attainable if the nitrogens in **6** are close to planar, as was found in the X-ray structure of a naphtho derivative of **6**.[19] The nearly perfect gauche conformations in the hydrocarbon bridges of **6** will make through-bond coupling in **6** very inefficient (see later).



Bicyclo[4.4.4]tetradecane structures, as in **3** and **9**, pose more complex conformational problems, more structures which are energy minima are possible, and it is impossible to be sure that the best structure has been located. The calculations for **3** have been reported earlier.[3] A C_3 structure with an inside lone pair ($\Delta H_f = +1.21$ kcal mol^{-1}, C–N–C = 112°) is strongly preferred to one with an outside lone pair ($\Delta H_f = +19.48$, C_3 symmetry, C–N–C = 117°). The results on **9** are in Table IV. Although the preference for an in,in structure may be exaggerated by the calculations a structure of this type is probably favored. A more extensive search of energy minima has been performed for bicyclo[4.4.4]tetradecane itself. The in,in isomer prefers a structure with C_2 symmetry, in which the inner hydrogens are displaced from a direct head-on clash; structures of this type have not been examined for **9**. The ^{13}C NMR of **9** shows only two types of carbon down to −140 °C, indicating that any energy minima involving nonequivalent bridges are quite shallow. In the in,in D_3 structure for **9** which is favored by the calculations, the N–C–C–C and C–C–C–C dihedral angles are 66 and 80°, respec-

---

(14) Method and basis set as described in: Huber, H. *Theor. Chim. Acta* **1980**, *55*, 117.

(15) Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1.

(16) Allinger (personal communication) has recently parameterized his MM2 force field for amines. For MM2 see: Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

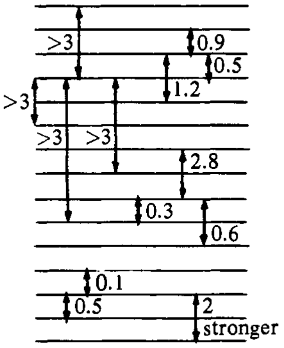
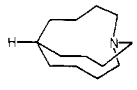
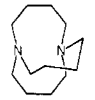
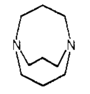
(17) Wang, A. H.; Missavage, R. J.; Byrn, R. S.; Paul, I. C. *J. Am. Chem. Soc.* **1972**, *94*, 7100. Murray-Rust, P.; Murray-Rust, J.; Watt, C. I. F. *Tetrahedron* **1980**, *36*, 2799.

(18) Lambert, J. B. *Acc. Chem. Res.* **1971**, *4*, 87.

(19) Alder, R. W.; Goode, N. C.; King, T. J.; Mellor, J. M.; Miller, B. W. *J. Chem. Soc., Chem. Commun.* **1976**, 173.

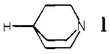
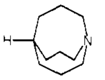
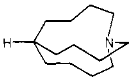
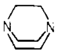
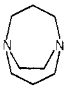
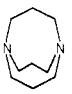
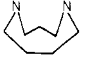
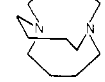
Table I. Standard Free Energies and Enthalpies of Proton Transfer and Proton Affinities Relative to Ammonia (kcal mol^{-1}) at 323 K

$$NH_4^+ + B \rightleftharpoons BH^+ + NH_3$$

standard[a]	$\Delta G°$	directly measured $\Delta G°$	$\Delta G°$	compd	$\Delta H°$
2-Cl pyridine	−11.0				
3-Cl pyridine	−11.5				
$CF_3CH_2N(CH_3)_2$	−11.7				
$C_6H_5CH_2NH_2$	−13.2		−12.1	 3	−11.3
pyridine	−17.7				
2-Me pyridine	−21.4				
Et_2NH	−22.2				
Et-*i*-PrNH	−23.8		−23.6	 9	−22.8
(*n*-Pr)$_2$NH	−24.3				
Et_3N	−29.4		−29.4	 6	−28.6
(*t*-Bu)$_2$NH	−29.9				
Pr_3N	−31.4				

[a] See ref 1b.

Table II. Ionization Energy and Proton Affinity Data for Some Tertiary Mono- and Diamines[a]

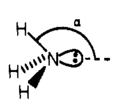
amine	$I_1^{m\,b}$	$I_1^{0\,c}$	I_2^{m}	I_2^{0}	PA	$D(N^+\text{-}H)^d$
Et_3N^e	8.08 (186.3)	7.11 (164)			234.0	84
n-Pr_3N^e	7.92 (182.6)	7.03 (162)			236.1	84
n-Bu_3N^e	7.90 (182.2)	6.98 (161)			237.6	85
 1	8.06 (185.9)[f]	7.50 (173)			233.6	93
 2	7.13 (164.4)	6.9_5 (160)			233.4	80
 3	7.84 (180.8)	7.4 (171)			217	74
 4	7.52 (173.4)[g]	7.2_4 (167)[g]	9.65 (222.5)[g]	9.0_2 (208)[g]	230.9	84
 5	7.5_5 (174)[h]	7.2 (166)[h]	7.8 ± 0.2 (180)[h]			
 6	6.85 (158.0)	6.4_5 (149)	7.9_0 (182)	7.7 (178)	234.1	69
 7	6.75 (155.6)[i]	6.3 (145)[i]	7.80 (179.9)[i]	7.5_5 (174)[i]		
 8	6.64 (153.1)	6.3 (145)	7.77 (179.2)	7.5 (173)		
 9	6.75 (155.6)	6.4_5 (149)	7.87 (181.5)	7.5_5 (174)	228.3	63

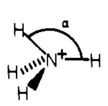
[a] Ionization energies in eV (kcal mol^{-1}). Data are from this work unless otherwise stated, and errors are then ±0.02 eV (±0.5 kcal mol^{-1}) if two decimals are quoted; ±0.05 eV (±1.2 kcal mol^{-1}) if the second decimal is a lower subscript; ±0.1 eV (±2.3 kcal mol^{-1}) otherwise. Proton affinities are in kcal mol^{-1}. Values are ±0.2 except for 3 where the error is estimated at ±1 kcal mol^{-1}; values are based on a figure of 205.5 kcal mol^{-1} for the PA of NH_3. The absolute PA of ammonia lies between 203.6 and 208.4 (Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* 1979, *101*, 4067). Eades, R. A.; Scanlon, K.; Ellenberger, M. R.; Dixon, D. A.; Marynick, D. S. *J. Phys. Chem.* 1980, *84*, 2840, recommend PA = 205.6 ± 0.1 as most probable value. [b] The experimental value I_2^m refers to the band maximum for those bands with smooth contours, and is assumed to represent the true vertical ionization energy I_2^v within the limits of error. For 2 and the second band of 6, an average of the positions of the two fine structure components (see Figure 2) has been taken as the best estimate. [c] The band onset I_i^0 has been determined by the tangential extrapolation technique used by: Aue, D. H.; Webb, H. M.; and Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 311. With the exception of I_1^a of 2 and I_2^a of 6, it is assumed that I_i^0 is the best available estimate of I_i^a, the latter could however well be lower by 0.1–0.2 eV. [d] $D(N^+\text{–}H) = I_1^0 + PA - 313.6$ kcal mol^{-1}. [e] Values from Aue et al., see footnote *c*. [f] Bieri, G.; Heilbronner, E. *Helv. Chim. Acta* 1974, *57*, 546. The value of 8.01 eV given in the first reference of footnote *g* is probably too low. [g] See ref 5 and 7. [h] Only the position of the first of the two overlapping bands can be assessed with some confidence. However, I_1^m could be associated with a larger error than the one suggested by the precision with which the double-band maximum can be located. I_2 is only a rough guess. [i] Mellor, J. M.; Rawlins, M. F., personal communication, see ref 9.

tively. These values are very far from the 0° or 180° angles which are optimal for through-bond coupling.

Calculations have not been performed on the less symmetrical diamines 7 and 8. 1,6-Diazabicyclo[4.3.3]dodecane (7) shows

Table III. FOGO Calculations on C_{3v} H_3N and H_3N^+-H

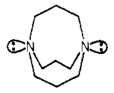
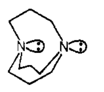
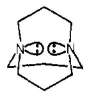
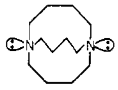
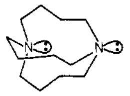
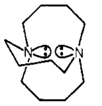




	α°						
	90	95	100	105	110	115	120
$E(NH_3)$,[a] kcal mol^{-1}	0	−0.7	−2.9	−5.5	−7.2	−7.1	−4.0
$E(H_3N^+$-H),[b] kcal mol^{-1}	−203.2	−214.9	−224.0	−229.5	−231.3	−228.5	−220.4
I^v (NH_3), eV	9.96	10.02	10.20	10.50	10.90	11.37	11.91

[a] Relative energies with respect to $E(NH_3)_{90°}$. [b] Relative energies with respect to the absolute energy of $E(NH_3)_{90°} = -56.1091E_h$.

Table IV. Force-Field Calculations on 1,5-Diazabicyclo[3.3.3]-undecane (6) and 1,6-Diazabicyclo[4.4.4]tetradecane (9)

structure	symmetry	C-N-C angle, deg	N-N distance, Å	ΔH_f, kcal mol^{-1}	strain energy, kcal mol^{-1}
	C_{3h}	114.8	3.34	26.24	32.99
	C_3	116.2 (out) 116.9 (in)	2.61	31.80	38.55
	C_{3h}	119.6	2.44	49.25	56.00
	D_3	117.2	4.27	43.07	66.57
	C_3	118.2 (out) 111.8 (in)	3.34	24.88	45.17
	D_3	113.8	2.61	2.70	26.20

14 lines in its ^{13}C NMR spectrum at −150 °C (vinyl chloride solvent), which means that a mixture of conformations must be present. There are five strong and nine weaker lines (~2:1 intensity ratio), so that two conformations, one with some symmetry, e.g., C_2, must be present. 1,6-Diazabicyclo[4.4.3]tridecane (8) shows six lines for carbons α to nitrogen and four lines for carbons β to N, in the ^{13}C spectrum at −146 °C in vinyl chloride. The compound could have a conformation without any symmetry (nonequivalent nitrogens) or could be a mixture of two conformations with C_2 symmetry—the latter is a reasonable possibility from models.

Discussion

Monoamines. The first band in the photoelectron spectrum of *out*-6*H*-1-azabicyclo[4.4.4]tetradecane (3) is similar both in position (I_1^m) and band profile to *n*-Bu_3N and is quite different from manxine (2). The broadness of the band suggests substantial changes in geometry on ionization of 3, while the normal value for the vertical ionization energy is consistent with a pyramidal nitrogen in 3. Force-field calculations favor an inwardly pyramidal nitrogen (C-N-C = 112°), in agreement with the unusual properties of 3 in solution.[3] On the other hand the adiabatic ionization energy of 3 is 0.4 eV (10 kcal mol^{-1}) higher than *n*-Bu_3N. Thus, at relaxed geometries $3^{+\cdot}$ is *more* strained than 3, a situation that is also found in quinuclidine ($1^{+\cdot}$ vs. 1). In manxine (2) the strain energies in amine and radical cation are more or less the same. According to the FOGO calculations there is a stronger driving force for $H_3N^{+\cdot}$ to be planar ($E(H_3N^{+\cdot})_{110°} - E(H_3N^{+\cdot})_{90°} = 15.5$) than for H_3N to be pyramidal ($E(H_3N)_{90°} - E(H_3N)_{110°} = 6.2$ kcal mol^{-1}). It seems that the hydrocarbon portion of 3 would impose inward pyramidality on a bridgehead atom which by itself showed no intrinsic preference for pyramid or planar geometry.

In contrast to the relatively ordinary ionization behavior of 3, its proton affinity is 20 kcal mol^{-1} lower than that of *n*-Bu_3N, making it the least basic known tertiary amine with purely saturated alkyl substituents. The pK_a of 3, measured in 48% v/v ethanol/water, is only +0.6,[3] so the extraordinarily weak basicity of 3 carries over into solution. We believe that in both the gas phase and solution we are observing the outside protonation of the nitrogen in 3. Proton transfers involving 3 in the gas phase are remarkably slow (see Results section). In CD_2Cl_2 solution, while proton transfers between amine 3 and its protonated ion are fast on the NMR time scale at room temperature, they become slow below −50 °C, which is unusual behavior for a simple tertiary amine. The formation of outside protonated 3, both in the gas phase and in solution, may involve the rapid capture of a tiny equilibrium concentration of outside pyramidalized 3. There is good agreement between the strain energy penalty for outside pyramidalization of 3 (17 kcal mol^{-1}) and the observed decrease in proton affinity compared to acyclic models. Based on experience with the inside protonation of the corresponding diamine 9[20] and related species,[21] there is likely to be a very high barrier to inside protonation of 3, although 3 may be quite a strong base in a thermodynamic sense as far as inside protonation is concerned. Force-field calculations on bicyclo[4.4.4]tetradecane itself show a preference for the in,out over the out,out structure of 12.3 kcal mol^{-1}. So far all attempts to induce inside protonation of 3 in solution have failed.

In comparison with 3 the proton affinity of manxine appears remarkably high. As the FOGO calculations attest there is a much greater driving force for the attainment of tetrahedral geometry in NH_4^+ than for pyramidality in NH_3 ($E(H_3N^+\text{-H})_{\alpha=90°} - E(H_3N^+\text{-H})_{\alpha=110°} = 28.2$ kcal mol^{-1}). In the crystal structure of manxine hydrochloride, α = 102°.[17] Formation of H_3N^+-H with this geometry from planar H_3N is calculated from the FOGO results to be ~2 kcal mol^{-1} more favorable than normal protonation of relaxed NH_3 to relaxed NH_4^+. The difference between this value and PA(*n*-Pr_3N) − PA(manxine), ca. 5 kcal mol^{-1}, might be ascribed to the strain introduced in the bicyclo[3.3.3]undecane skeleton by protonation. This strain is also evident in the bond dissociation energy $D(N^+\text{-H})$ for manxineH^+ which is 4 kcal mol^{-1} lower than normal. The $D(N^+\text{-H})$ value for 3-H^+ is 10 kcal mol^{-1} below normal reflecting a much greater strain relief on loss of $H\cdot$.

Diamines. The first ionization energies of diamines 6–9 are exceptionally low—these molecules must be among the most easily ionized saturated organic compounds. In solution too these compounds are very easily oxidized giving very long-lived radical cations, which are presumed to contain 3-electron σ bonds.[9,10,22] This implies that the ground state of these radical cations is $n_+(\uparrow\downarrow)$

---

(20) Alder, R. W.; Casson, A.; Sessions, R. B. *J. Am. Chem. Soc.* **1979**, *101*, 3652.

(21) Cheney, J.; Kintzinger, J. P.; Lehn, J.-M. *Nouv. J. Chim.* **1978**, *2*, 411.

(22) Nelsen, S. F.; Alder, R. W.; Sessions, R. B.; Asmus, K.-D.; Hiller, K.-O.; Gobl, M. *J. Am. Chem. Soc.* **1980**, *102*, 1429.

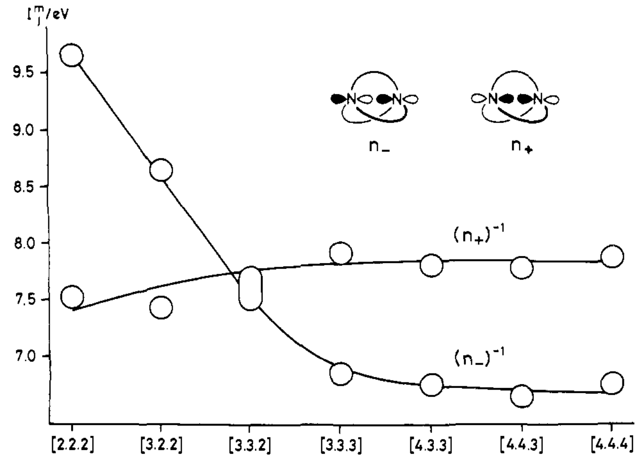


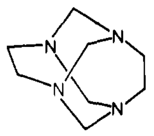
Figure 2. Vertical ionization energies for the first two bands in the photoelectron spectra of diamines: [2.2.2] = 1,4-diazobicyclo[2.2.2]octane (**4**), etc.

$n_-(1)$ (see the introduction), i.e., that through-space interaction dominates any through-bond effects at least at the equilibrium (relaxed) geometries of these ions. Before discussing the photoelectron spectra of these diamines, it is as well to emphasize the simple-minded arguments for this assignment. All the stable radical ions $\mathbf{6}^{+}\cdot\mathbf{9}^{+}$, can be oxidized in solution to stable dications $\mathbf{6}^{2+}$–$\mathbf{9}^{2+}$ which are plainly propellanes with a normal N–N 2-electron bond ($n_+(\uparrow\downarrow)$ $n_-(0)$ configuration). In all these structures inward pyramidalization at the bridgehead atoms is strongly favored by the geometrical constraints of the bicyclic medium ring system. Thus the $n_+(\uparrow\downarrow)$ $n_-(1)$ configuration which requires a short N–N distance is surely favored at the relaxed $\mathbf{6}\cdot\mathbf{9}^{+}$. of $\mathbf{6}^{+}\cdot$ –$\mathbf{9}^{+}\cdot$.

These arguments do not ensure that the radical ions from **6**–**9** formed by the first vertical ionization in the photoelectron spectrometer have the same $n_+(\uparrow\downarrow)$ $n_-(\uparrow)$ configuration, but we shall argue that this is indeed the case. Figure 2 shows the first two ionization energies through the sequence from 1,4-diazabicyclo[2.2.2]octane (**4**) to 1,6-diazabicyclo[4.4.4]tetradecane (**9**). Data for 1,5-diazabicyclo[3.2.2]nonane are taken from the work of Nelsen and Buschek.[23] We propose that the data are best interpreted in terms of the trend lines and assignments on Figure 2. Through-bond coupling is known to be dominant in Dabco (**4**). According to theory, through-bond coupling should place n_+ above n_- for a $(CH_2)_2$ bridge, n_- above n_+ for a $(CH_2)_3$ bridge, and n_+ above n_- for a $(CH_2)_4$ bridge. If this were occurring, there should be a strong alternating effect, which is not observed. However, through-bond coupling is crucially dependent on conformation within the bridges. As the bridges lengthen, the probability of achieving a favorable conformation decreases sharply. In fact the evidence from NMR data, the results from force-field calculations see the Results section), and the simple examination of models suggest that while $(CH_2)_2$ bridges in these molecules are in favorable conformations for through-bond coupling, this is not the case for $(CH_2)_3$ and $(CH_2)_4$ bridges. The outcome is that the effect of through-bond coupling simply dies away to insignificance as the $(CH_2)_2$ bridges are replaced by $(CH_2)_3$ and $(CH_2)_4$ bridges.

At the same time as through-bond coupling dies away, two other effects must make their appearance. The strained medium ring structures in **6**–**9** should have flattened nitrogen atoms. As discussed above for the monoamines this should cause a general lowering of lone-pair ionization energies. The same structural constraints should enforce direct through-space overlap of the nitrogen lone pairs causing n_- to be destabilized relative to n_+. The observed values for I_1^m and I_2^m are remarkably constant in the series **6**–**9**. These diamines are probably best visualized as consisting of two nitrogen atoms pushed into as close proximity as their mutual repulsion will allow by the three hydrocarbon bridges. The overlap integral between the lone-pair orbitals may well be fairly constant despite changing $(CH_2)_n$ bridges and changing conformations. Both N–N distance and hybridization at N affect the overlap, but there may be a trade-off between these. Thus the N–N distance may be shorter in **6** than in **9**, but the nitrogen atoms in **9** are probably inwardly pyramidalized, increasing the overlap. In the absence of detailed structural data, this model must be qualitative. It seems to explain the facts, however, including the observation that diamines **7** and (probably) **8** are conformational mixtures but that this has no noticeable effect on the photoelectron spectra.

1,5-Diazabicyclo[3.3.2]decane (**5**) is of special interest, since n_+ and n_- are virtually degenerate. It is structurally related to the tetramine **10**, whose radical cation, it has been argued, exists in a different electronic state in solution from that produced by the lowest energy gas phase ionization process.[24] The radical cation $\mathbf{5}^{+}\cdot$ is apparently very short lived in solution, and our attempts to characterize it by ESR have so far proved fruitless.



10

For the medium-ring diamines **6**–**9** the first band is always broad and structureless. Removal of a n_- electron should precipitate a large change of structure with the N–N distance decreasing sharply. In solution the radical cations $\mathbf{6}^{+}\cdot$ –$\mathbf{9}^{+}\cdot$ show very broad absorption centered at ~480 nm which must be the $n_+(\uparrow\downarrow)$ $n_-(\uparrow) \rightarrow n_+(\uparrow)$ $n_-(\uparrow\downarrow)$ transition. Thus *at the geometry of the diamines* these two states are separated by ~1 eV, but *at the relaxed geometry of the radical ions* the two states are separated by ~2.7 eV. This is somewhat larger than the energy difference between the *onset* of the first PE band and the *demise* of the second one, as it should be. The second PE band for **6** is remarkably sharp indicating little change in structure on going to the $n_+(\uparrow)$ $n_-(\uparrow\downarrow)$ cation. It is difficult to regard this as more than a fortuitous circumstance, though it should be pointed out that outward movement of the nitrogens is strongly resisted by the hydrocarbon bridges of **6**. The larger diamines are perhaps more flexible in this respect.

The proton affinities of diamines **6** and **9** show the same trends as the solution pK_a values (pK_{a1} = 10.3, pK_{a2} ~ 6.5 for **6**,[9] pK_{a1} = 6.5 ± 0.5, pK_{a2} = −3.25 for **9**[20]); as with monoamine **3**, the major factors affecting protonation of these diamines are of a type (strain, etc.) which are not much altered by solvation. The common trends make us confident that it is the proton affinity for outside protonation which is being observed. The proton affinity of **9**, for inside protonation, should be very high indeed, the strong hydrogen bond in the inside protonated ion providing strong "solvation" of the proton.[1a,20,25] The possibility of very slow isomerization to the inside protonated form in the ICR spectrometer was looked for, but not found. In the absence of special effects the proton affinity is expected to show a substantial increase on going from **4** to **6** to **9**, due to a decreased inductive effect from the second nitrogen and increased polarizability (cf. Et_3N, n-Pr_3N, n-Bu_3N). In practice the proton affinity of the [3.3.3] diamine **6**, while less than that of n-Pr_3N, is quite high and is actually higher than that of the structurally related monoamine **2**. A possible explanation of this is that the nonprotonated nitrogen in monoprotonated **6** is more flexible than a CH group and can adopt a flattened or even inside pyramidalized geometry. A more clear-cut example of the same phenomena is probably responsible for the much higher proton affinity of diamine **9** than monoamine **3**. Outside monoprotonated **9** probably resembles amine **3** in geometry with the unprotonated lone pair inside. For diamine **9** it is the *second*

---

(23) Nelsen, S. F.; Buschek, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 7930.

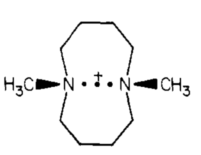
(24) Nelsen, S. F.; Haselbach, E.; Gschwind, R.; Klemm, U.; Lanyova, S. *J. Am. Chem. Soc.* **1978**, *100*, 4367.

(25) Meot-Ner, M.; Hamlet, P.; Hunter, E. P.; Field, F. H. *J. Am. Chem. Soc.* **1980**, *102*, 6393. Lau, Y. K.; Saluja, P. P. S.; Kebarle, P.; Alder, R. W. *Ibid.* **1978**, *100*, 7328.

outside protonation which occurs with such reluctance.

The $D(N^+-H)$ values for **6** and **9** are exceptionally low. As discussed in the introduction, Staley and Beauchamp suggested[8] that comparison of $D(N^+-H)$ values for **1** and **4** provided a direct measure of the resonance stabilization of the radical cation from **4** (by through-bond coupling in this case). According to the values in Table II, this amounts to 9 kcal mol^{-1}. Application of the Staley-Beauchamp argument to the pairs **2**/**6** and **3**/**9** leads to estimated stabilization energies of 11 kcal mol^{-1} for both $\mathbf{6}^{+\cdot}$ and $\mathbf{9}^{+\cdot}$, presumably by through-space interaction. This argument however relies on the strain energies of the monoprotonated ions of the mono- and diamines being the same. As we have argued above, this is probably not the case, the monoprotonated ions of the *mono*amines being more strained. This means that the estimated stabilization energies are too small, perhaps by 1-3 kcal mol^{-1} for $\mathbf{6}^{+\cdot}$, but by perhaps as much as 10 kcal mol^{-1} for $\mathbf{9}^{+\cdot}$. A better model for **9** would probably be the inside CH isomer of **3**, which is unknown at present.

Recently the kinetics of decomposition of the radical ion **11** were studied.[22] The rate-limiting step is probably cleavage of the 3-electron σ bond. The free energy of activation for this process (14.5 kcal mol^{-1}) is therefore a reasonable estimate of the bond dissociation energy for the 3-electron σ bond, since the reverse process probably has no activation energy. There seems to be encouraging semiquantitative agreement on the strengths of the 3-electron σ-bonding interaction in **6**, **9**, and **11**.



11

Acknowledgment. Work at Bristol has been assisted by S.R.C. studentships to R.J.A., A.C., and R.B.S. Work at Basel constitutes part 129 of project No. 2.011-2.78 of the Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung. Branka Kovač thanks the "Ruđer Bošković" Institute (Zagreb, Yugoslavia) for a leave of absence. Work at Irvine has been supported in part by a grant from the National Science Foundation.

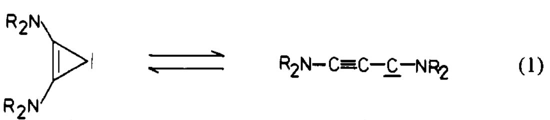
The First Bis Gem Donor-Acceptor Substituted Allene: Synthesis, Geometry, and Electronic Structure

Robert Weiss,*[1] Hilmar Wolf,[1] Ulrich Schubert,[2] and Timothy Clark[1]

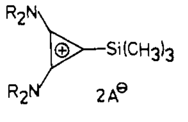
Contribution from the Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg, D-8520 Erlangen, Federal Republic of Germany, and the Institut für Anorganische Chemie der Technischen Universität München, D-8046 Garching, Federal Republic of Germany. Received February 23, 1981

Abstract: The synthesis of 1,3-bis(dimethylamino)-1,3-bis(triphenylphosphonio)allene diiodide (**12**), the first bis gem donor-acceptor substituted allene, is reported. the X-ray structure of this salt shows geometrical features such as a twist toward a trans planar geometry and tilt of the $Ph_3P^+CNMe_2$ units, which are reproduced by MNDO calculations on the 1,3-diamino-1,3-diphosphonioallene dication. Strong interactions between the allene π orbitals, the σ^*_{CP} orbitals (negative hyperconjugation), and the amine lone pairs are responsible for the geometric distortions.

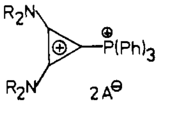
During investigations on the generation and reactions of nucleophilic cyclopropenylidenes[3] **1**, we became interested in the isomeric nucleophilic propargylene **2**—a hitherto unknown species. In particular, we were intrigued by the possibility that these two (singlet) species might be connected by a carbene-carbene rearrangement, (1). For clarification of this question, generation of **2** from some open-chain precursors was indicated. In view of the successful generation of **1** from precursors **3** and **4** by F$^-$ induced α-elimination,[3,4] we felt that a phosphonium salt, **5**, would be a suitable precursor for **2** by analogy. In this paper we report on the attempted synthesis of such a propargylene precursor which resulted in the formation of an allene with novel structural features.



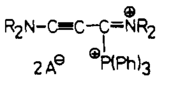
1 2



3

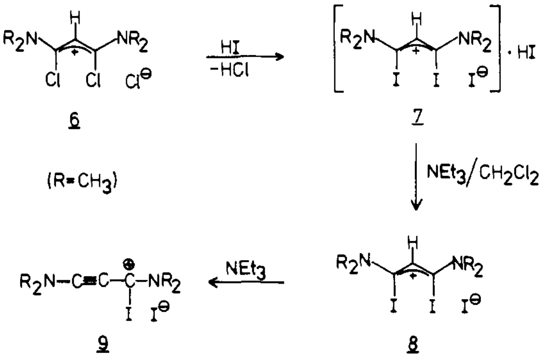


4



5

Scheme I



Synthesis of a Stable Propargyl Salt. A conventional synthesis of the dication salt **5** necessitates generation of a halopropargyl salt and its subsequent reaction with triphenylphosphine. We were able to obtain for the first time a stable, isolable propargyl salt by the strategy shown in Scheme I. When the easily available[5]

---

(1) University of Erlangen.
(2) Technical University of Munich.
(3) (a) Weiss, R.; Wolf, H.; Priesner, C. *Angew. Chem.* **1978**, *90*, 486. Weiss, R.; Hertel, M.; Wolf, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 473.
(4) Wolf, H. Ph.D. Dissertation, University of Erlangen, 1980.
(5) Janousek, Z.; Viehe, H. G. *Angew. Chem.* **1971**, *83*, 615.

0002-7863/81/1503-6142$01.25/0