where X represents unidentified *oxidant*. The driving force of this reaction is probably stabilization of the ruthenium(II) nitrile species due to ability of the Ru(II) to back-bond to unsaturated nitrogen ligands;[9,10] a similar explanation has been involved to explain formation of the Ru(II) diimine species.[5] It is of interest, however, that the diimine case requires the participation of an unidentified *reductant* to obtain an overall balanced equation.[11]

The possibility that the reaction goes through the ruthenium(III) nitrile intermediate seems unlikely because ruthenium(III) nitriles are rapidly hydrolyzed by base to amide complexes.[12]

Investigations are continuing to establish the nature of the oxidant(s), elucidate the kinetics, and explore synthetic usefulness of this reaction.

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Photoelectron Spectrum and Gas-Phase Basicity of Manxine. Evidence for a Planar Bridgehead Nitrogen

Sir:

The bicyclic amine manxine, **1**, has recently been prepared by Leonard and coworkers.[1] Space-filling (CPK) molecular models of this amine show that it is highly strained as a result of transannular interactions between the hydrogens in the three three-membered bridges. The crystal structure of the hydrochloride salt of manxine indicates that these bridges flatten by expanding the C-C-C angles in the three-membered bridge to 117–120°, while the bridgehead C-C-C and C-N-C angles are 114–116°.[2,3] Molecular models of manxine suggest that much of the transannular strain can be relieved by permitting the nitrogen to assume a planar geometry. Recent force field calculations and the high solvolytic reactivity of manxyl chloride have placed the strain relief for conversion of manxyl chloride (bridgehead C-C-C $\angle \simeq$ 115°) to a planar manxyl cation at ca. 6–8 kcal/mol.[4] Since the inversion barriers of alkylamines are only ca. 4–6 kcal/mol,[5] it is expected that there should be more than sufficient strain energy relief to overcome the nitrogen inversion barrier for manxine to adopt a planar bridgehead configuration. We report here the gas-phase photoelectron spectrum and gas-phase basicity of manxine, which provide evidence for a planar configuration at nitrogen in manxine.

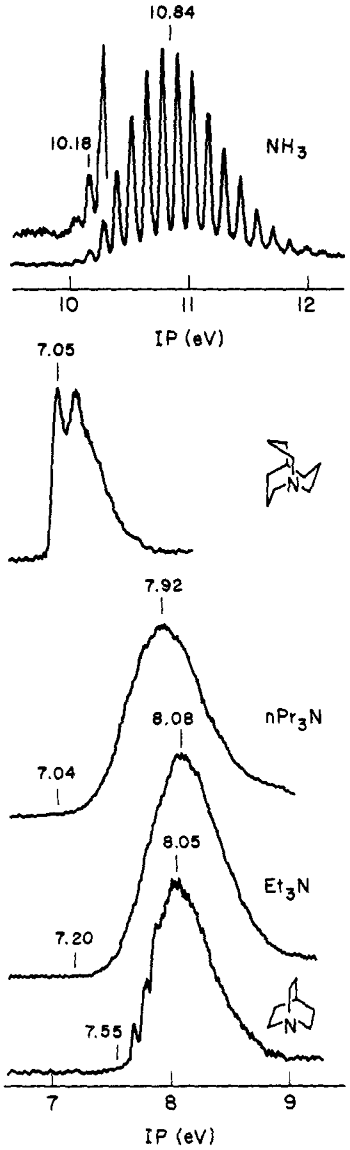

Figure 1. Photoelectron spectra for the first (lone pair) bands in manxine and related amines at 25°. The energy scale for NH_3 has been offset to show its peak shape relative to the alkylamines.

The photoelectron spectrum of ammonia (Figure 1) shows vibrational structure with a frequency (ca. 970^{-1}) characteristic of the nitrogen inversion.[6] The radical cation produced is expected to have a planar equilibrium geometry.[6a] From magnified scans near the onset of the first band in the ammonia spectrum, weak bands appear at 10.07 and at 10.18 eV.[7] Although alkyl substitution generally shifts the position of the nitrogen lone pair band strongly and broadens and obscures the vibrational fine structure, the shapes and widths of the bands stay remarkably similar to the envelope of the ammonia peaks with the difference between the onset (adiabatic IP) and the vertical IP usually 18–21 kcal/mol.[7,8] This is illustrated for triethyl- and tri-*n*-propylamine in Figure 1 and Table I.

Table I. Proton Affinities and Adiabatic and Vertical Ionization Potentials and Hydrogen Affinities of Manxine and Related Amines at 25°[a]

Amine	PA[b]	aIP[c]	aHA[d]	vIP	vHA[d]
NH_3	207 ± 3	235	128 ± 3	250.0[e]	143 ± 3
Et_3N	235.6	166	88	186.3	108.3
Quinuclidine	235.8	173	95	185.6	107.8
n-Pr_3N	237.8	162	86	182.6	107.0
Manxine	235	160	82	161.7	*f*

[a] All values in kcal/mol. [b] PA's are relative to methylamine (218.4 kcal/mol) (see ref 8). [c] The aIP's are quoted to ±2 kcal/mol and are taken at the peak onset except for NH_3 where a 10.18 eV adiabatic value is taken (see ref 7). [d] The adiabatic and vertical hydrogen affinities correspond to the homolytic bond dissociation energies of the $\equiv N^+$—H bonds and can be derived from the IP and PA data (see ref 8 and 13). It is assumed that the geometry of NH_3 and the alkylamines is unchanged on protonation, so that the PA's are near vertical. The vHA's are then calculated from the PA's. [e] The vIP of ammonia was taken halfway between the two largest vibrational bands at 10.78 and 10.90 eV to make the value most comparable to the vIP's derived from the broadened alkylamine bands. [f] Since manxine appears to change geometry from ∠CNC ≅ 120° to 115° on protonation, no vHA can be directly calculated.

Typically, bridgehead amines like quinuclidine, **2,** show a vertical IP very similar to an acyclic model (triethylamine in Figure 1), but they have a narrower band width because of the strain introduced into the bicyclic structure as the bridgehead becomes more planar.[9,10] The photoelectron spectrum for the bridgehead lone pair in manxine, however, has a remarkably different appearance (Figure 1). We interpret the sharp onset and narrow band width in this spectrum as indicative of vertical ionization from a preferred planar geometry in manxine to a planar radical cation.[11] The assignment of the adiabatic band in ammonia and the model acyclic tri-*n*-propylamine reinforces this interpretation, since the vertical IP of manxine is nearly identical with the adiabatic IP (onset) of tri-*n*-propylamine, as expected.

The intrinsic basicity of the lone pair p electrons in manxine was measured by equilibrium ion cyclotron resonance techniques in the gas phase relative to tri-*n*-propylamine.[8,12,13] The proton affinity (PA) of manxine was found to be only 3 kcal/mol lower than that for tri-*n*-propylamine. Competition between large hybridization[14] and strain energy effects[3,4] apparently results in a small net effect on the PA of manxine relative to tri-*n*-propylamine. On the basis of hybridization effects and its low vertical ionization potential, manxine's PA would be expected to be greater than that of a comparable sp^3 hybridized amine like tri-*n*-propylamine.[14] Strain energy effects associated with bond angle distortion at nitrogen in the manxinium ion and steric interactions within the ring oppose this hybridization effect, however.[15]

Not only is manxine less basic than tri-*n*-propylamine by 3 kcal/mol in the gas phase but it is also less basic in aqueous solution by ca. 1.0 kcal/mol than tri-*n*-propylamine or ca. 1.5 kcal/mol than quinuclidine in terms of $\Delta G°_{\text{prot}}$.[1] Thus, these gas-phase and solution-phase basicities show similar, though small, effects.

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Proton Affinities, Ionization Potentials, and Hydrogen Affinities of Nitrogen and Oxygen Bases. Hybridization Effects[1]

Sir:

The effect of alkyl group polarizabilities on quantitative proton affinities has been reported previously and the proton affinity changes analyzed in terms of changes in ionization potentials (IP's) and hydrogen affinities (HA's).[2] These quantities are related according to eq 1. In this report we describe how changes in hybridization at nitrogen and oxygen affect the PA's, IP's, and HA's of several amines and oxygenated compounds.

$$\text{B:} + \text{H}^+ \longrightarrow \text{BH}^+ \quad -\Delta H° = \text{PA}$$
$$\text{B}^{+\cdot} + \text{H}\cdot \longrightarrow \text{BH}^+ \quad -\Delta H° = \text{HA}$$
$$\text{PA(B:)} = \text{HA(B}^{+}\cdot) - \text{IP(B:)} + \text{IP(H}\cdot) \qquad (1)$$

Nitrogen compounds with lone-pair electrons of high s character are compared in the first part of Table I with saturated model compounds of similar polarizability[3] but with sp^3 hybridization at nitrogen. Differences between the proton affinities of pairs of compounds with similar polarizabil-