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Formation of Three- and Four-Membered-Ring Structures for the Li$^+$ Adducts of Appropriate Azines[1a]

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Abstract: Wide deviations (enhanced stabilities) from a linear relationship between the corresponding stability constants (given as Gibbs standard free energies of complexing) for gaseous Li$^+$ and H$^+$ adducts of monodentate diazines and pyridines are found for pyridazine, 2-fluoropyridine, and 1,8-naphthyridine. These results are interpreted to indicate the formation of a bidentate ring structure for the latter three compounds (and others of similar structures) with Li$^+$ but not with H$^+$. Ab initio calculations of structures and energies show the most stable forms of all of the H$^+$ adducts to be monodentate, whereas three- and four-membered-ring bidentate structures are confirmed for the Li$^+$ adducts of the three above-mentioned compounds. The charge distributions obtained support the previous conclusion that bonding to H$^+$ is largely covalent, whereas that to Li$^+$ is largely ionic.

Stability constants in the gas phase for a limited series of 1:1 univalent cation–molecule adducts (for ions such as Li$^+$,[2-4] K$^+$,[5] Mg$^+$,[6] Al$^+$,[7,8] Mn$^+$,[9] NO$^+$,[10] and I$^+$[11]) have been reported in relatively recent years. For these adducts, corresponding series of stability constants (expressed as Gibbs standard free energies, $\Delta G°$) have been found to frequently give linear trends (approximate linear free energy relationships, LFERs), particularly for given functional group families. Furthermore, the LFERs are found to apply to corresponding gaseous adducts of H$^+$ for which the bonding is much stronger and more covalent. That is, the LFERs transcend wide variations in covalent/electrostatic components of the bonding.

Currently the most extensive investigations of functional and substituent group variations are for the corresponding gaseous adducts of Li$^+$[2-4] and H$^+$.[4] These results led to the conclusion[4] that three kinds of effects of molecular structure strongly limit general LFERs between corresponding series of stability constants: (1) the nature of the interactions of the addends to different monodentate coordination centers (functional groups); (2) chelation effects involving certain bidentate (or polydentate) adducts of one addend compared to monodentate adducts with the other addend; (3) changes in the relative contributions of substituent polarizability, field/inductive, and resonance effect contributions between two series of adducts.

This paper reports an experimental and theoretical study of the second kind of structural effects within the gaseous alkali cations and H$^+$ adducts of azines. The experimental results for Li$^+$ adducts of selected azines, pyridazine, 2-fluoropyridine, and 1,8-naphthyridine have been interpreted by making use of the LFER between corresponding stability constants relative to pyridine for Li$^+$ and H$^+$ with the following monodentate bases: pyridine, 3- and 4-(dimethylamino)pyridines, 3-methyl-, 3-chloro-, and 4-(trifluoromethyl)pyridines, pyrimidine, and pyrazine. The results for these eight compounds are assumed to be typical of monodentate azines.

There are some precedences for the enhanced stabilities and bidentate structures ascribed to the three selected bidentate Li$^+$ adducts. The lowest energy form of the Li$^+$ adduct of hydrazine, a simpler analogue of pyridazine, was shown by a structure optimized ab initio calculation[12] to be a symmetric three-membered ring. In contrast, these calculations showed the stable form of the H$^+$ adduct of hydrazine to have the open monodentate structure.. The 1,8-naphthyradine is a nonplanar molecule in which the nitrogens of the two rings are twisted in opposite directions. Upon four-membered-ring formation with Fe$^{\text{II}}$ the entire molecular complex becomes coplanar.[13] Theoretical calculations for the Li$^+$ adducts of ethylenediamine[14] indicate the most stable form is a five-membered-ring bidentate structure. Gaseous diamine complexes of K$^+$ have enhanced stabilities that support the bidentate structures.[15] Ab initio calculations for Li$^+$ adducts of polyazoles show the bidentate three-member-ring structures to be the most stable forms.[16] Polydentate structures for H$^+$ adducts are relatively rare, although these have been found with polyethers.[17,18]

Results and Conclusions

Experimental and theoretical adduct stability constants relative to pyridine, $\delta\Delta G°_{(\mathrm{A}^+)}$, obtained in this study are given in Table I. The $\delta\Delta G°_{(\mathrm{A}^+)}$ values correspond to the standard free energies of transfer equilibria for the indicated azine and A$^+$ cation:

$$\text{azine–A}^+ + \mathrm{C_5H_5N} \rightleftarrows \text{azine} + \mathrm{C_5H_5N\text{–}A^+} \qquad (1)$$

Figure 1 gives a plot of $\delta\Delta G°_{(\mathrm{Li}^+)}$ values vs the corresponding $\delta\Delta G°_{(\mathrm{H}^+)}$ values of Table I. The azines that form monodentate complexes with both Li$^+$ and H$^+$ give an approximate LFER, according to eq 2.

$$\delta\Delta G°_{(\mathrm{Li}^+)} = (0.502 \pm 0.020)\delta\Delta G°_{(\mathrm{H}^+)} - 0.62 \pm 0.19 \qquad (2)$$

$$n = 8;\ R^2 = 0.990;\ s = 0.6\ \text{kcal/mol}$$

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Table I. Gibbs Free Energies of Transfer of Gaseous Cations in the Azine Family and Corresponding ab Initio Calculations[a]

$$\text{pyr} + \text{azineA}^+ \rightleftarrows \text{azine} + \text{pyrA}^+$$

Azine	$\delta\Delta G°_{H^+}$	$\delta\Delta G°_{Li^+}$	$\delta\Delta G°_{K^+}$	$\delta\Delta E_{H^+}$[d]	$\delta\Delta E_{Li^+}$[d]	$\delta\Delta E_{Na^+}$[d]
4-NMe_2pyr	15.6	7.1	3.2	19.3[b]		
3-NMe_2pyr	9.7	3.7	1.5	7.0[b]		
1,8-naph	6.2	8.5	9.2	8.1	26.0	22.6
4-Me(pyr)	3.5			4.6	2.6	2.1
3-Me(pyr)	3.0	1.5		2.6	1.5	1.2
pyr	(0.0)	(0.0)	(0.0)	0.0	0.0	0.0
pyridazine	−5.0	6.5	4.8	−6.4	10.6	10.4
3-Cl(pyr)	−6.1	−3.4				
4-CF_3pyr	−8.2	−5.5		−15.5 (−6.8)[c]	−10.5 (−5.1)[c]	−9.1 (−4.0)[c]
pyrimidine	−10.1	−5.7		−12.3	−6.8	−5.8
2-F(pyr)	−10.2	0.1		−13.9	1.0	3.4
pyrazine	−12.4	−6.9		−16.5	−9.5	−7.9

[a] $A^+ = H^+, Li^+, Na^+, K^+$; pyr = C_5H_5N; naph = naphthyridine. [b] STO-3G/Indo, Fabero and Catalán, unpublished. [c] STO-3G/STO-3G. [d] $\delta\Delta E$ values are 6-31G/3-21G.

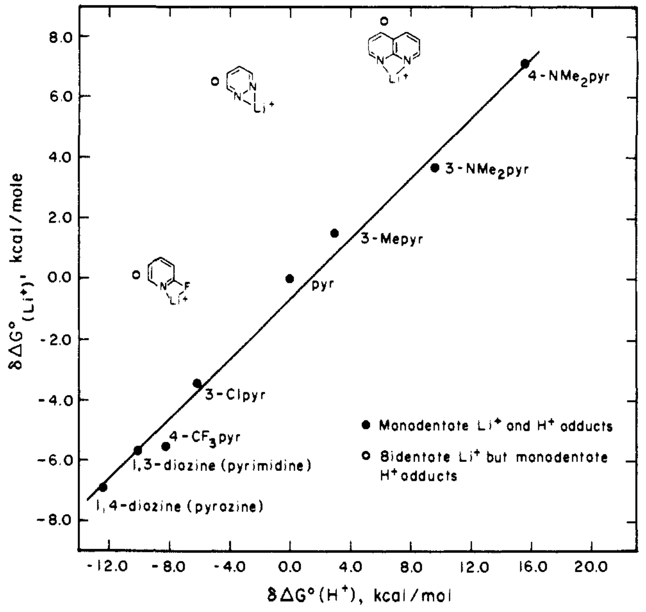


Figure 1. Plot of $\delta\Delta G°_{(Li^+)}$ vs $\delta\Delta G°_{(H^+)}$ for reaction 1 transfer equilibria (Table I): ordinate, $\delta\Delta G°_{(Li^+)}$ (kcal/mol); abscissa, $\delta\Delta G°_{(H^+)}$ (kcal/mol).

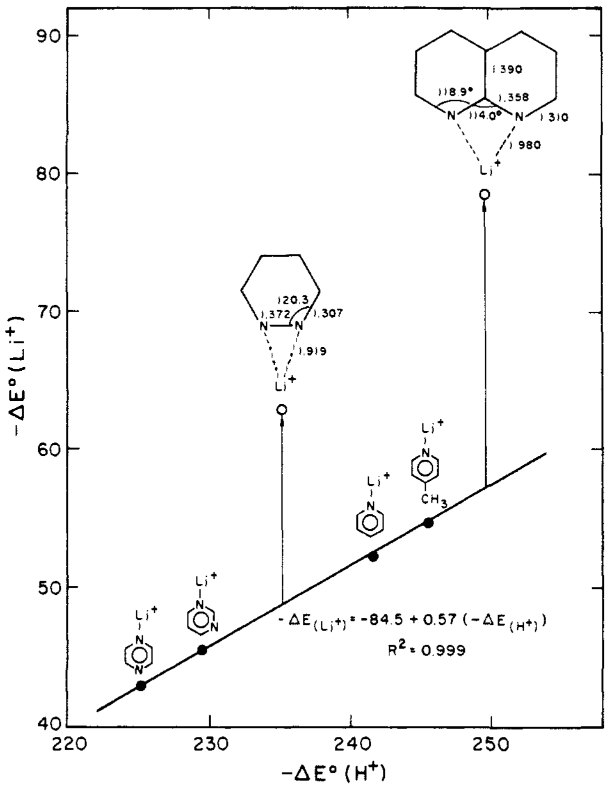
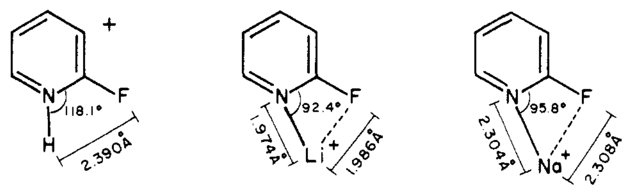


Figure 2. Plot of calculated complexation energies, $-\Delta E°_{(Li^+)}$ vs $-\Delta E°_{(H^+)}$: ordinate, $-\Delta E°_{(Li^+)}$ (kcal/mol); abscissa, $-\Delta E°_{(H^+)}$ (kcal/mol). Closed circle points are for monodentate Li^+ and H^+ adducts. Bidentate Li^+ adducts are given by open circle points and corresponding structural schematics.

Chart I



Values of $\delta\Delta G°_{(A^+)}$ for pyrimidine and pyrazine have been statistically corrected. Equations similar to eq 1 have been obtained for gaseous I^+ adducts of 3- and 4-substituted pyridines[11] and for families of azoles[19] and of formyl derivatives.[4] The three azines that form bidentate structures with Li^+ show markedly greater stabilities than expected from eq 1; the deviations are the following:[20] 2-fluoropyridine, 5.6 kcal/mol; 1,8-naphthyridine, 6.0; and pyridazine, 9.5. Table I shows that the calculated stability constants relative to pyridine, given as the $\delta\Delta E_{(A^+)}$ values of Table I, follow the same general pattern of behavior as the corresponding $\delta\Delta G°$ values. Quantitative agreement between corresponding values of $\delta\Delta E_{Li^+}$ and $\delta\Delta G°_{Li^+}$ is as good as can be expected considering that corrections for entropy changes for adduct formation have not been made and that the theoretical calculations involve some problems with the different levels of structure optimization and calculation of the $\delta\Delta E_{(A^+)}$ values (see Computational Section). It has also been noted earlier that there are shortcomings (severe over-calculation) with 6-31G calculations

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(20) We have also observed similar deviations for pentafluoropyridine and 2,6-difluoropyridine.

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Table II. Calculated 6-31G//3-21G Results

compound	energy, au	R(N–A$^+$), Å	Mulliken population,[e]
1,8-naphthyridine	−415.162 458		
1,8-naphthyridine–H$^+$	−415.560 416	1.009	0.533
1,8-naphthyridine–Li$^+$	−422.523 057	1.980	2.174
1,8-naphthyridine–Na$^+$	−576.916 677	2.292	10.110
1,2-diazine	−262.523 790		
1,2-diazine–H$^+$	−262.898 566	1.006	0.513
1,2-diazine–Li$^+$	−269.859 529	1.919	2.118
1,2-diazine–Na$^+$	−424.258 577	2.244	10.066
pyridine	−246.593 806		
pyridine–H$^+$	−246.978 831	1.007	0.541
pyridine–Li$^+$	−253.912 678	1.901	2.124
pyridine–Na$^+$	−408.311 999	2.243	10.076
1,3-diazine	−262.564 426		
1,3-diazine–H$^+$	−262.929 848	1.007	0.527
1,3-diazine–Li$^+$	−269.872 470	1.911	2.116
1,3-diazine–Na$^+$	−424.273 411	2.244	10.071
1,4-diazine	−262.557 038		
1,4-diazine–H$^+$	−262.915 759	1.009	0.525
1,4-diazine–Li$^+$	−269.860 839	1.918	2.180
1,4-diazine–Na$^+$	−424.262 610	2.255	10.065
3-CH$_3$-pyridine	−285.615 571		
3-CH$_3$-pyridine–H$^+$	−286.004 772	1.006	0.544
3-CH$_3$-pyridine–Li$^+$	−292.937 770	1.897	2.126
3-CH$_3$-pyridine–Na$^+$	−447.335 502	2.237	10.078
4-CH$_3$-pyridine	−285.616 722		
4-CH$_3$-pyridine–H$^+$	−286.009 066	1.006	0.545
4-CH$_3$-pyridine–Li$^+$	−292.939 602	1.892	2.129
4-CH$_3$-pyridine–Na$^+$	−447.338 167	2.234	10.079
2-F-pyridine	−345.421 865		
2-F-pyridine–H$^+$	−345.784 595	1.009	0.481
2-F-pyridine–Li$^+$	−352.742 306	1.974	2.137
2-F-pyridine–Na$^+$	−507.145 434	2.304	10.157
Li$^+$	−7.235 480		2.000
Na$^+$	−161.659 276		10.000

of the energy effects of strong "electron-withdrawing" substituents (e.g., CF$_3$) in cations.[21] Nevertheless, plots of $\delta\Delta E_{(\mathrm{Li}^+)}$ vs $\delta\Delta E_{(\mathrm{H}^+)}$ (cf. Figure 2), $\delta\Delta E_{(\mathrm{Li}^+)}$ vs $\delta\Delta E_{(\mathrm{Na}^+)}$, and $\delta\Delta G^\circ_{(\mathrm{K}^+)}$ vs $\delta\Delta G^\circ_{(\mathrm{H}^+)}$ (not shown) are all consistent with the conclusions from Figure 1 that bidentate cyclic structures are formed as the lowest energy forms of the Li$^+$, Na$^+$, and K$^+$ adducts of pyridazine, 1,8-naphthyridine, and 2-fluoropyridine. It is also shown by $\delta\Delta G^\circ_{(\mathrm{Li}^+)}$ and $\delta\Delta G^\circ_{(\mathrm{K}^+)}$ values that Li$^+$ favors pyridazine whereas K$^+$ favors 1,8-naphthyridine in accord with size considerations.

The ab initio 3-21G optimized calculations (cf. Computational Section) confirm that the coplanar symmetrical three- and four-membered-ring structures are the most stable forms of the Li$^+$ and Na$^+$ adducts of pyridazine and 1,8-naphthyridine, respectively. Figure 2 plots absolute values of $-\Delta E_{(\mathrm{Li}^+)}$ vs $-\Delta E_{(\mathrm{H}^+)}$ for complexing of these two Li$^+$ bidentate bases and of four typical H$^+$ and Li$^+$ monodentate azines. In addition to the large enhancements in stability of the Li$^+$ bidentate bases, Figure 2 shows some of the details of the calculated structures. For 2-fluoropyridine, structural details of interest are given in Chart I. Table II gives the electronic energies for the most stable forms of all the species involved in the equilibrium results of Table I.[28] Also given in Table II are the N–A$^+$ bond lengths and the Mulliken electronic population of the addend A$^+$ in the adducts.

Upon Li$^+$ adduct formation, the azine bond lengths increase, but the endocyclic angle subtended by the nitrogen atom joined to Li$^+$ changes very little (less than 1 deg). N–Li$^+$ bond lengths are ~1.9, and Mulliken electronic populations of Li are in the range of 2.1–2.2 electrons. That is, Li$^+$ is indicated to retain 0.8–0.9 electronic unit of its positive charge in the adducts. This is to be contrasted with the relatively large change in the endocyclic angle upon protonation (at least 3 deg), the N–H$^+$ bond lengths (near 1.0 angstrom), and the proton populations showing retention of 0.4 electron unit of its positive charge. These results are all consistent with largely ionic Li$^+$ bonding, but largely covalent H$^+$ bonding.[29,30] The N–Na$^+$ distances are ~2.2 Å, and the Mulliken population shows that Na$^+$ retains in its adducts ~0.9 electronic unit of its original charge.

Computations

Hartree–Fock ab initio calculations have been performed to investigate the structures and stabilities of neutral azines and their H$^+$, Li$^+$, and Na$^+$ adducts. No calculations could be performed for azine–K$^+$ complexes because SCF convergence was not achieved for these compounds using our IBM VM/CMS version of the GAUSSIAN 80 series of programs.[22] Population analyses have been done by using the very well known Mulliken method. 3-21G geometries[23] were obtained by a gradient method[24] and are available from the authors. For neutral and H$^+$ adducts of pyridine, 1,2-diazine, 1,3-diazine, and 1,4-diazine calculations have been previously published at 3-21G//3-21G, 6-31G//6-31G, and 6-31G*//6-31G levels.[25]

It has been shown[26] that relative basicities calculated at split-valence level reproduce the majority of the experimental data accurately. Due to the size of the 1,8-naphthyridine molecule we were restricted for consistency to optimized geometries at the 3-21G level. Using this geometry, we made single-point 6-31G calculations.[27] Basis set superposition error (BSSE) corrections are greater for Li$^+$ adducts than for the corresponding H$^+$ adducts but are practically constants for the homologous series of compounds and have not been found to have an important influence on relative basicities.[12,16] Zero-point vibrational energies (ZPVE) for systems of this size are beyond our computational capabilities. It has been shown[12] that these corrections are five times smaller for Li$^+$ complexes than for the corresponding H$^+$ complexes, and we assume they are constants in a series of homologous compounds.

Experimental Methods

The general ICR method has been employed.[2–4,6–11] Details of the FT-ICR method used are given in ref 4 and 19. Absolute values of $-\Delta G^\circ_{\mathrm{H}^+} = 213.2$ kcal/mol and $-\Delta G^\circ_{\mathrm{Li}^+} = 37.7$ kcal/mol for complexing with pyridine are taken from ref 4. The corresponding value for $\Delta G^\circ_{\mathrm{K}^+} = 20.7$ kcal/mol is from ref 5.

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