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Enhanced Li$^+$ binding energies of some azines: a molecular orbital study

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Summary. Hartree–Fock calculations with the 6-31G* basis have been performed to investigate the structure and Li$^+$ binding energies of the complexes between Li$^+$ and pyridine, diazines, triazines and tetrazines. Structures have been fully optimized at the 3-21G level. As for azole-Li$^+$ and methyldiazole-Li$^+$ complexes, a topological analysis of the Laplacian of the electronic charge density reveals that the azine-Li$^+$ is a typical closed-shell interaction and that the stabilization of the complex is mainly electrostatic. BSSE is quite significant, specially for Li$^+$-bridging complexes. The correlation between calculated Li$^+$ binding energies and proton affinities follows two different linear relationships, one for those cases where Li$^+$ is singly coordinated and a different one for those cases in which an additional three-membered ring is formed. The enhanced stability of these particular conformations explains why while polyazines are less basic than pyridine when the reference acid is a proton; pyridazine and 1,2,4 triazine are more basic than pyridine when the reference acid is Li$^+$. The effect on Li$^+$ binding energies of systematic nitrogen substitution roughly follows an additive model.

Key words: Azines — Li$^+$ binding energies — Intrinsic basicities

1. Introduction

The intrinsic basicity of a molecule is defined by its binding energy to a reference acid in the gas phase. Although, in general, proton affinities are used to measure these intrinsic basicities, it is obvious that they depend on the reference acid [1, 2], and it is not uncommon to find that basicity trends along a given family of compounds change from one reference acid to another [1, 3]. In this sense, particular attention was devoted to the evaluation of binding energies of π- and n-donor bases to alcaline cations [1, 4–7], as well as to the analysis of possible correlations between these binding energies and the corresponding proton affinities.

The difference between Li^+ and H^+ complexation is mainly due to the quite different character of the bonds between the base and the proton and between the base and Li^+ [4, 8–10]. In the former case a strong covalent bond is formed, while in the latter a closed-shell interaction, typical of a practically pure ionic bond, is found. Moreover, the ability of the Li^+ ion to form bridging structures with bases which present two atoms having lone pair of electrons [8–10] singularizes its behaviour as an acid, since the formation of these bridging conformations are responsible for the enhanced basicity of some bases with respect to Li^+. It is for this reason that we have lately focused our attention on the study of Li^+ complexes with azoles [10] and methyl-diazoles [11] in an effort to analyze both the characteristics of the Li^+-complexes with typical polidentate bases and the influence of the substituents on their relative stability. As a logical progression in this effort we shall present in this paper an *ab initio* molecular orbital study of the azine-Li^+ complexes. Besides the intrinsic interest of this set of compounds in view of their versatile chemistry [12], it would be of interest to compare, on the one hand, their calculated Li^+ binding energies with the corresponding proton affinities reported earlier [13] and with the Li^+ binding energies to the azoles [10], on the other. This comparison can be quite illustrative since azoles are considered traditionally as prototypes of π-excessive systems, while azines are not. Furthermore, all members of the azole series have a non-zero dipole moment, and therefore the ion-dipole interaction is always a dominant contribution to the stability of the Li^+-complexes [8–10], which is not the case within the azine series, since several members of it are non-polar.

It should also be noted that the information on basicities of bidentate bases is scarce and most of it is of theoretical origin [8, 14–21]. Actually, *ab initio* studies are a powerful tool for evaluating not only binding energies for complexes involving different ions, but also for elucidating their most stable structures, information which is seldom available from experiments. We shall illustrate in this study that such information can be crucial, as mentioned above, for the interpretation of experimentally measured gas phase basicities, which are often related to the formation of three-membered ring structures for the Li^+ adducts [10]. In this respect it will be very interesting to investigate which factors favor and which ones do not favor the formation of this additional ring.

2. Computational details

The geometries of the complexes of azines with Li^+ were fully optimized at the Hartree–Fock level of theory using suitable gradient optimization techniques [22]. These optimizations were carried out using the split-valence 3-21G basis set [23], which is a reasonable choice for Li-containing compounds, as has been shown in many different studies [18, 21, 24, 25]. The optimized geometries of the neutral bases were taken from [13]. In order to take into account polarization effects which proved to be significant in Li^+-base interactions [9, 10], 6-31G* [26] single-point calculations on these 3-21G optimized geometries were performed. These calculations will be denoted hereafter as 6-31G*//3-21G. The complete set of systems studied in this work is presented in Fig. 1. This figure actually shows only those lithiated species which have been found to be stable although, as we shall show later, many other conformations have in fact been studied.

Li^+ binding energies were obtained by subtracting from the energy of each complex the sum of the energies of the isolated azine and the Li^+ ion. Since the basis set superposition error (BSSE) has been found to be particularly important for Li^+ complexes [10, 11] and given that we are interested in a comparison between protonation and lithiation energies, we shall pay special attention to the magnitude of this error, which will be evaluated using the counterpoise procedure of Boys and Bernardi [27].

To analyze the characteristics of Li^+-azine interactions we shall discuss the topological characteristics of the Laplacian of the electronic density, ϱ. As it has been shown by Bader [28–30], the Laplacian of ϱ identifies regions of space wherein the electronic charge of a given system is locally concentrated or depleted. In the first situation $\nabla^2\varrho(r) < 0$, whereas in the latter $\nabla^2\varrho(r) > 0$. In the first case there is a covalent interaction, while in the second case there is a closed-shell interaction such as in typical ionic bond, hydrogen bond [30] or van der Waals molecules. We have also characterized, for the N–Li linkages, the critical bond points, i.e., points where the electronic charge density has one positive curvature and two negative curvatures, because the value of ϱ and $\nabla^2\varrho$ at these

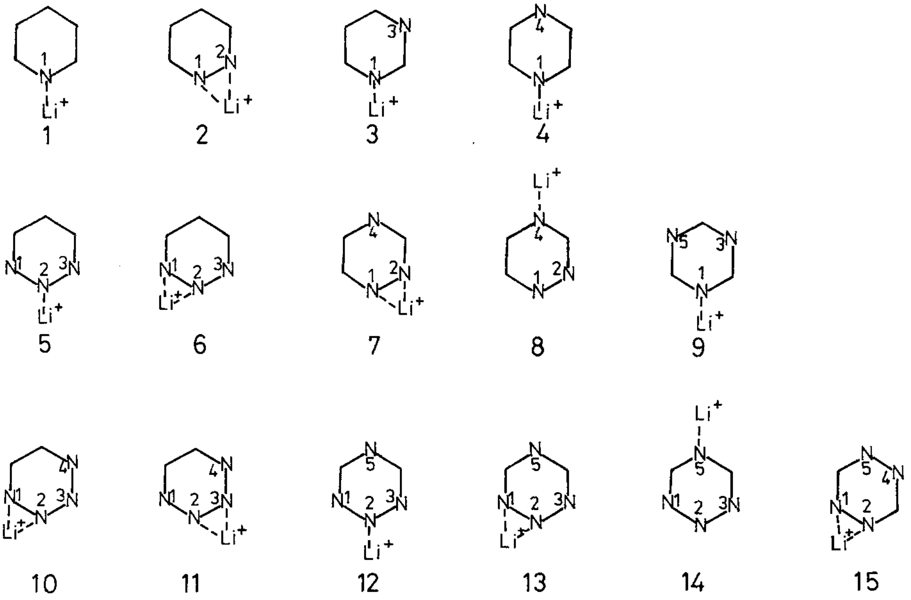


Fig. 1. Azine-Li^+ complexes included in this study. This figure shows only those conformations which are minima of the corresponding potential surface, with the exception of form 5 (see text)

points offer quantitative information on the bonding between the pyridinic nitrogen and the attaching ion. The evaluation of the gradient and the Laplacian of the charge density, as well as the Hessian matrix has been programmed by one of us (MA) and implemented in the framework of the Gaussian-80 series of programs [31].

Finally, it should be mentioned that correlation effects were not taken into account for economic reasons. Nevertheless, we can reasonably assume that, as for other bases [9, 32], inclusion of electron correlation would not significantly change the relative Li^+ binding energies reported here.

The evaluation of zero-point vibrational energies (ZPVE) for systems of this size is beyond our computational capacity. It has been proved [9, 11], however, that ZPVE corrections are about five times smaller for Li^+ complexes than for protonated species. On the other hand we can reasonably assume that they are practically constant along a homologous series of compounds [11] such as the one considered in this study. Therefore we may be confident that the no inclusion of ZPVE corrections in our calculations will not affect our conclusions in a significant way.

3. Results and discussion

3.1. Geometries

The optimized structures of neutral azines have been reported previously [13] and those for the corresponding azine-Li^+ complexes are not going to be discussed in detail here, but are available from the authors. It should be indicated that, as has been found for azole-Li^+ systems [10], the structure of the azine ring changes very little upon lithiation, although it changes significantly upon protonation [13]. There is however an important difference between azines and azoles. When the azine presents two contiguous nitrogen atoms having lone pairs of electrons the Li^+-bridging structure is always the most stable one, at least at the 3-21G level, while this is not the case for azoles. We shall come back to this problem in following sections.

Regarding the structural changes just mentioned, we may consider, for instance, as a significative geometrical parameter, the XNY ($X, Y = C$ or N) endocyclic bond angle where N is the basic center. This angle, which in pyridine is about 118.7°, opens 4.0° upon protonation while it remains unchanged upon lithiation. Similar variations are observed for diazines, triazines and tetrazines, with the only exceptions being 1,2,3-triazine and 1,2,3,4- and 1,2,3,5-tetrazines, where this angle opens more than 6° in the protonation process and about 3° upon lithiation. In general, these geometric features reflect the different nature of the azine-H^+ and azine-Li^+ interactions: the formation of a new covalent bond in the first case, but not in the second, where the interaction is a closed-shell one. Actually, for bent azine-Li^+ complexes, the value of ϱ at the N–Li critical bond point (i.e. the maximum value of the charge density between the N and Li nuclei) is quite small ($\simeq 0.037$ e/au^3) and $\nabla^2\varrho$ always positive ($\simeq 0.28$ e/au^5). Furthermore, these values are very similar to those reported by Bader and Essén [28] for ClLi, which is a prototype of an ionic bond.

The exceptions mentioned above do not imply a change in the nature of the interaction, as it clearly illustrated, for instance, by the characteristics of the Laplacian of the charge density of complexes 5 and 6. As shown in Figs. 2 and 3, the electronic charge is depleted ($\nabla^2\varrho > 0$) in the region between the basic nitrogens and the Li^+ ion, both for bent (5) or bridged (6) conformations. This indicates that, as for the other azine-Li^+ complexes, the N–Li bond is still basically ionic. Fig. 2b also shows a slight polarization towards the Li^+ of the electronic density which surrounds N2. It is more important to realize that a similar polarization is undergone by the charge density around N1 and N2 in complex 6 (see Fig. 3b). As we shall show later, this effect will be, in part, responsible for the enhanced stability of bridged structures since, in general, the N–Li^+ distances are only slightly greater in these systems (2,6,7 . . .), than in singly coordinated species (1,3,4 . . .), and therefore polarization effects are considerably greater in the former where Li^+ interacts with two pyridinic nitrogens.

At this point it may be of interest to investigate whether a three-membered ring is really formed, when the azine presents two neighboring nitrogen atoms. To answer this question it is necessary to localize the corresponding critical bond points (where ϱ has two negative and one positive curvature) since the presence of such a point is a necessary condition for the existance of a bond. In addition, if the nuclei are linked so as to form a ring, then a critical ring point (where ϱ has two positive and one negative curvature) must be found in its interior. In our case there are, in principle, two different situations, those where the three-membered ring shows a clear asymmetry (as in complex 6) and those where it is symmetric (as in complex 2), so we shall take these two systems as typical examples. The electronic density maps of complexes 2 and 6, in the region of interest, have been plotted in Fig. 4. For the first system, two N–Li critical bond points and one critical ring point have been found, all of them quite close to the Li^+ valence shell, as is expected from a closed-shell interaction. We can conclude, therefore, that in this case a three-membered ring is formed upon lithiation of the azine. The situation is different for complex 6, where only one N–Li critical bond point has been found, corresponding to the shortest N–Li linkage. Figure 4b shows that on the line which joins Li and N1 there is a critical point with one of the curvatures practically equal to zero. Although in complex 6 we cannot strictly say that a three-membered ring has been formed, the amount of electronic charge concentrated in that region is practically the same as that in complex 2, and therefore, the stability of the structures formed should not be very different, in agreement with the results discussed in the next sub-section.

3.2. Li^+ binding energies

We present in Table 1 the Li^+ binding energies corresponding to the formation of the stable complexes of Fig. 1 obtained at the two levels of accuracy considered (3-21G and 6-31G*//3-21G) before and after BSSE correction.

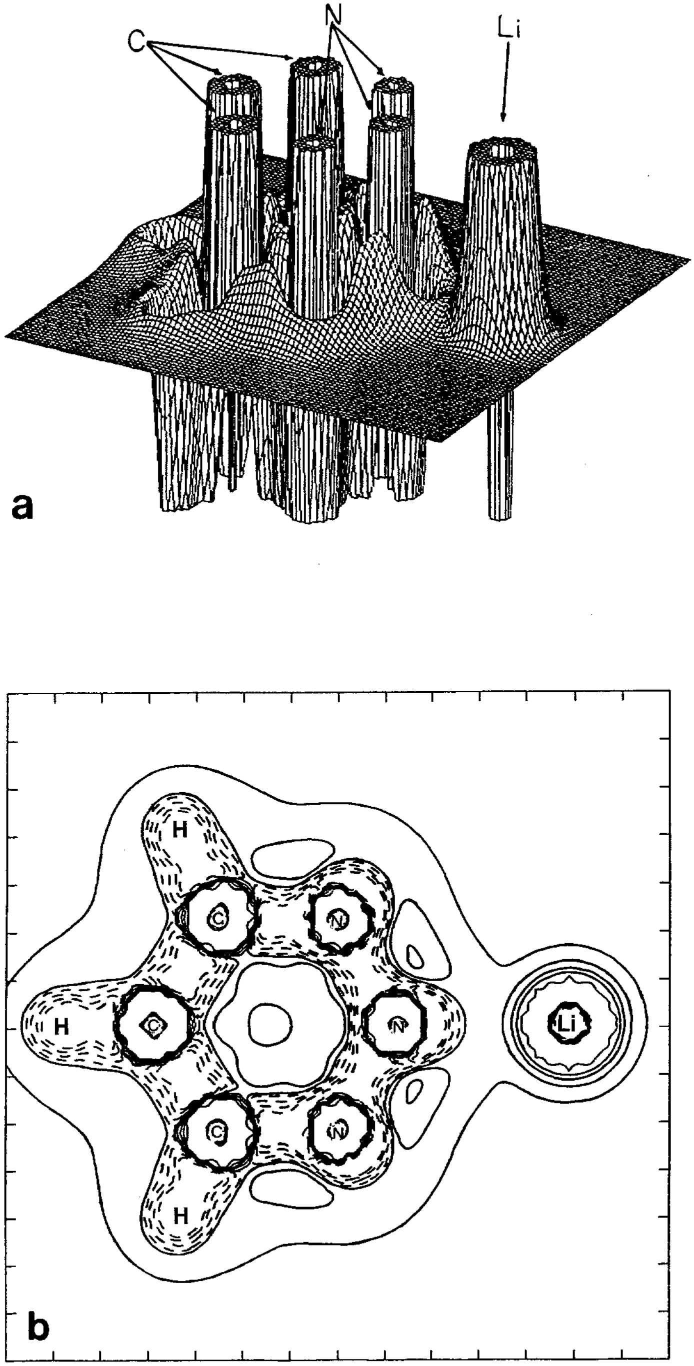
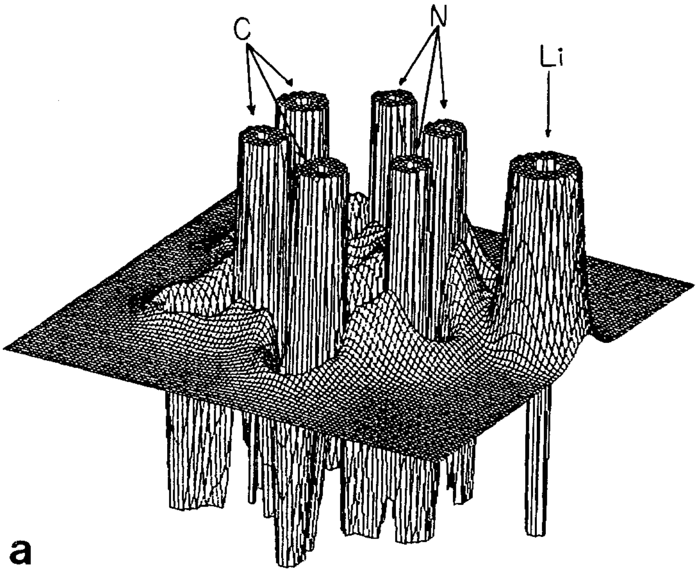


Fig. 2a,b. Laplacian of the charge density for 1,2,3-triazine-Li^+ complex (5). **a** Three dimensional plot; **b** corresponding contour map. Positive values of $\nabla^2\rho$ are denoted by *solid lines* and negative values by *dashed lines*



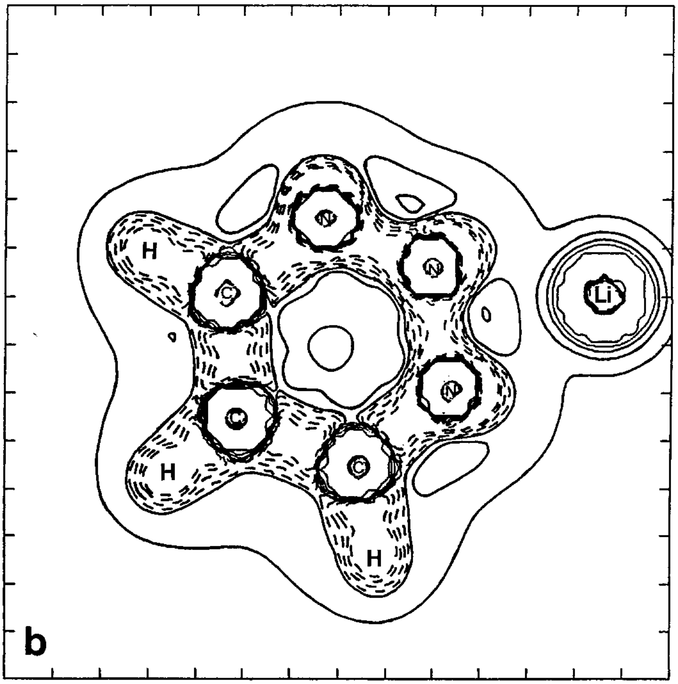


Fig. 3a,b. Laplacian of the charge density for 1,2,3-triazine-Li$^+$ complex (6). **a** Three dimensional plot; **b** corresponding contour map. Conventions as the same as in Fig. 2

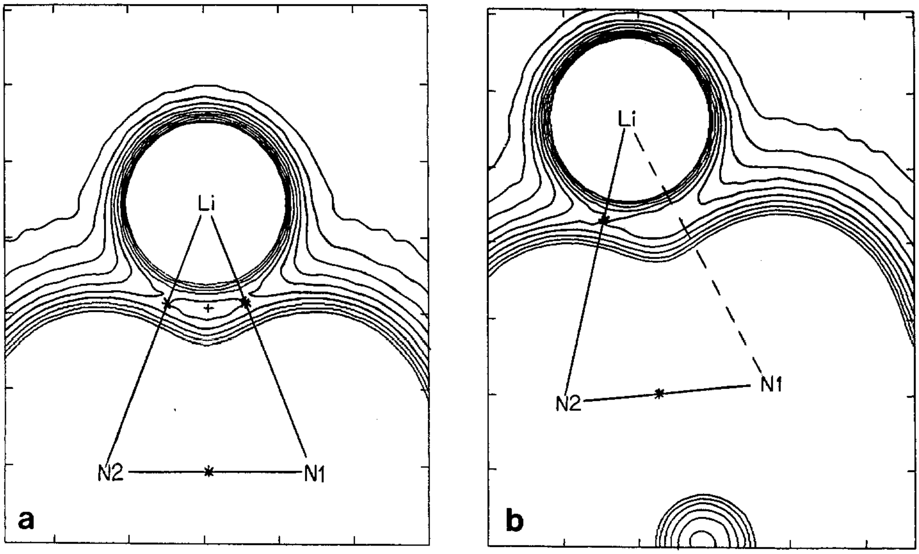


Fig. 4a,b. Contour map of the charge density showing the critical bond points (*) and the critical ring points (+) for **a** complex 2: the values of ϱ and $\nabla^2\varrho$ are: at the N–Li critical bond points: 0.030 e/au^3 and 0.25 e/au^5; at the ring critical point: 0.027 e/au^3 and 0.25 e/au^5; at the N–N critical bond point: 0.360 e/au^3 and -0.78 e/au^5, respectively. **b** Complex 6: the values of ϱ and $\nabla^2\varrho$ are: at the N–Li critical bond point: 0.030 e/au^3 and 0.21 e/au^5; at the N–N bond critical point: 0.385 e/au^3 and -0.91 e/au^5, respectively

The first conspicuous fact of Table 1 is that 1,2-diazine is predicted as the most basic azine in the gas-phase when the reference acid is Li^+, in clear contrast with its behavior when the reference acid is a H^+ which is in agreement with recent experimental measurements [7]. When the reference acid is a proton, experimental [33–36] and theoretical [13] results show, as a trivial general rule, that additional nitrogens decrease the overall absolute basicity. Obviously, this rule does not apply when the reference acid is Li^+ due to its ability to yield quite stable bridged structures when the base presents two neighboring nitrogens having lone pairs of electrons. Then, one may observe that, in general, gas-phase protonation energies [13] are about 5 times greater than gas-phase Li^+ binding energies, but this factor reduces to about 4 when the lithiated species is a bridged structure. More significantly, the basicity trends along the family are clearly affected by the formation of this three-membered arrangement, so that while protonated the intrinsic basicities decrease along the series (pyridine > diazines > triazines > tetrazines), whereas upon lithiation, not only pyridazine, but also 1,2,3- and 1,2,4-triazines are predicted to be more basic than pyridine and considerably more basic than 1,3- and 1,4-diazines, which are in turn less basic than 1,2,3,4-tetrazine. In this respect, it would be illustrative to compare the calculated proton affinities with the Li^+ binding energies for this set of compounds. For this purpose we have plotted in Fig. 5 the (6-31G*//3-21G) calculated protonation energies vs. the calculated Li^+ binding energies, including, in both cases, the corresponding BSSE corrections. For the particular case

Table 1. Proton ($E(H^+)$) and Li+ ($E(Li^+)$) binding energies (kcal/mol) for the compounds included in this study

	Complex[a]	3-21G			6-31G*//3-21G			
		$E(H^+)^b$	$E(Li^+)$	$E_c(Li^+)^c$	$E(H^+)$	$E(Li^+)$	$E_c(Li^+)^c$	
1	Pyridine (1)	241.3	57.0	52.4	235.5	47.3	45.7	
2	1,2-Diazine (1–2)	235.1	70.9	64.4	231.2	57.1	54.8	
3	1,3-Diazine (1)	230.4	50.8	46.3	224.9	41.4	39.8	
4	1,4-Diazine (1)	226.0	48.3	43.9	220.1	38.6	37.0	
5	1,2,3-Triazine (2)	222.5	58.7	53.8	217.0	48.6	46.9	
6	(1–2)	220.1	61.7	55.6	220.9	49.7	47.7	(48.9)[d]
7	1,2,4-Triazine (1–2)	218.7	61.3	55.1	214.7	48.0	46.0	(46.1)
	(2)	222.9	—	—	219.9	—	—	—
8	(4)	212.2	40.2	35.9	206.9	31.3	29.8	(31.1)
9	1,3,5-Triazine (1)	218.5	44.2	39.6	213.1	35.0	33.5	(33.9)
10	1,2,3,4-Tetrazine (1–2)	203.0	51.0	45.1	198.9	39.5	37.6	(37.4)
11	(2–3)	206.1	52.4	45.8	207.1	43.0	41.1	(43.0)
12	1,2,3,5-Tetrazine (2)	204.0	48.3	43.8	202.7	40.0	38.3	
13	(1–2)	207.0	51.1	45.2	203.9	39.2	37.3	(40.2)
14	(5)	197.7	32.0	28.0	193.3	26.2	24.8	(25.2)
15	1,2,4,5-Tetrazine (1–2)	202.5	48.7	42.8	200.0	36.3	34.5	(37.4)

[a] The numbers within parenthesis indicate the ring nitrogens to which Li^+ is attached in the complex. In azine-H^+ complexes the H^+ is always attached to the first indicated position

[b] Values taken from [13]

[c] Values obtained after BSSE correction

[d] Li^+ binding energies predicted assuming constants increments of +9.51, −5.9 and −8.7 kcal/mol for ortho-, meta- and para-nitrogen substitution, respectively

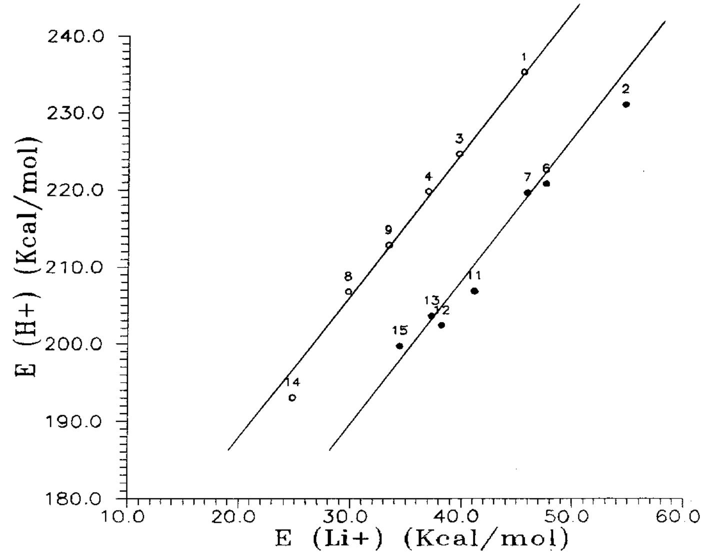


Fig. 5. Linear correlations between protonation energies ($E(H^+)$) and Li^+ binding energies ($E(Li^+)$) for azines. ○, Complexes where Li^+ is singly coordinated; ●, complexes where Li^+ yields bridging structures. *1.* Pyridine; *2.* 1,2-diazine; *3.* 1,3-diazine; *4.* 1,4-diazine; *6.* 1,2,3-triazine (1–2); *7.* 1,2,4-triazine (1–2); *8.* 1,2,4-triazine (4); *9.* 1,3,5-triazine (1); *11.* 1,2,3,4-tetrazine (2–3); *12.* 1,2,3,5-tetrazine (2); *13.* 1,2,3,5-tetrazine (1–2); *14.* 1,2,3,5-tetrazine (5); *15.* 1,2,4,5-tetrazine (1–2)

of bridged Li^+-complexes we have used, for the correlation, the protonation energy corresponding to the most basic position of the azine. Figure 5 shows the existance of two linear relationships with approximately the same slope. That with the smaller x-axis intercept corresponds to complexes where Li^+ is singly coordinated and that with the greater intercept to those complexes with bridging conformations. On the other hand, the fact that both slopes are significantly greater than unity ($\simeq 1.8$) means that relative Li^+ binding energies are smaller than relative protonation energies. A similar finding was already reported and explained for the case of azoles [10]. The same arguments apply in this case and they are not repeated here for the sake of conciseness.

The second conspicuous feature of Table 1 is that the BSSE is very important, mainly at the 3-21G level, accounting for 6–7 kcal/mol of the total stabilization energy of the complex. Although this error decreases appreciably when the basis set is enlarged, at the 6-31G* level it still amounts to 1.5–2 kcal/mol. Since the absolute value of this error is non negligible, its most outstanding effect is observed on relative basicities. The BSSE for bridged structures is in fact systematically greater than for bent ones, because in the former the atomic orbitals of lithium can simultaneously supplement the atomic basis of several atoms. The consequences are that, for instance, at the 3-21G level 1,3-diazine has a Li^+ binding energy slightly smaller than those of 1,2,3,4- and 1,2,3,5-tetrazines, but after the BSSE correction it becomes more basic than them. Furthermore, this problem is not completely corrected by enlarging the basis set since, when the 6-31G* basis is employed, it is only after the BSSE correction is included that the right basicity ordering is obtained.

The third feature of Table 1 that deserves to be commented on is that the inclusion of polarization functions in the basis set leads to a noticeable decrease of the calculated Li^+ binding energies because of the more realistic description of the multipoles of the base and, accordingly, of the ion-molecule interaction. This decrease is about 2–3 kcal/mol greater for bridged complexes, implying that their enhanced stabilization is slightly overestimated at the 3-21G level. Actually, it may be observed that when the energy difference between the two alternative configurations: bridged and bent is not very large, as for instance in 1,2,3,5-tetrazine, the latter is predicted to be slightly more stable than the former, when a 6-31G* basis set is used. We shall come back in the next sub-section to this point.

Finally, it should be mentioned, from a practical point of view, that it can be assumed that Li^+ binding energies roughly follow an additive scheme. In other words, assuming constant increments of $+9.1$, -5.9 and -8.7 kcal/mol in the basicity of the azine when an additional pyridine nitrogen is introduced at ortho-, meta- and para-positions, respectively, one gets Li^+ binding energies in fairly good agreement with those obtained in the *ab initio* SCF calculation (see Table 1).

3.3. The performance of the electrostatic model

We have shown in previous sections that the azine-Li^+ interaction is a typical closed-shell one. Accordingly, one should expect to find that most of the calculated stabilization energy of the complex comes from electrostatic and polarization interactions. On the other hand, one may reasonably assume that the polarizability of the ring would not change dramatically along the series and therefore that polarization interactions should be, to a first approximation, constant along it. To confirm this we have evaluated, at the 3-21G level, the electrostatic potential created by the isolated azine at the point of space physically occupied by the Li^+ ion in the complex. The values so obtained are represented in Fig. 6 vs. the SCF calculated Li^+ binding energies.

Figure 6 shows the existence of two linear correlations of slope of practically unity. That with the smaller intercept ($E(Li^+) = 1.05V + 9.01$, $r = 0.998$) involves all complexes where Li^+ is singly coordinated and that with a greater intercept ($E(Li^+) = 1.02V + 18.89$, $r = 0.997$) involves all complexes where the Li^+ is bridging two pyridinic nitrogens.

The slope of 1 seems to confirm that factors different from the pure electrostatic ones are practically constant along the series. The intercept ($\simeq 9$ kcal/mol) indicates that polarization and covalent effects are small but not negligible, since they amount to 20% of the whole stabilization energy.

It is important to note that the intercept for the correlation of the bridged complexes ($\simeq 19$ kcal/mol) is practically twice that for the bent ones. Two factors may be responsible for the enhanced stability of bridging complexes. On one hand, we have already mentioned that this conformation greatly favors the polarization of both ring nitrogens, while in bent configurations only the

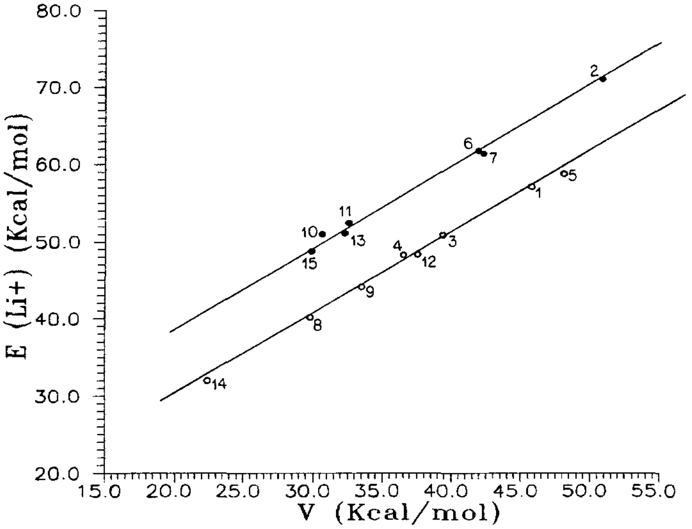
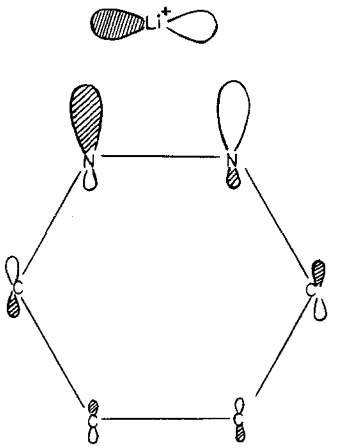


Fig. 6. Linear correlations between the electrostatic potential energy (V) and Li$^+$ binding energies for azines. Same conventions as in Fig. 5. *1.* Pyridine; *2.* 1,2-diazine; *3.* 1,3-diazine; *4.* 1,4-diazine; *5.* 1,2,3-triazine (2); *6.* 1,2,3-triazine (1–2); *7.* 1,2,4-triazine (1–2); *8.* 1,2,4-triazine (4); *9.* 1,3,5-triazine (1); *10.* 1,2,3,4-tetrazine (1–2); *11.* 1,2,3,4-tetrazine (2–3); *12.* 1,2,3,5-tetrazine (2); *13.* 1,2,3,5-tetrazine (1–2); *14.* 1,2,3,5-tetrazine (5); *15.* 1,2,4,5-tetrazine (1–2)

nitrogen which is closer to the Li$^+$ ion becomes appreciably polarized. On the other hand, the possible contribution of the lithium *p* functions to the highest occuplied molecular orbital of the complex must also be considered as proposed in [9]. To check this possibility we have examined the molecular orbitals of the azine-Li$^+$ complexes which are bridged structures and we have found that, in these cases, there is a systematic interaction between the out of phase combination of the nitrogen lone pairs (LPN$^-$) and the lithium *p* orbital of the appropriate orientation (see Scheme 1). Obviously, this interaction is neither possible for bent complexes nor for protonated species, since the hydrogen atom is devoid of valence *p* orbitals. Both factors would also explain why the Li$^+$ binding energies for bridged complexes are considerably greater than is expected from the values of the corresponding protonation energies, as shown in Fig. 5. Nevertheless, the former must be clearly dominant, since the interaction between the lithium *p* functions and the LPN$^-$ orbital is always quite small. Furthermore, the stabilization due to the formation of the additional three-membered ring seems to be constant along the series since both linear regressions have the same slope. It must be also remarked that the enhanced stability of the bridged structures, which Fig. 5 illustrates, becomes smaller when BSSE corrections and polarization functions are included in the basis set. Nevertheless, the intercepts of both correlations decrease by about the same factor ($\simeq 2$) so that the correlation followed by bridged complexes still has an intercept of about 4 kcal/mol greater than the bent complexes.

Figure 6 also shows that Li$^+$ does not have a stronger electrostatic interaction with the two nitrogen atoms when it occupies an intermediate position [9].



Scheme 1

To better visualize this point let us concentrate our attention on 1,2,3-triazine, as a suitable example. The electrostatic potential felt by the Li^+ ion in complex 5 is 48 kcal/mol, while that felt in the bridged situation (6) is 6 kcal/mol lower. Therefore, if the electrostatic interaction were the only contributor to the stability of the cation it would exhibit a bent conformation. However, the SCF results indicate that the bridged arrangement (6) is about 1 kcal/mol more stable than the bent one (5), showing that the stabilization of the former due to both the polarization of two nitrogens and the role of the lithium *p* functions compensates the smaller electrostatic interaction between the Li^+ ion and the base when the former is in an intermediate position. Something similar can be observed for species 12 and 13 and for 1,2,3,4-tetrazine. On the contrary, pentazole, which can be considered the result of substituting a $CH=CH$ group of 1,2,3,4-tetrazine by a $-NH$ group, yields only bent complexes [10]. This is so, because, in this case, the electrostatic potential felt by the Li^+ ion in the bridged arrangement is 11 kcal/mol lower than in the bent conformation and the stabilization due to polarization and covalent effects are not able to counterbalance this difference.

A quantitative analysis of the potential energy curve corresponding to the different paths along which the Li^+ ion approach 1,2,3,4-tetrazine (see Fig. 7) confirms that only species 14 and 15 are local minima, while bent arrangements correspond to saddle points close to the maxima between them. This potential energy curve was obtained by fully optimizing the structure of the complex for values of the angle α (defined in Fig. 7) from 40°–180°, in steps of 10°. A similar analysis for the case of 1,2,3-triazine showed that the bent conformation (5) is not a minimum but a flat maximum of the potential surface, lying 3 kcal/mol above the minimum which corresponds to conformation 6.

A comparison of Figs. 5 and 6 leads to another useful conclusion. Within each subset of systems (those with bridged and non-bridged structures) the basicity trends are clearly given by pure electrostatic interactions of the nature of the reference acid. However, it can be easily shown that there is only a rough

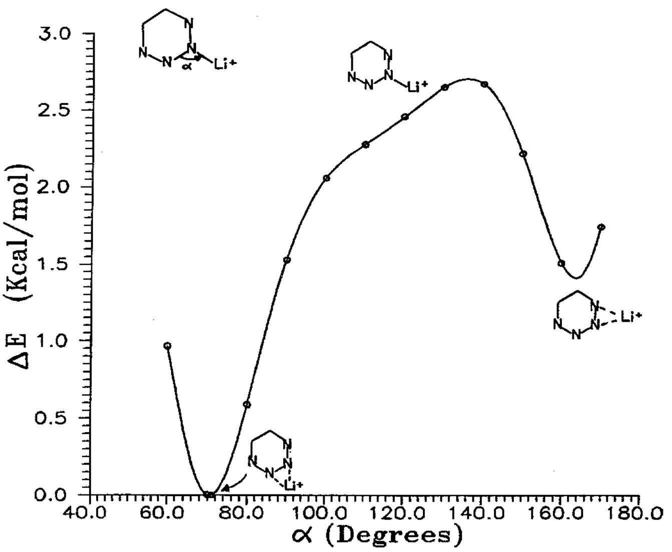


Fig. 7. Potential energy curve corresponding to the clustering between 1,2,3,4-tetrazine and Li^+. Values are referred to the absolute minimum

correlation between Li^+ binding energies and the ion-dipole interaction term, i.e., although the ion-dipole term is the dominant it would yield only a rough basicity ordering. Only when contributions from higher order multipoles are included does the correlation become reliable.

4. Conclusions

Pyridazine has the highest Li^+ binding energy of all the monocyclic azines, in contrast with its proton affinity and in agreement with recent experimental measurements. The enhanced basicity of this and other azines when the reference acid is Li^+ is related to the formation of a three-membered ring in which Li^+ bridges two nitrogen atoms with lone pairs of electrons. As a consequence, the correlation between Li^+ binding energies and proton affinities follows two different linear relationships, one for bent complexes and another for bridged systems.

A topological analysis of the electronic charge density and its Laplacian shows that, in all cases, the azine-Li^+ interaction is a closed-shell one, so that the stabilization of the complex is dominated by electrostatic effects. In fact, there are good linear correlations between the electrostatic potential felt by the Li^+ ion in the complex and the calculated Li^+ binding energies. Nevertheless, the enhanced stability of bridged complexes when the Li^+ occupies an intermediate position is not due to the stronger electrostatic interaction of Li^+ with both nitrogen atoms but to the polarization of the nitrogens and to the participation of the lithium *p* orbitals in the occupied molecular orbitals of appropriate symmetry. The preference for bridging conformations is the result of the competition between three factors: (i) a smaller electrostatic interaction between the base and the Li^+ ion, (ii) a stronger polarization of the two nitrogen atoms of the ring, and (iii) a more efficient contribution of the lithium *p* orbitals, on the other. When the first one dominates the complex presents a bent conformation, if (ii) and (iii) are dominant then the complex will exhibit a bridging structure.

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