

# Stabilization of Nitrogen-Containing Three-Membered Rings by H<sup>+</sup> and Li<sup>+</sup> Association in the Gas Phase

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**Abstract:** Ab initio calculations have been performed for three-membered nitrogen-containing rings, including all saturated and unsaturated compounds and their protonated and lithiated species. Geometry optimizations were carried out at the HF/6-31G\* level and, for some suitable examples, at the MP2/6-31G\* level. Protonation energies and Li<sup>+</sup> binding energies were evaluated at the MP4/6-31+G(d,p) level including ZPVE corrections. We have found that the intrinsic basicities of saturated nitrogen-containing three-membered rings decrease as the number of basic centers increases. However, the same trend is not observed in the series of unsaturated analogues, where triazirine is predicted to be much more basic than diazirine. This finding is related to the considerable alleviation of the antiaromatic character of the former when it becomes protonated. This enhanced gas-phase basicity is observed for all of the antiaromatic compounds studied, explaining why some antiaromatic species become more stable than the nonaromatic counterparts when protonated in the gas phase. When the reference acid is Li<sup>+</sup> this enhancement is considerably smaller, but sizable. Saturated systems with two or more basic centers also present enhanced Li<sup>+</sup> binding energies due to the ability of Li<sup>+</sup> to bridge between two neighbor centers bearing pairs of electrons. No stable bridged structures were found for unsaturated compounds. The Li<sup>+</sup> derivative of triaziridine in which the alkali cation is tricoordinated is a minimum of the potential energy surface which lies about 3 kcal/mol above the global one, in which Li<sup>+</sup> appears dicoordinated.

## 1. Introduction

Gas-phase ion chemistry has experienced an impressive development in the last two decades.<sup>1</sup> Besides protonation and deprotonation processes, a great deal of attention was also devoted to the study of metal cation binding energies to organic molecules,<sup>1,2</sup> and in many cases, a comparison between these binding energies and the corresponding proton affinities, within a homologous series of compounds, has permitted<sup>3-13</sup> a better understanding of the factors governing the stability of ion-molecule complexes in the gas phase. Alkali metal cations provide a good illustration of this. In most cases the alkali metal ion binding energies are linearly correlated with the corresponding protonation energies,<sup>8-10,13</sup> even though in alkali metal ion complexes the interactions are essentially electrostatic,<sup>8,13,14</sup> while

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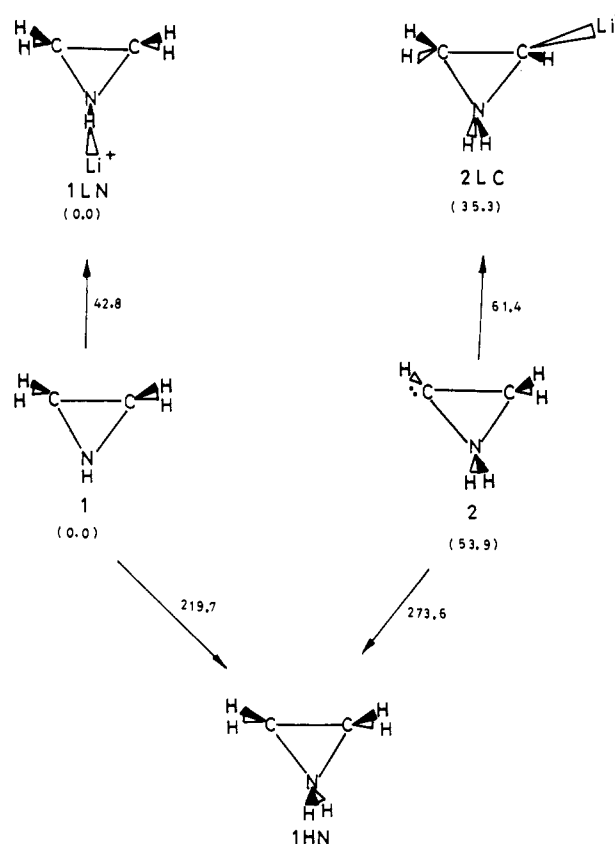
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**Figure 1.** Protonated and lithiated species of aziridine (1) and their isomers. All values (in kcal/mol) were obtained at the MP4/6-31+G(d,p) level using MP2/6-31G\* optimized structures.

in protonated molecules the interaction with the incoming proton leads to the formation of a covalent bond. There are however noticeable exceptions to this general rule when the organic base presents two (or more) basic centers close to each other. Diazirines<sup>10,11</sup> and some triazoles and tetrazoles<sup>9</sup> constitute suitable

Table I. Total Energies<sup>a</sup> (au) and ZPVE (kcal/mol)

compd	6-31G*//6-31G*		6-31+G(d,p)//6-31G*	
	HF//HF	ZPVE	MP2//MP2	MP4//MP2
1	-133.038 56	47.6	-133.473 09	-133.554 42
2	-132.948 04	46.6	-133.376 34	-133.467 62
1HN	-133.407 95	57.2	-133.834 27	-133.918 73
1LN	-140.349 00	49.5	-140.786 49	-140.860 94
2LC	-140.292 01	49.5	-140.727 34	-140.805 06
3	-131.840 03	30.7	-132.270 37	-132.325 40
4	-131.796 88	30.0	-132.211 78	-132.277 85
5	-131.775 54	30.0	-132.206 58	-132.266 12
3HN	-132.168 65	39.1	-132.584 00	-132.645 07
5HN	-132.156 99	39.7	-132.577 15	-132.638 51
3LN	-139.145 23	32.2	-139.574 44	-139.624 42
4LC	-139.108 78	32.1	-139.530 10	-139.585 23
5LN	-139.092 31	31.7	-139.525 00	-139.576 70
6(cis)	-148.993 14	40.2		-149.534 11
6(trans)	-149.004 03	40.5		-149.544 31
7(cis)	-148.900 96	39.2		-149.444 33
7(trans)	-148.909 12	39.5		-149.452 52
8	-148.949 28	39.1		-149.490 02
6HN	-149.347 11	49.6		-149.884 14
7HN	-149.247 85	48.6		-149.787 29
6LN	-156.300 44	42.0		-156.837 32
6LNN	-156.311 19	42.0		-156.848 87
7LN	-156.203 34	41.1		-156.743 86
7LC	-156.240 26	42.0		-156.777 55
8LN	-156.284 60	41.6		-156.819 49
9	-147.836 09	23.0		-148.343 19
10	-147.789 94	22.6		-148.306 65
11	-147.759 10	22.0		-148.262 60
12	-147.794 99	22.3		-148.298 70
9HN	-148.113 44	31.4		-148.618 48
10HN1	-148.133 79	31.9		-148.641 44
10HN2	-148.089 38	29.6		-148.597 75
9LN	-155.115 46	24.4		-155.619 99
10LN1	-155.093 36	24.0		-155.604 44
10LN2	-155.087 16	23.8		-155.598 46
11LC	-155.050 34	23.3		-155.552 92
12LN	-155.085 78	24.1		-155.586 01
12LC	-155.092 35	24.6		-155.595 96
13(cis)	-164.922 02	32.0		-165.489 93
13(trans)	-164.942 44	32.5		-165.508 53
14	-164.881 09	31.6		-165.448 23
13HN(cis)	-165.255 93	41.8		-165.819 68
13HN(trans)	-165.268 06	42.0		-165.830 57
13LN	-172.221 79	34.3		-172.786 16
13LNN	-172.238 25	33.4	-172.747 96	-172.804 32
13LPL	-172.232 97	33.4	-172.743 01	-172.798 22
14LN	-172.205 38	33.8		-172.766 65
15	-163.778 68	14.6		-164.316 87
15HN1	-164.085 57	23.6		-164.619 04
15HN2	-164.010 84	22.7		-164.552 08
15LN1	-171.065 52	16.0		-171.599 50
15LN2	-171.041 12	15.8		-171.578 86

<sup>a</sup> The 6-31+G(d,p) energy for Li<sup>+</sup> is -7.23554 au.

examples of systems which present enhanced alkali metal ion binding energies in the gas phase, due to the ability of these metal cations to bridge between two basic centers bearing electron pairs. In this respect the contributions of the theoretical investigations<sup>3-15</sup> have been crucial in elucidating the structure and energetics of these molecular ions.

Pursuing our research along these lines we have extended our investigation to nitrogen-containing three-membered rings reacting with H<sup>+</sup> and Li<sup>+</sup>. Three-membered rings constitute the simplest aromatic or antiaromatic systems and for this reason they have received a great deal of attention<sup>16-25</sup> over the last two

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Table II. Protonation Energies<sup>a</sup> and Li<sup>+</sup> Binding Energies<sup>a</sup>

compd	position	process	6-31G*//6-31G*		6-31+G(d,p)//6-31G*	
			HF//HF	MP2//MP2	MP4//HF	MP4//MP2
1	N	H <sup>+</sup>	223.3	218.2	220.1	219.7
		Li <sup>+</sup>	41.6	37.2	42.9	42.8
2	C	H <sup>+</sup>	219.2	278.0	273.7	273.6
		Li <sup>+</sup>	65.5	71.7	61.4	61.4
3	N	H <sup>+</sup>	198.7	189.3	193.1	192.1
		Li <sup>+</sup>	42.3	41.6	38.4	38.0
4	C	H <sup>+</sup>	225.2	225.5	222.4	222.8
		Li <sup>+</sup>	46.0	50.1	43.2	43.4
5	N	H <sup>+</sup>	230.7	223.9	225.1	224.5
		Li <sup>+</sup>	49.5	50.5	45.6	45.4
	C	H <sup>+</sup>	238.6	228.8	229.8	229.2
6	N	H <sup>+</sup>	207.2		205.2	
		Li <sup>+</sup>	36.8		34.7	
	NN	Li <sup>+</sup>	43.6		42.0	
7	N	H <sup>+</sup>	204.5		202.0	
		Li <sup>+</sup>	35.5		33.6	
	C	H <sup>+</sup>	265.9		261.9	
		Li <sup>+</sup>	57.8		53.9	
8	N	H <sup>+</sup>	240.3		238.0	
		Li <sup>+</sup>	60.4		56.7	
9	N	H <sup>+</sup>	156.6		165.3	
		Li <sup>+</sup>	26.3		24.7	
10	N1	H <sup>+</sup>	207.5		201.9	
		Li <sup>+</sup>	41.4		37.8	
	N2	H <sup>+</sup>	181.7		176.5	
		Li <sup>+</sup>	37.6		34.2	
	C	H <sup>+</sup>	195.2		187.9	
11	C	H <sup>+</sup>	200.6		203.6	
		Li <sup>+</sup>	33.8		33.3	
12	C	H <sup>+</sup>	204.1		206.6	
		Li <sup>+</sup>	36.8		36.7	
	N	Li <sup>+</sup>	33.1		30.9	
13	N	H <sup>+</sup>	195.9		193.6	
		Li <sup>+</sup>	25.9		24.8	
	NN <sup>b</sup>	Li <sup>+</sup>	37.0		37.0	
	P1 <sup>c</sup>	Li <sup>+</sup>	33.3		32.8	
14	N	H <sup>+</sup>	233.6		230.7	
		Li <sup>+</sup>	53.7		50.1	
15	N1	H <sup>+</sup>	184.6		181.6	
		Li <sup>+</sup>	31.0		28.4	
	N2	H <sup>+</sup>	138.5		140.4	
		Li <sup>+</sup>	15.9		15.6	

<sup>a</sup> The reported values include the ZPVE corrections, which have been scaled by the empirical factor 0.89. All values (kcal/mol) are referred to the *trans* conformer. <sup>b</sup> NN indicates that the Li<sup>+</sup> bridges between the two nitrogen atoms. <sup>c</sup> Li<sup>+</sup> is located above the plane of the molecule bridging the three nitrogen atoms.

decades. In fact, they are suitable model compounds for studying the general influence of ring strain upon chemical reactivity and, for the particular case of nonsaturated systems, the degree to which the system is destabilized by conjugation of the nitrogen lone pair with the  $\pi$ -bond. In fact, we shall show in forthcoming sections that some typically antiaromatic systems are considerably stabilized either by protonation or Li<sup>+</sup> association in the gas phase. On the other hand, although the protonation of some nitrogen-containing small rings, such as aziridine and azirine, already has been described in the literature,<sup>26-31</sup> to our knowledge, systematic

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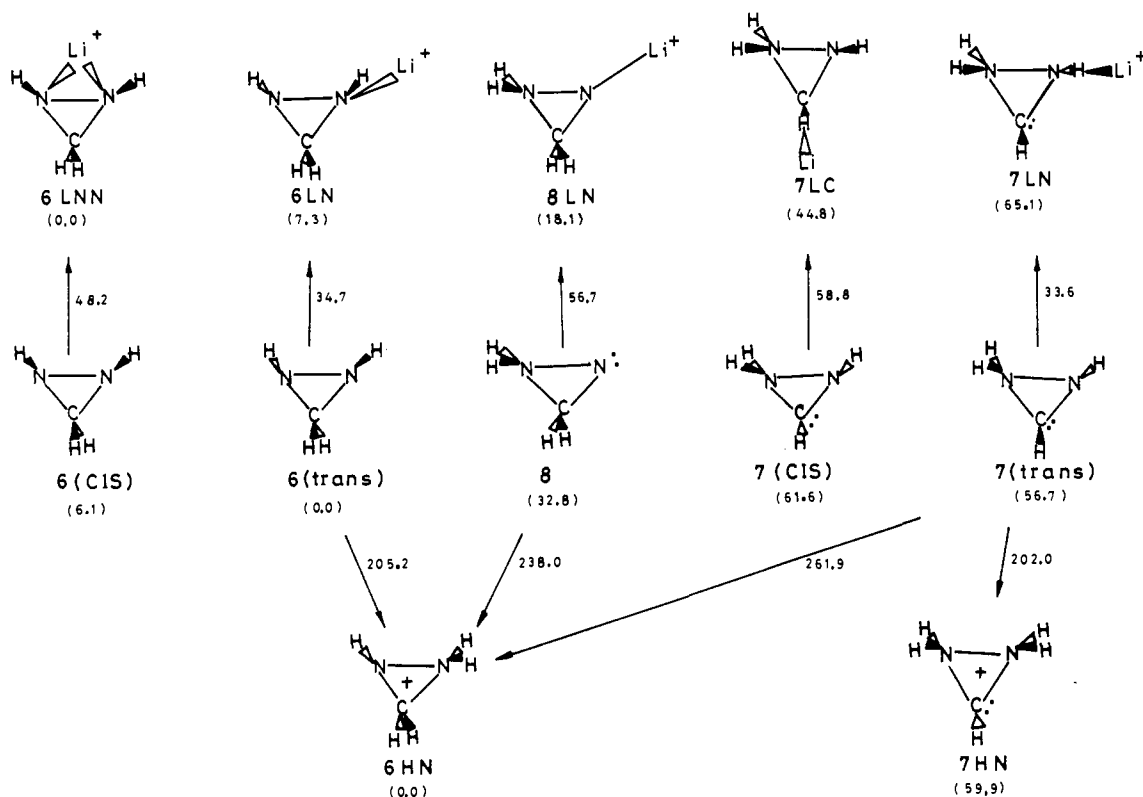
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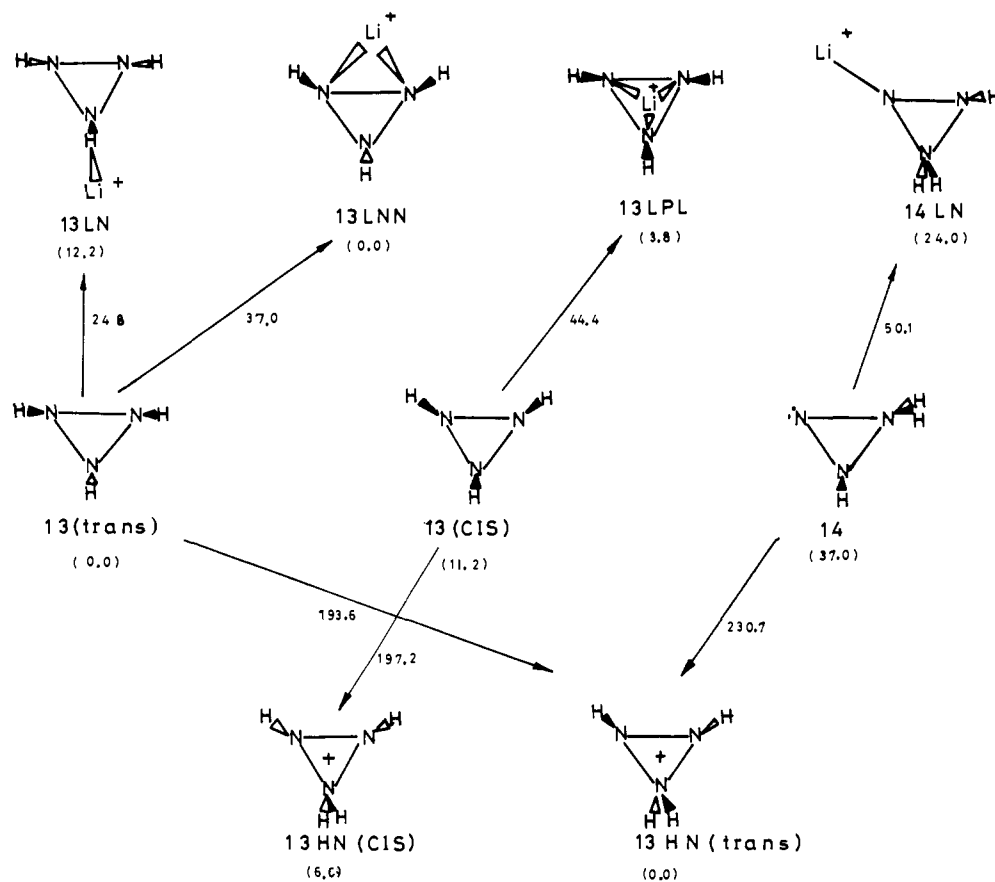
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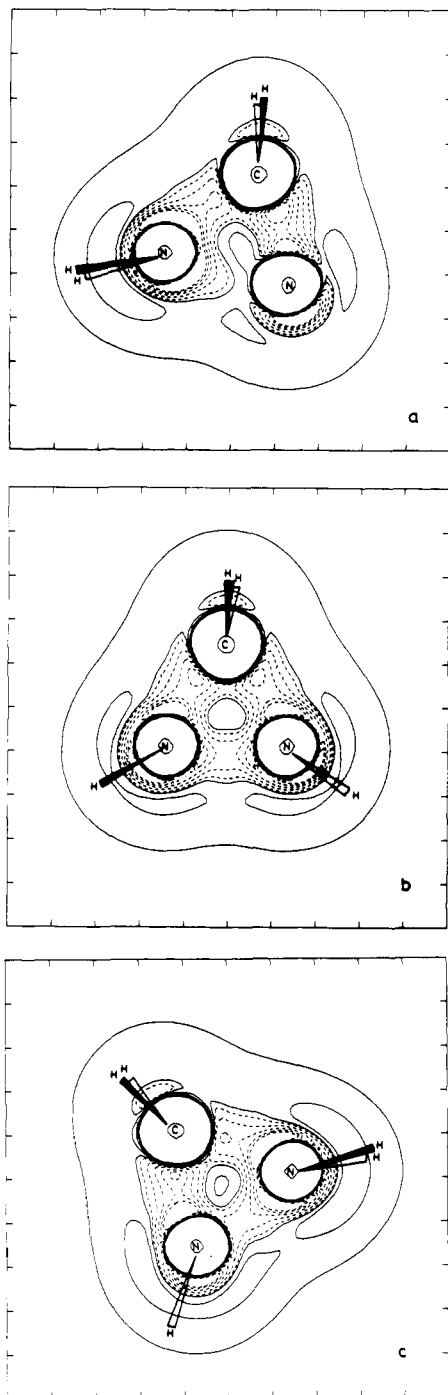
**Figure 2.** Protonated and lithiated species of diaziridine (6) and their isomers. All values (in kcal/mol) were obtained at the MP4/6-31+G(d,p) level using HF/6-31G\* optimized structures.



**Figure 3.** Protonated and lithiated species of triaziridine (13) and their isomers. All values (in kcal/mol) were obtained at the MP4/6-31+G(d,p) level using HF/6-31G\* optimized structures.

studies including all possible nitrogen-containing three-membered rings have not been published. As a consequence, no investigation

has been carried out, so far, on the possible influence of protonation (or Li<sup>+</sup> association) on the stability of some three-membered



**Figure 4.** Contour map of the Laplacian of the charge density of (a) **8**, (b) **6**, and (c) **6HN**. Positive values of  $\nabla^2\rho$  are denoted by full lines and negative values by dashed lines. Contour values are  $\pm 0.05$ ,  $\pm 0.25$ ,  $\pm 0.50$ ,  $\pm 0.75$ , and  $\pm 0.95$  au.

rings such as 2-azirine which may be considered as prototypes of  $4n-\pi$  antiaromatic systems. Another important subject we are interested in is the possible existence of  $\text{Li}^+$  complexes that exhibit enhanced  $\text{Li}^+$  binding energies and, in particular, the existence of complexes in which  $\text{Li}^+$  appears tricoordinated. In this respect, triaziridine constitutes a suitable benchmark case for studying this possibility.

Therefore, we present in the present paper ab initio calculations on the protonation and  $\text{Li}^+$  association to aziridine (**1**), 1-azirine (**3**), 2-azirine (**5**), diaziridine (**6**), 1-diazirine (**9**), 2-diazirine (**11**), triaziridine (**13**), and triazirine (**15**). It must be noted that our study has not been limited to the most stable neutral forms but includes all possible isomers (**2**, **4**, **7**, **8**, **10**, **12**, **14**). As we shall illustrate later, most of these isomers, which are considerably

unstable with respect to the global minimum, become strongly stabilized by protonation or  $\text{Li}^+$  association.

## 2. Computational Details

The structures of the different neutrals and cations were fully optimized at the HF/6-31G\* level.<sup>32</sup> For the particular set of compounds that includes aziridine, azirine, and their isomers as well as their protonated and lithiated species, these geometries were refined at the MP2/6-31G\* level. The inclusion of polarization functions is required for a correct description of both three-membered-ring structures<sup>33</sup> and the valence angles at the heteroatom.<sup>34</sup> Since, as we shall indicate later, the use of HF or MP2 optimized geometries leads to energetics which differed by less than 1 kcal/mol, for the remaining species and for the sake of economy, the geometry optimizations were only performed at the HF level of theory. Harmonic vibrational frequencies were evaluated at the HF level by using analytical second derivative techniques to both characterize the stationary points of the potential energy surface and evaluate the corresponding zero-point vibrational energies (ZPVE). The final energies used in our discussions were obtained by including electronic correlation effects to fourth order by means of the Møller-Plesset perturbation theory,<sup>35,36</sup> (MP4), keeping the core electrons frozen. The basis set used in these post-Hartree-Fock calculations (6-31+G(d,p))<sup>37</sup> includes a set of diffuse functions on the heavy atoms and polarization functions on hydrogens, since it has been proved<sup>38</sup> that a proper description of electronic correlation effects for systems containing alkali monocations requires the inclusion of these diffuse components in the basis set.

Protonation energies were obtained as the energy difference between the protonated and the unprotonated species. The  $\text{Li}^+$  binding energies were calculated by subtracting from the energy of the corresponding  $\text{Li}^+$  complex the energy of the  $\text{Li}^+$  cation plus that of the neutral from which the complex can be derived. All these calculations have been carried out using the Gaussian-90 series of programs.<sup>39</sup>

As we shall illustrate in forthcoming sections, protonation or  $\text{Li}^+$  association implies, in many cases, drastic redistributions of the electronic charge density of the base. These effects will be discussed by carrying out a topological analysis of the corresponding electronic charge densities,  $\rho$ , and its Laplacian,  $\nabla^2\rho$ . As we have shown recently,<sup>40</sup> bond activation in protonation processes can be detected by comparing the Laplacian of the charge densities of the protonated and neutral species. Actually, Bader et al.<sup>41-44</sup> have demonstrated that the Laplacian of the electronic charge density ( $\nabla^2\rho$ ) identifies regions of space wherein  $\rho$  is locally concentrated ( $\nabla^2\rho < 0$ ) or depleted ( $\nabla^2\rho > 0$ ). Hence, bond activation should be accompanied by a decrease in the absolute value of  $\nabla^2\rho$ , while bond reinforcement would imply a more negative value of the Laplacian. Therefore, in general, an inspection of the topological characteristics of the Laplacian of the charge density will reveal the most significant charge

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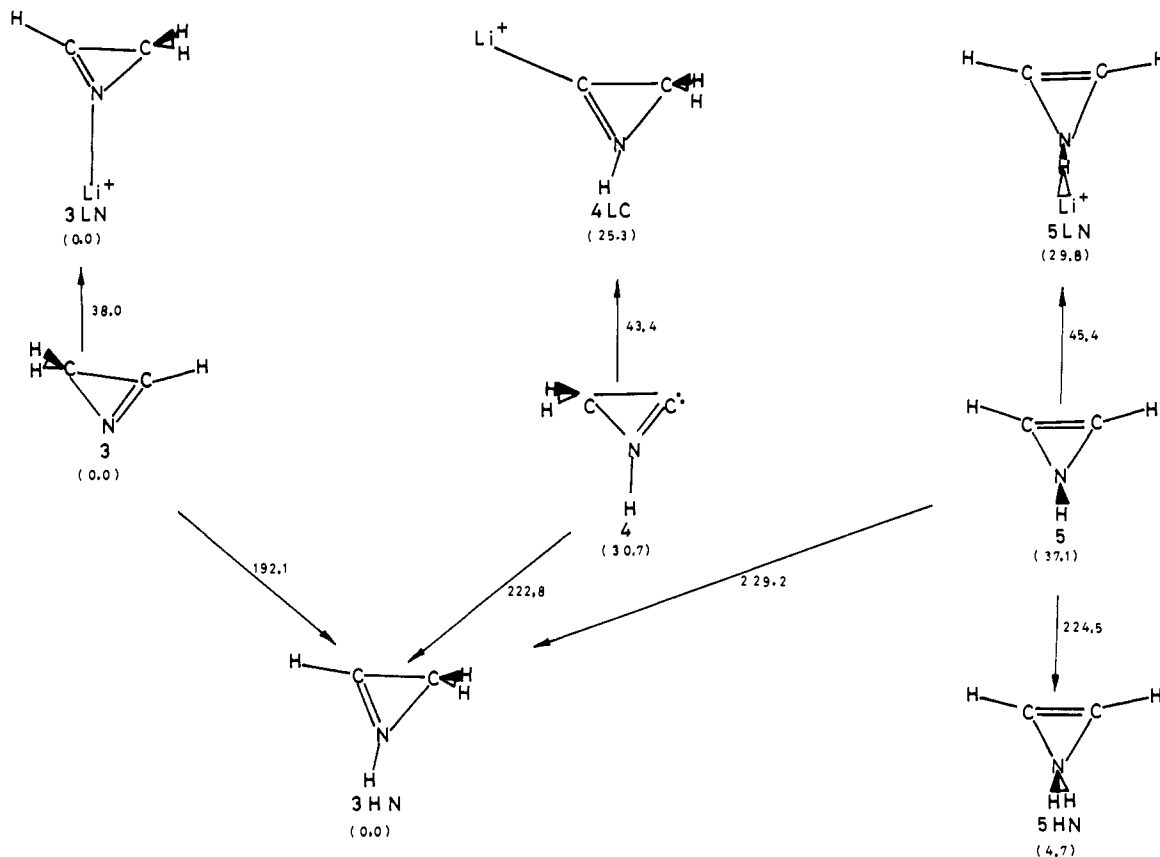
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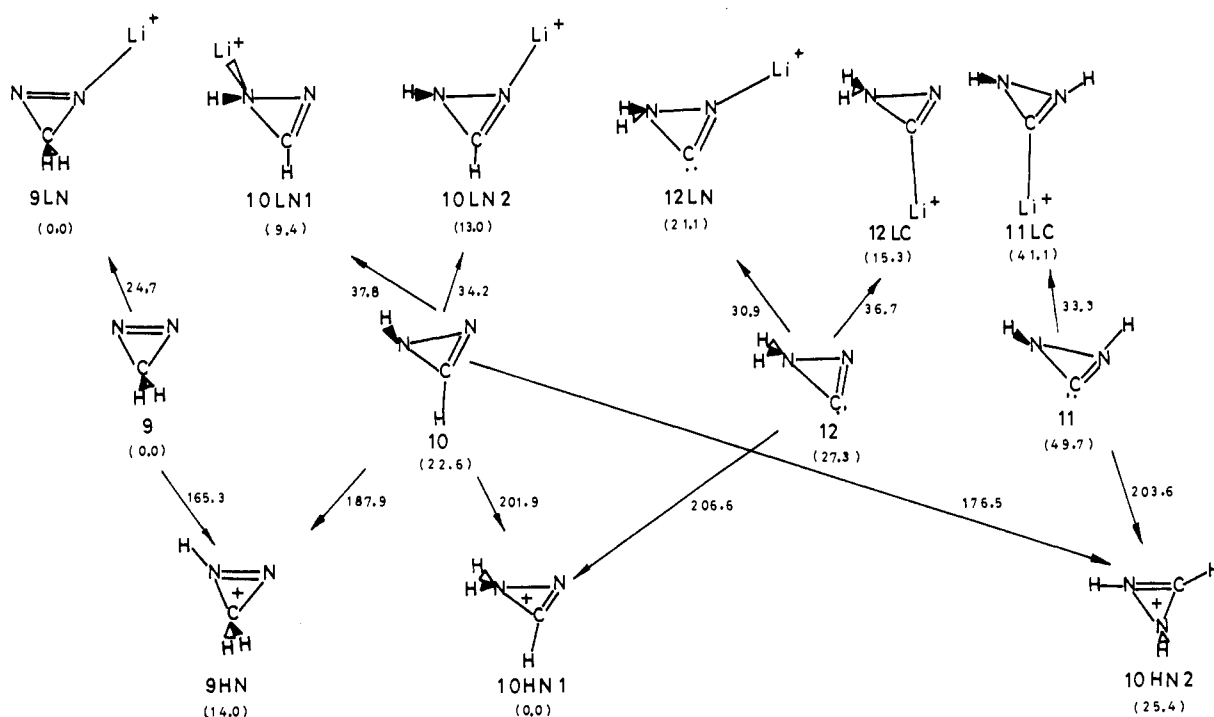
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**Figure 5.** Protonated and lithiated species of 1-azirine (**3**) and their isomers. All values (in kcal/mol) were obtained at the MP4/6-31+G(d,p) level using MP2/6-31G\* optimized structures.



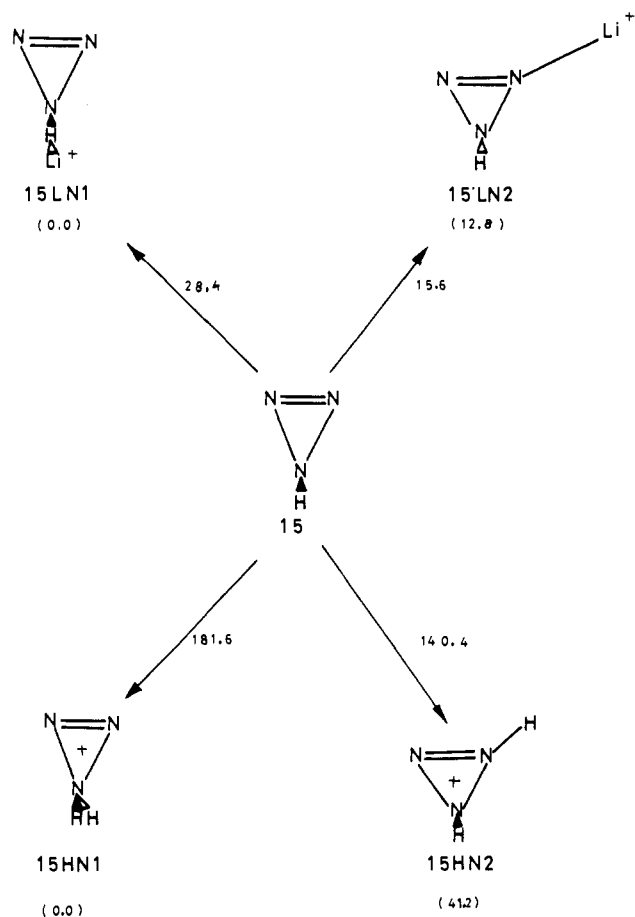
**Figure 6.** Protonated and lithiated species of 1-diazirine (**9**) and their isomers. All values (in kcal/mol) were obtained at the MP4/6-31+G(d,p) level using HF/6-31G\* optimized structures.

redistributions undergone by the neutral upon H<sup>+</sup> or Li<sup>+</sup> association. These calculations have been carried out using the AIMPAC series of programs.<sup>45</sup>

(45) The AIMPAC programs package has been provided by J. Cheeseman and R. F. W. Bader.

### 3. Results and Discussion

To make our discussion more systematic and easy to follow we have adopted the following nomenclature for the complexes included in our study. After the number that identifies the neutral, we have first added the symbol H or L to indicate that the complex



**Figure 7.** Protonated and lithiated species of triazirine (**15**). All values (in kcal/mol) were obtained at the MP4/6-31+G(d,p) level using HF/6-31G\* optimized structures.

is formed by protonation or  $\text{Li}^+$  association, respectively. The second symbol identifies the basic center. For instance, **1LN** designates the complex obtained by  $\text{Li}^+$  association to the nitrogen atom of aziridine (**1**), while **2LC** identifies the complex formed when the association takes place on the carbon atom of neutral **2**. The **6LNN** notation indicates that  $\text{Li}^+$  bridges between the two nitrogen atoms of diaziridine (**6**).

The total energies obtained at the different levels of theory considered as well as the ZPVE are presented in Table I. The corresponding optimized geometries are given as supplementary material. All species included are minima of the corresponding potential energy surfaces.

The protonation energies as well as the  $\text{Li}^+$  binding energies are summarized in Table II. Both sets of values include the corresponding ZPVE correction, scaled by the empirical factor 0.89.<sup>46</sup>

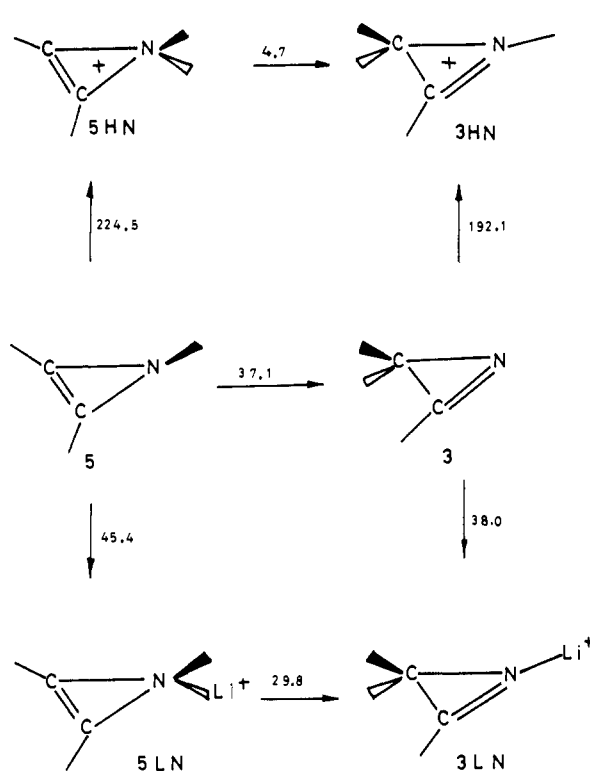
Table II shows, for a reasonably large set of compounds, that protonation or  $\text{Li}^+$  association energies obtained in the MP4 calculations based on HF optimized geometries differ by less than 1 kcal/mol from those obtained using MP2 optimized structures. This permits us to constrain our geometry optimizations to the HF level for the remaining systems of the series.

**General Basicity Trends.** Table II indicates that for the saturated series of compounds, as has been found for other nitrogen bases such as azines<sup>1,47</sup> and azoles,<sup>48</sup> the increase in the number of basic centers within the system reduces its intrinsic basicity. Hence, aziridine (**1**) is more basic than diaziridine (**6**), which is

(46) Pople, J. A.; Ragavachari, K.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem. Symp.* **1979**, *13*, 225.

(47) M6, O.; de Paz, J. L. G.; Yáñez, M. *J. Mol. Struct. (Theochem)* **1987**, *150*, 135.

(48) M6, Q.; de Paz, J. L. G.; Yáñez, M. *J. Phys. Chem.* **1986**, *90*, 5597.



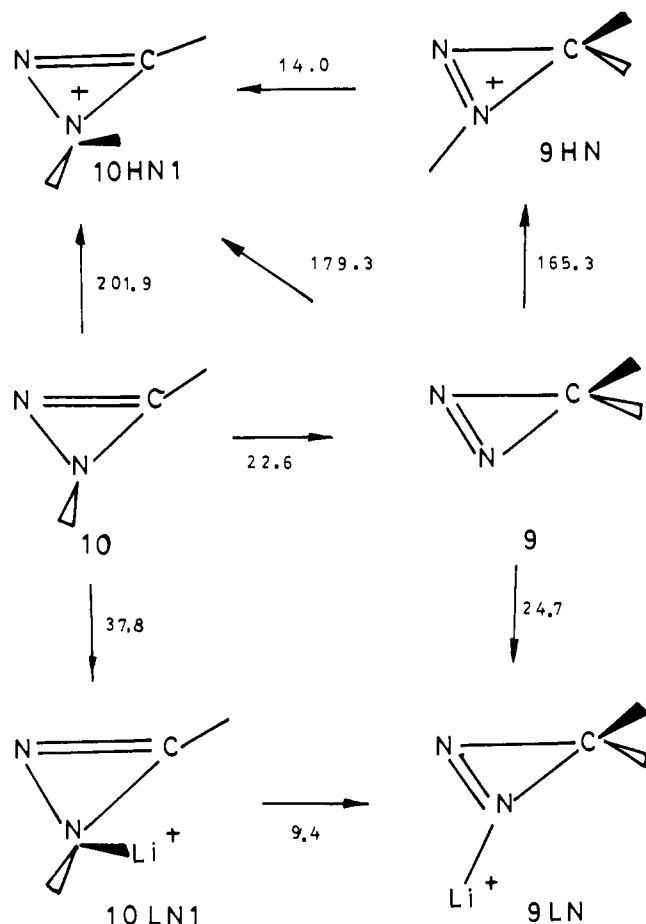
**Figure 8.** Influence of protonation and  $\text{Li}^+$  association on the relative stabilities of **3** and **5**. All values (in kcal/mol) were obtained at the MP4/6-31+G(d,p) level using MP2/6-31G\* optimized structures.

more basic than triaziridine (**13**). However, the same trend is not observed within the unsaturated series. Actually, while 1-azirine (**3**) is more basic than 1-diazirine (**9**), the latter is less basic than triazirine (**15**). As we shall discuss below, this finding is related to the attenuation of the antiaromatic character of the latter compound upon protonation. Regarding the reliability of our theoretical calculations, it must be mentioned that for aziridine (**1**) (which is the only system for which the experimental proton affinity has been reported in the literature) the agreement between our estimates and the experimental value<sup>17</sup> (215.7 kcal/mol) is fairly good. On the other hand, our estimate for the proton affinity of 1-diazirine (**9**) is also quite close to the experimental proton affinity<sup>49</sup> of its isomer  $\text{H}_2\text{NCN}$  (164.0 kcal/mol).

It must also be observed that due to the ability of the  $\text{Li}^+$  cation to bridge between two basic centers having lone pairs of electrons, the basicity trends found upon protonation are not always coincident with those observed for the  $\text{Li}^+$  binding energies. As mentioned above, aziridine (**1**) is more basic than diaziridine (**6**) as far as gas-phase protonation is concerned, but it is not when the reference acid is  $\text{Li}^+$ . This is not the case, however, within the unsaturated series, where the  $\text{Li}^+$  binding energies follow the same qualitative trend as the protonation energies. We shall come back later to this question when discussing the relative stabilities of  $\text{Li}^+$ -bridged structures.

**Complexes Involving Saturated Compounds.** In Figures 1–3 we have schematized the different complexes that are minima of the potential energy surface corresponding to the  $\text{H}^+$  and  $\text{Li}^+$  association to saturated compounds. These figures also show the corresponding protonation or lithiation energies. It can be seen that the neutrals considered present three different kinds of active centers: nitrogen atoms with one electron pair (**1**, **6**, **13**), nitrogen atoms with two electron pairs (**8**, **14**), and carbon atoms (**2**, **7**). For our discussion we are going to select the subset formed by the tautomers **6**, **7**, and **8** as suitable examples, because within this subset the three types of basic centers can be found.

(49) Beach, D. B.; Eyermann, C. J.; Smit, S. P.; Xiang, S. F.; Jolly, W. *J. Am. Chem. Soc.* **1984**, *106*, 536.



**Figure 9.** Influence of protonation and  $\text{Li}^+$  association on the relative stabilities of **9** and **10**. All values (in kcal/mol) were obtained at the MP4/6-31+G(d,p) level using HF/6-31G\* optimized structures.

Protonation of these three systems (see Figure 2) yields a common cation, **6HN**. Hence, the very large protonation energies of species **7** and **8** are a consequence of the low stabilities of these neutrals. The dramatic stabilization of these two species upon protonation is related to the strong charge redistribution induced by the interaction with the incoming proton. As is clearly illustrated in Figure 4, in species **8** there is not a true N–N bond. In other words, strictly speaking species **8** is not a three-membered ring, since the location of two pairs of electrons on one of the nitrogen atoms significantly affects its coordination ability. Actually, the N–N “linkage” presents the typical characteristics of the interaction between closed shell systems. It can be seen in fact that the Laplacian between these two atoms is clearly positive and the charge density quite small, corresponding to a situation in which the charge concentrates preferentially on the two nitrogen atomic basins. Quite on the contrary, in species **6** all bonds are normal covalent linkages (see Figure 4b). Upon nitrogen protonation a strong charge transfer to the incoming proton takes place, but this charge transfer has opposite effects on the ring electronic charge densities of **6** and **8**. In both cases there is a strong charge transfer to the incoming proton, but while in species **6** the nitrogen atom recovers part of the charge transferred to the proton by depopulating the C–N bond, which accordingly becomes weaker (see Figure 4c) and longer (from 1.422 to 1.642 Å), in species **8** the nitrogen atom is an electron excessive center and the charge transfer to the incoming proton is made without depopulating the ring bonds. Simultaneously, the engagement of one of the nitrogen lone pairs in the new N–H linkage allows the interaction with the neighbor nitrogen atom, leading to the formation of a covalent N–N bond, which is reflected in a shortening of the N–N distance from 1.513 to 1.445 Å.

The products obtained in the lithiation processes are different for the three neutrals (namely, **6LN**, **7LC**, and **8LN**, respectively). Again, the  $\text{Li}^+$  binding energies of species **7** and **8** are significantly large, and almost twice those calculated when  $\text{Li}^+$  association takes place at a nitrogen atom with only one electron pair (**6LN** or **7LN**) (see Figure 2 and Table II). The enhanced  $\text{Li}^+$  basicity of **7(cis)** and **8** is a direct consequence of the nature of the interactions between the base and the alkali cation. As already has been proved<sup>8,13,14</sup> for very different kinds of complexes, the  $\text{Li}^+$ -molecule interactions are essentially electrostatic and therefore clearly dominated by the ion–dipole terms. The presence in species **7** and **8** of an electron excess center results in a very large dipole moment directed to this center, and therefore in an enhancement of the electrostatic interactions with the  $\text{Li}^+$  cation.

Similar findings are also observed for the other saturated systems considered. Actually, species **2** and **14** have much larger  $\text{Li}^+$  binding energies than aziridine (**1**) and triaziridine (**15**), respectively (see Figures 1 and 3).

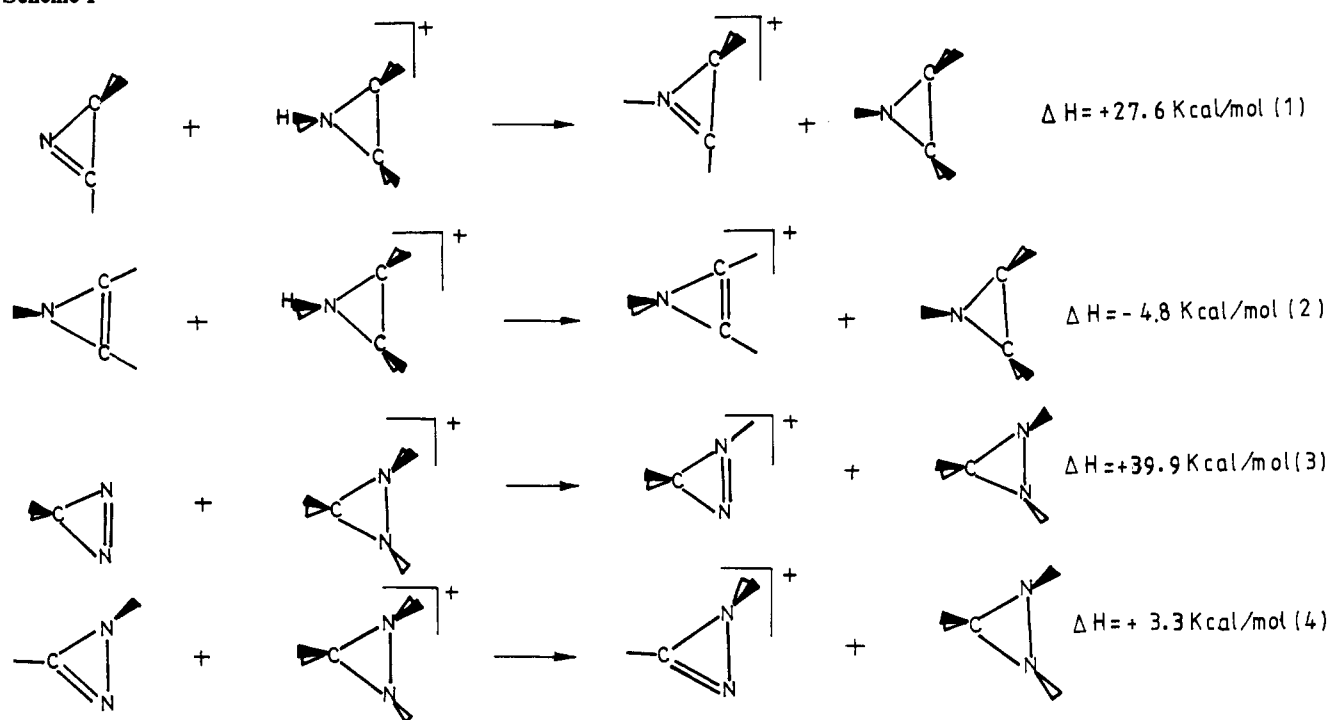
**Complexes Involving Unsaturated Compounds.** We present in Figures 5–7 the different complexes that are minima of the potential energy surface corresponding to the  $\text{H}^+$  and  $\text{Li}^+$  association to nonsaturated compounds. These figures also show the corresponding protonation or lithiation energies.

Some of the conclusions found in the previous section apply to the series of unsaturated compounds. In general, those species such as **4** which present an electron excessive atom exhibit quite high basicities. It is however very significant to realize that although **4** is more basic than **3**, it is less basic than **5**, even though the latter does not present electron excessive atomic centers. Something similar can be said of species **10** which presents an intrinsic basicity only ca. 2 and 5 kcal/mol smaller than those of **12** and **11**, respectively, both of which have an electron excessive carbon atom. It is interesting to note that all the species which present this enhanced basicity have in common their antiaromatic character. Hence, the high basicity of triazirine (**15**) (which is also antiaromatic) with respect to diazirine (**9**) probably has the same origin.

Let us analyze this phenomenon in more detail. As expected species **5** is 37.1 kcal/mol (see Figure 8) less stable than its isomer **3**, because in the former the conjugation of the nitrogen lone pair with the  $\pi$  bond destabilizes the system. Upon protonation this energy gap reduces to 4.7 kcal/mol (see Figure 8), because the antiaromatic character of **5** decreases considerably. Actually, in the neutral form **5** the degree of pyramidalization at the nitrogen atom is considerably high and the H atom bends 69.6° out of the plane in an attempt to minimize the destabilizing cyclic  $\pi$ -interaction. Coherent with this, the nitrogen inversion barrier of this system is also high, since as explained in ref 31 an increase of N-pyramidalization implies a decrease of the  $\pi$ -antibonding character of the HOMO of the system. Nitrogen protonation stabilizes this antibonding orbital and, as a consequence, the degree of N-pyramidalization decreases significantly. Actually in the protonated species **5HN** the amino hydrogens bend out of plane by only 57.1°. Something similar is observed in systems **10** and **10HN1**. In the former the H atom bends 70.4° out of the ring plane, while in the latter this angle is only 58.6°. It is interesting to note that these findings agree with those reported by Kroeker et al.<sup>50</sup> for the deprotonation process of 1-diazirine. In fact, it has been found by the aforementioned authors that the formation of the antiaromatic diazirinyl anion is accompanied by a noticeable increase in the degree of pyramidalization at the carbon atom, in an effort by the system to decrease the interaction between the remaining C lone pair and the  $\pi$ -electronic system. Also, a stabilization mechanism similar to that described above has been reported recently by Davy et al.<sup>25</sup> regarding the stabilization of  $\text{P}_2\text{O}$  cyclic species by protonation. The aforementioned effects

(50) Kroeker, R. L.; Bachrach, S. M.; Kass, S. R. *J. Org. Chem.* **1991**, *56*, 4062.

Scheme I



are more dramatic when considering species **9** and **10**. The latter is 22.6 kcal/mol **less** stable than the former, while its protonated form (**10HN1**) is 14.0 kcal/mol **more** stable than that of the latter (**9HN**) (see Figure 9). This implies that the proton affinity of 1-aziridine can be considerably higher than what should be expected from its intrinsic basicity (as shown in Figure 9) if the thermodynamically favored isomerization between **9HN** and **10HN1** takes place.

As it has been pointed out before for other cyclic systems,<sup>51</sup> these stabilizations can be modeled by appropriate isodesmic reactions in which the unsaturated systems may be compared with the corresponding saturated counterparts. For this purpose, we have taken aziridine (**1**) as the saturated reference system for compounds **3** and **5** (reactions 1 and 2) and diaziridine (**6**) for compounds **9** and **10** (reactions 3 and 4). It can be seen that while reaction 1 is clearly endothermic, reaction 2 is slightly exothermic. Therefore, while in relative terms the protonated species of the unsaturated compound **3** is less stable than that of the saturated counterpart, the opposite is true for the antiaromatic system **5**. Reactions 3 and 4 show the same qualitative trends for compounds **9** and **10**. Reaction 3 is also strongly endothermic, while reaction 4 is only slightly endothermic. Hence, in this case, the protonated species of form **10** is slightly less stable than the protonated species of the saturated counterpart, in relative terms. However, the stabilization of **10** by protonation is quantitatively more important than the stabilization of **5**. This is reflected, as mentioned above, in the reverse stability of the protonated forms of **9** and **10** with respect to the neutrals.

These findings are also mirrored in the topological characteristics of the electronic charge distributions of these systems. As illustrated in Figure 10, which presents the Laplacian of the charge densities of **9**, **10**, and their protonated species evaluated in the plane of the three-membered ring, the protonation of **9** implies an activation of all bonds of the three-membered ring, in particular the C—N bond, while protonation of **10** leads to a reinforcement of the C=N and the N=N bonds, due to the alleviation of its antiaromatic character, and only the C—N bond becomes activated.

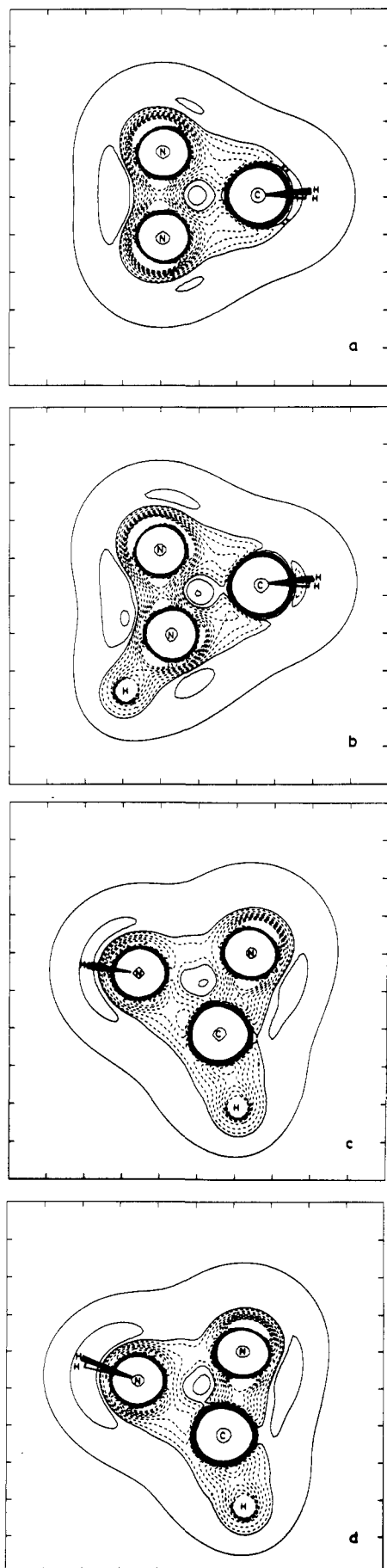
A similar analysis allows us to conclude that the enhanced basicity of triazirine, which renders this species more basic than diazirine, is also a consequence of a significant attenuation of its antiaromatic character upon protonation. The same arguments explain why the protonation at the NH position of **15** to yield **15NH1** is much more favorable than the protonation at the other two nitrogen atoms to yield **15NH2**. Similar to what has been discussed above for **9** and **10**, protonation of triazirine (**15**) is accompanied by a significant decrease of the pyramidalization at the nitrogen atom. In the neutral form (**15**) the H atom bends 74.1° out of the plane of the molecule, while in the protonated species (**15NH1**) this angle is reduced to 60.9°.

The effects observed upon Li<sup>+</sup> association are qualitatively similar to those described above for H<sup>+</sup> association but quantitatively much smaller. This is a reasonable result if one takes into account that the interaction between the neutrals and Li<sup>+</sup> is essentially electrostatic, and therefore no new N—Li covalent bonds are formed. Accordingly, Li<sup>+</sup> does not change the antiaromatic character of the system, but it decreases it a little by polarizing the nitrogen lone pair away from the π-bond.

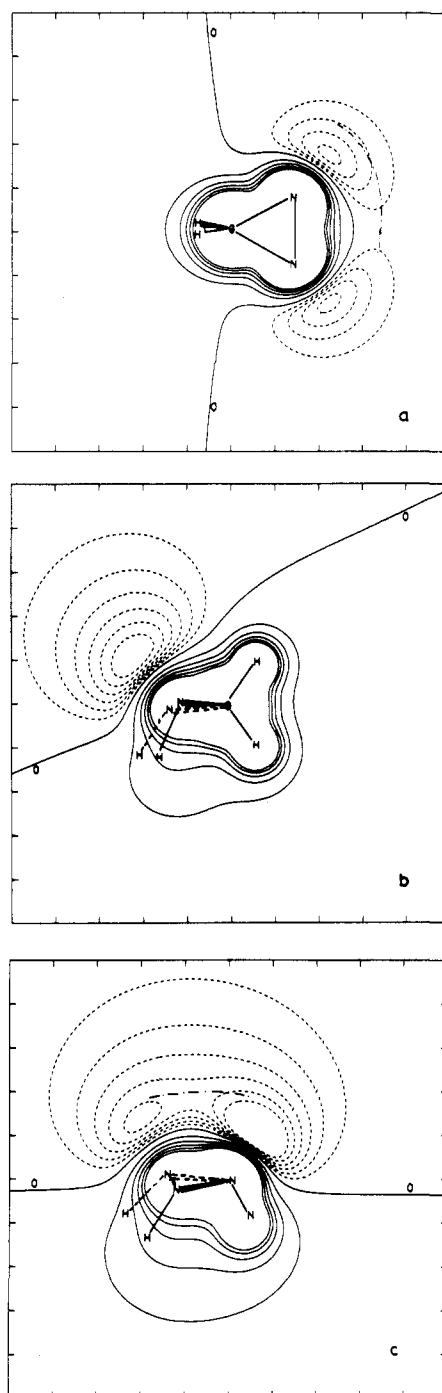
**Stability of Bridging Structures.** A comparison of Figures 1–3 and 5–7 clearly shows that structures in which the Li<sup>+</sup> bridges between two basic centers are only stable for the saturated series. To illustrate this point let us choose, as suitable model compounds diaziridine (**6cis**) and 1-diazirine (**9**). Since, as mentioned before, the Li<sup>+</sup>–neutral interactions are essentially electrostatic, the different behavior of saturated vs unsaturated systems should be reflected in their molecular electrostatic potentials, which have been plotted in Figure 11. It can be observed that the electrostatic potential around 1-diazirine presents two well-defined local minima, but more importantly, at distances typical of N—Li linkages (≈1.9 Å), there are no isopotential energy lines connecting both minima. Therefore, when Li<sup>+</sup> approaches this system it is trapped in one of these minima yielding a single coordinated Li<sup>+</sup> complex. The situation is completely different for diaziridine in its *cis* conformation. Due to the different spatial orientation of the two nitrogen lone pairs, the potential minima associated with them overlap, as is reflected by the existence of a local minimum in the plane that bisects the NCN bond angle (see Figure 11). On the other hand, when the Li<sup>+</sup> occupies this central position

(51) Winkelhofer, G.; Janoschek, R.; Fratev, F.; Spitznagel, G. W.; Chandrasekhar, J.; Schleyer, P.v.R. *J. Am. Chem. Soc.* **1985**, *107*, 332.





**Figure 10.** Contour map of the Laplacian of the charge density of (a) 9, (b) 9HN, (c) 10, and (d) 10HN1. Contour values are  $\pm 0.05$ ,  $\pm 0.25$ ,  $\pm 0.50$ ,  $\pm 0.75$ ,  $\pm 1.00$ ,  $\pm 1.25$ , and  $\pm 1.50$  au.



**Figure 11.** Contour map of the molecular electrostatic potential of (a) 1-diaziridine (9), (b) *cis*-diaziridine (6(*cis*)), and (c) *cis*-triaziridine (13(*cis*)). The former has been evaluated in the plane of the ring. The latter two have been evaluated in the plane that bisects the CNC and NNN angles, respectively. Positive values of the potential (0.05, 0.10, 0.15, 0.20, 0.20 au) are denoted by solid lines and negative values ( $-0.02$ ,  $-0.03$ ,  $-0.04$ ,  $-0.05$ ,  $-0.06$ ,  $-0.07$  au) by dashed lines. The -.-.- line shows the relative position of the  $\text{Li}^+$  cation within the complex.

it polarizes both basic centers,<sup>10</sup> which also contributes to stabilizing the complex. It must be observed however that the bridged conformation can only be formed if the two amino hydrogens are in a *cis* conformation. This implies a non-negligible energetic cost (about 6.1 kcal/mol, see Figure 2) which is counterbalanced by the enhanced interaction of  $\text{Li}^+$  with both basic centers. Actually, according to our calculations, the interactions to yield 6LNN is 13.5 kcal/mol more stabilizing than the interaction to yield 6LN.

A very interesting case is represented by form 13LPL where  $\text{Li}^+$  appears tricoordinated. It must be observed however that

this species is not the global minimum of the potential energy surface; instead it lies 3.8 kcal/mol above the minimum (**13LNN**). An inspection of the molecular electrostatic potential in the plane that bisects the N–N–N bond angle of the corresponding neutral (**13cis**) indicates that the global minimum is closer to the nitrogen atom which lies in that plane. However, at the typical N–Li<sup>+</sup> bond distances there are isopotential curves that extend over the three-membered ring, favoring the migration of the Li<sup>+</sup> toward the center of the ring where it is able to polarize the three nitrogen lone pairs. Since these interactions are always stabilizing, the **13LPL** conformation is the preferred one. It must be observed however that this coordination of Li<sup>+</sup> forces the three amino hydrogens to be on the same side of the molecular plane. This causes a significant destabilization of the system (about 11.2 kcal/mol) while the stability gain on going from the dicoordinated to the tricoordinated complex is only 7.4 kcal/mol (see Figure 3), which explains why the latter is 3.8 kcal/mol less stable than the former. Quite significantly, the relative stabilities of species **13LNN** and **13LPL** do not change appreciably when the theoretical estimations are obtained from MP2/6-31G\* optimized structures rather than from HF/6-31G\* optimized ones. Actually, at the higher level of accuracy considered in this work, the energy difference between these two systems reduces to 3.0 kcal/mol (see Table I).

#### 4. Conclusions

As has been found for other nitrogen bases,<sup>1,47,48</sup> the intrinsic basicity of saturated nitrogen-containing three-membered rings decreases as the number of basic centers increases. However, the same trend is not observed in the series of the unsaturated analogues, where triazirine is predicted to be much more basic than diazirine. This finding is related to the considerable decrease of the antiaromatic character of the former when it becomes protonated. The attenuation of the antiaromatic character of the protonated species with respect to the neutral one is reflected (a) in the topological characteristics of the Laplacians of their charge densities, since the nitrogen lone pair which interacts in

the neutral, in an antibonding manner, with the  $\pi$ -system in the protonated species is engaged in the new N–H  $\sigma$ -bond, and (b) in a significant decrease of the degree of nitrogen pyramidalization by protonation. This enhanced gas-phase basicity is observed in all of the antiaromatic compounds studied, explaining why for some of the species investigated the relative stability of the protonated form is reversed with respect to that of the neutral. When the reference acid is Li<sup>+</sup> this enhancement is considerably smaller because the interaction between the base and Li<sup>+</sup> is essentially electrostatic and the nitrogen lone pair does not truly participate in a new covalent bond but is simply polarized toward the attaching ion.

Saturated systems with two or more basic centers also display enhanced Li<sup>+</sup> binding energies due to the ability of Li<sup>+</sup> to bridge between two neighbor centers bearing pairs of electrons. The extra stability of these bridged structures is the consequence of two concomitant factors: (a) the overlap of the electrostatic potentials associated with each basic center and (b) the fact that at this intermediate position Li<sup>+</sup> is able to polarize simultaneously the charge distributions around both basic centers.

The first of these two effects is not present in the unsaturated three-membered rings due to the different spatial distribution of the nitrogen lone pairs, and therefore no bridged structures were found to be stable for unsaturated compounds.

The Li<sup>+</sup> derivative of triaziridine in which the alkali cation is tricoordinated is a minimum of the potential energy surface which lies about 3 kcal/mol above the global surface, in which the Li<sup>+</sup> bridges between two nitrogen atoms. This is due to the high energetic cost of forcing the three amino hydrogens to be on the same side of the molecular plane.

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**Supplementary Material Available:** Table of bond distances and angles (4 pages). Ordering information is given on any current masthead page.