

References and Notes

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A Theoretical Study of Proton Addition to Oxirane, Aziridine, and 2-Azirene

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Abstract: We have performed an ab initio study on the influence of protonation on the structure of some three-membered rings, using an extended basis set. According to our results no shortening of the C-C bond takes place upon protonation. The protonation energies calculated using the optimized geometries or those obtained from the electrostatic potential of the neutral molecules are in good agreement with experimental values.

I. Introduction

Protonation of organic molecules has been the subject of many experimental¹⁻¹⁰ and theoretical¹¹⁻¹⁹ studies in the last 7 years. Some factors involved in the protonation process (effects of hybridization,⁷ substituent effects,^{5b,8b,19} polarization¹⁵ and solvation^{8b} effects, etc.) have also been investigated.

In most calculations the geometry of the protonated species was determined by means of electrostatic potential maps.^{12,15,16,18} This simple treatment is qualitatively valid¹⁵ as a first-order prediction of protonation sites and affinities. It is, in general, accepted that the bare proton perturbs the molecule to a considerable extent. However, the effect of protonation on molecular geometry and electrostatic potentials (therefore on the protonation energies calculated) has not been well studied.

Three-membered rings have received particular attention mainly because their size make them very suitable for ab initio calculations.

Protonation is sometimes followed by ring opening leading to different recombination products.²⁰ Stohrer and Hoffmann¹⁴ postulated that protonation or other coordination of the heteroatom lone pair, in oxiranes and aziridines, strengthens the C-C bond. However, this theoretical conclusion is not in complete agreement with experimental results. The structure of aziridinium salts²¹ show no shortening of the C-C bond and when aziridine forms a coordination compound with borane, the shortening of the C-C bond (from 1.48 Å²² to 1.46 Å²³) is not significant.

In this paper we present the results of an ab initio study of the effects of protonation on the structure of oxirane and aziridine (the first member of each family) and 2-azirene. We also investigate the influence of geometry on the calculated electrostatic potentials and the proton affinity values obtained by computing the SCF energy with the proton placed at the position of the electrostatic potential minimum.

II. The Effect of Protonation on Geometry

To establish the effects of protonation on a given molecule it is necessary to know the structure of the neutral and protonated species. We use experimental geometries for neutral oxirane and aziridine. Since experimental information on the structure of 2-azirene and all the protonated species is not available we have chosen the SCF optimized geometry for those species. This procedure leads, in general, to geometries in good agreement with the experimental ones.²⁴

In order to save computation time the optimization process was divided into two parts: (a) full optimization with a (STO-3G) minimal basis set²⁵ and (b) full optimization of the geometry of neutral molecules using the final result of (a), as a starting point, and a split-valence (6-31G) basis set.²⁶ For the protonated species only those parameters directly involved in the possible shortening of the C-C bond (CXC angle and CX bonds) were optimized in this step.

Figure 1a contains the results of part (a) for aziridine²⁷ along with experimental values (in parentheses) determined by microwave spectroscopy.²² The agreement is excellent. We have found²⁷ that the dihedral angle between the CH₂ groups and the ring is 87°. This value is also found in the most recent microwave studies.²² These planes do not bisect the NCC angle, but divide it into two parts (see Figure 1c), $\alpha = 33.6^\circ$ and $\beta = 26.5^\circ$, again in good agreement with experimental values;²² $\alpha = 33.7^\circ$, $\beta = 26.2^\circ$.

Step (b) introduces no significant changes in the geometry obtained in (a). The most important one is the change in γ (Figure 1a), whose value is now 61°.

The results of Figure 1b correspond to the protonated molecule. It is clear that some changes have taken place. γ decreases by 9°, owing to the change in the nitrogen atom, when the second proton is bound to the lone pair.

The changes in the ring affect mainly the CNC angle that

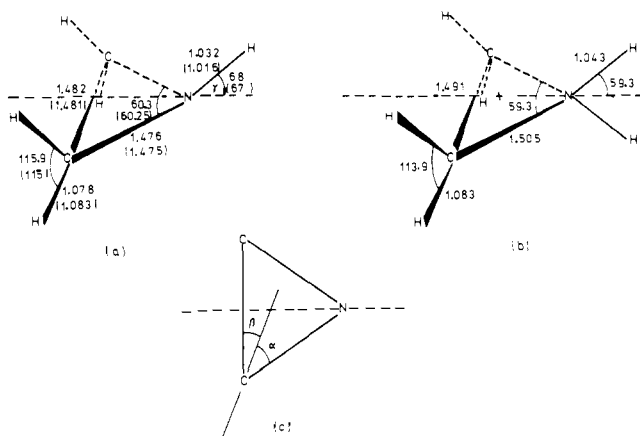


Figure 1. Optimized geometry for aziridine. (a) neutral molecule, (b) protonated molecule, (c) intersection of a CH₂ and the NCC planes.

Table I. 6-31G Overlap Populations of the C-C Bond

	A	AH ⁺
Aziridine	0.123	0.204
Oxirane	0.184	0.189
2-Azirene	0.203	0.388

closes by 1°, but as the CN bond increases 0.029 Å, the C-C bond is practically unchanged.

Geometry optimization with the 6-31G basis set does not change the CNC angle or the CN bond length in any appreciable way.

The STO-3G results for oxirane appear in Figure 2. The agreement with experimental values²⁸ (in parentheses) is very good for the neutral molecule (Figure 2a). The calculated values of α and β (see Figure 1c) are in this case 34.4 and 24.6°, respectively, in fairly good agreement with experimental determinations²⁸ ($\alpha = 37.2^\circ$ and $\beta = 22.6^\circ$).

The main change caused by the 6-31G basis is in the COC angle that comes down to 61.45° and the C-C bond distance that is now 1.466 Å.

In the protonated form (Figure 2b) the CH₂ planes are now "twisted" 2° with respect to the perpendicular plane (neutral molecule), owing to the presence of the proton bound to the oxygen atom. The COC angle closes 1.3° and the C-O bond lengths 0.047 Å and correspondingly the C-C bond increases only 0.019 Å. However, when using the 6-31G basis set the COC angle is 59.3° and C-C distance 1.464 Å, 0.002 Å shorter than in the neutral molecule.

The results obtained for 2-azirene are shown in Figure 3. Comparing Figures 3a and 3b it is clear that in this case the changes produced by the protonation are not significant and only γ varies by 1.5°.

With the 6-31G basis the results for neutral molecule are CNC = 50.2° and C-C distance = 1.271 Å and for the protonated form CNC = 49.7° and C-C distance = 1.269 Å (0.002 Å shorter).

In conclusion, the structural changes of oxiranes and aziridines due to protonation are not very important. The greater

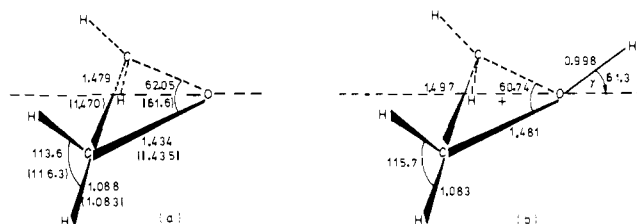


Figure 2. Optimized geometry for oxirane. (a) neutral molecule, (b) protonated molecule.

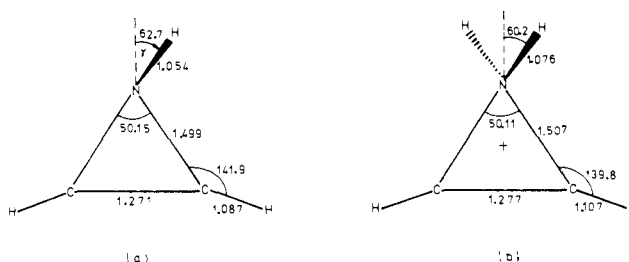


Figure 3. Optimized geometry for 2-azirene. (a) neutral molecule, (b) protonated molecule.

variations involve the parameters related to the heteroatom (angle γ , angle CXC, and CX bonds). In the three systems considered here, the CX bond is more labile than the C-C bond, which remains unchanged.

To complete our discussion, we present in Table I the (6-31G) overlap populations of the C-C bond for neutral and protonated species. The overlap population increases in going from the neutral to the protonated system, in agreement with other calculations,^{12,14} although that increase is very small for oxirane.²⁹

In the systems we studied we find no relationship between increase in the overlap population and shortening of the C-C bond. This result is not surprising if we consider that three-membered rings are very rigid structures.

III. Protonation Energies

In Table II we present the 6-13G total and protonation energies. According to these results aziridine and 2-azirene present a very similar basicity. Both are stronger bases than oxirane. The agreement between the calculated and experimental⁷ values is fairly good. Unfortunately we could not find in the literature any experimental value of PA for 2-azirene, but other calculations¹¹ indicate that its proton affinity is practically equal to that of aziridine.

The small values obtained by Ghio et al,¹⁵ (fifth column in Table II) when the proton is placed at the minimum of electrostatic potential corresponding to the neutral system are discussed in section IV.

IV. Molecular Electrostatic Potentials

In this section we present molecular electrostatic potentials corresponding to a symmetry plane perpendicular to the ring (Figures 4, 5, and 6, respectively), calculated using the 6-31G

Table II. 6-31G Energies and Proton Affinities

	A <i>E</i> , au	AH ⁺ <i>E</i> , au	PA, kcal/mol	PA ^a	PA ^b
Aziridine	-132.9638	-133.3424	237.6	220.1	186.5
Oxirane	-152.7825	-153.0903	193.2	185.0	141.0
2-Azirene	-131.6954	-132.0771	239.2		

^a Experimental values from ref 7. ^b Theoretical values from ref 15.

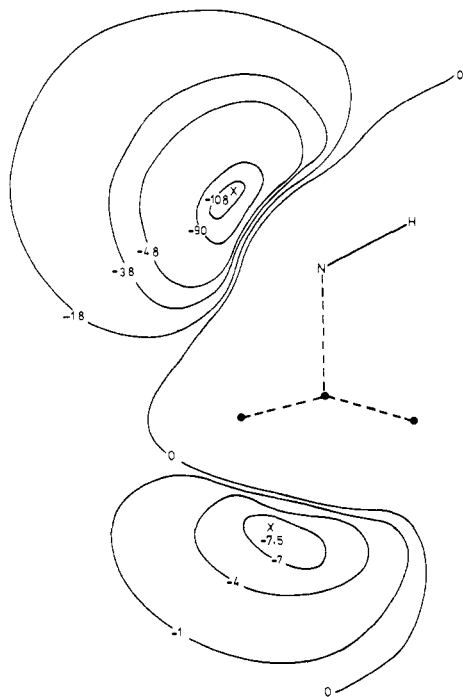


Figure 4. (6-31G) Electrostatic potential map for aziridine in the symmetry plane perpendicular to the ring.

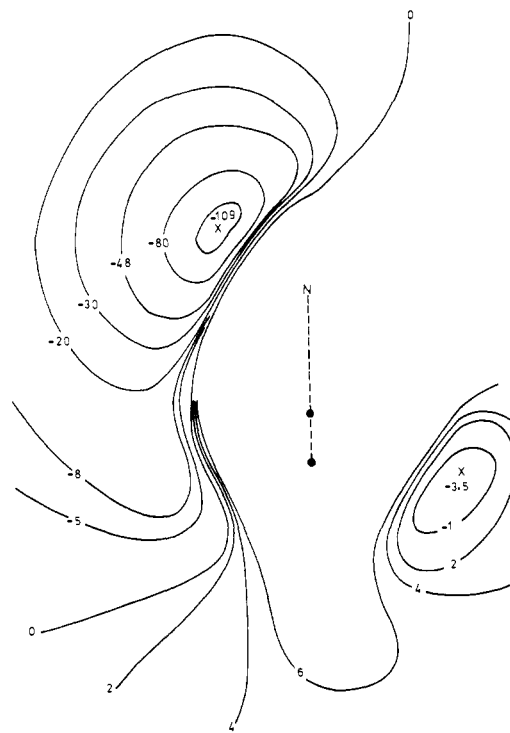


Figure 6. (6-31G) Electrostatic potential map for 2-azirene in the symmetry plane perpendicular to the ring.

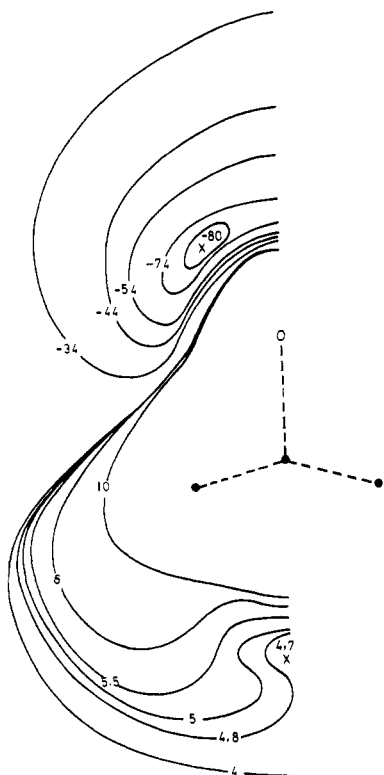


Figure 5. (6-31G) Electrostatic potential map for oxirane in the symmetry plane perpendicular to the ring.

results of section II and the equations from ref 30. The qualitative predictions on the basicity of the three molecules are in perfect agreement with those obtained in section III.

For aziridine, our minimum—due to the nitrogen lone pair—is deeper, and that corresponding to the carbon region is shallower and away from the CNC bisector than those reported in ref 15. This fact is, no doubt, a consequence of the “twisting” of the CH₂ groups.

Table III. Values of the Parameters γ and X-H Obtained from the Electrostatic Potential of the Neutral Molecules

	γ , deg	X-H, Å
Aziridine	54.5	1.14
Oxirane	45	1.12
2-Azirene	54.5	1.14

Table IV. 6-31G Energies and Proton Affinities Using the Geometry Obtained from the Electrostatic Potential of the Neutral Molecule

	AH ⁺ , au	PA, kcal/mol
Aziridine	-133.3303	229.0
Oxirane	-153.0721	182.0
2-Azirene	-132.0699	235.0

For oxirane our results predict a single protonation site, in the region of the oxygen lone pairs. In the carbon region we found a repulsive minimum justified by the net charge (-0.002 electrons) on the carbon atoms.

The coordinates of the potential minima are presented in Table III. The values of γ are always smaller and the bond lengths a little longer than those obtained optimizing the energy.

Protonation energies are calculated placing the proton on these heteroatom minima. The results obtained appear in Table IV.

All protonation energies are very close to those obtained with the optimized geometry, indicating that they are not much influenced by geometrical changes.

It has been established³¹ that minimal basis sets significantly overestimate protonation energies. We have found that extended basis give results a good agreement with experimental values. As the small values reported in ref 15 were obtained with a basis set intermediate between minimal basis and the extended basis we used, the differences must be due not only

to the basis set used, but perhaps to the geometry used for the neutral molecule, not indicated in the paper.

It seems that a split-valence basis set produces reliable information on this type of process because it is flexible enough to describe the charge transfer to the proton and lead to accurate values of the protonation energies, even when the electrostatic potential model is used.

Acknowledgments. All calculations were performed in the IBM 360/65 computer at the UAM/IBM Center (Madrid).

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Sources of Line Width in Boron-11 Nuclear Magnetic Resonance Spectra. Scalar Relaxation and Boron-Boron Coupling in B_4H_{10} and B_5H_9

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Abstract: The factors responsible for line broadening in ^{11}B NMR spectra have been investigated by analysis of the spectra of B_4H_{10} and B_5H_9 . It is demonstrated that unresolved boron-boron spin-spin coupling is not the sole source of extra broadness in ^{11}B spectra, as scalar relaxation and partially collapsed spin-spin multiplets also play a significant role in broadening ^{11}B NMR lines. The consequences of these conclusions in spectral simulation and in analysis of boron spectra are discussed.

A characteristic feature of ^{11}B NMR spectra is the broadness of the peaks, a quality which greatly impairs resolution and is particularly striking when compared to the much narrower lines observed in ^1H and ^{13}C NMR spectra. Although it might be tempting to attribute these line widths (usually 10–100 Hz) to the short relaxation time of the quadrupolar ^{11}B nuclei (spin $3/2$), this is not a satisfactory explanation since the first measurements of ^{11}B spin-lattice relaxation times demonstrated that the “natural line width” due to quadrupolar relaxation is generally less than 10 Hz.¹ Consequently, unresolved boron-boron coupling was proposed¹ as the source of the “extra” line width, and this suggestion was shown² to be correct for some resonances in selected boron hydrides via a technique which artificially narrows the broad ^{11}B resonance to reveal the unresolved boron-boron coupling. There are, however, two situations in which line narrowing will not expose the coupling. First, since the experimental lower limit of resolution of the line narrowing technique is about 10 Hz,² any coupling smaller than this will probably be unresolvable. The second case arises when, as a result of rapid relaxation of the

coupled nucleus, S, the nucleus under observation, I, “sees” only the average spin state of S and therefore appears as a singlet with no observable coupling (e.g., H-Cl coupling in CHCl_3 is not observed owing to rapid relaxation of ^{35}Cl and ^{37}Cl). A further complication is that under certain circumstances, the rapid relaxation of the spin S may act as a spin-spin relaxation mechanism for the spin I, thereby adding broadness to the peak (owing to shortening of T_2) which may be misinterpreted as unresolved coupling.

In an attempt to overcome the resolution problem, a recent study³ employed a line-shape analysis program to extract ^{11}B - ^{11}B coupling constants from experimental spectra, such as that of B_4H_{10} , that failed to yield to the line narrowing technique. The program in that work considered only unresolved coupling, neglecting collapsed coupling and scalar contributions to T_2 (and hence line width). The justification offered for this procedure was based on measurements of ^{10}B spin-lattice and spin-spin relaxation times in $^{11}\text{B}_4\text{H}_{10}$.

In this paper we examine the origin of line width in the ^{11}B spectra of B_4H_{10} and B_5H_9 and demonstrate that (1) scalar