

The Protonation of Three-Membered Ring Molecules: The *ab initio* SCF versus the Electrostatic Picture of the Proton Approach

Caterina Ghio and Jacopo Tomasi

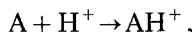
Laboratorio di Chimica Quantistica ed Energetica Molecolare del CNR, Via Risorgimento 35,
56100 Pisa, Italy

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The protonation processes for eight three-membered ring molecules have been investigated using the SCF LCAO MO method with Gaussian basis sets and the results are compared with those obtained at the first order approximation, i.e. the electrostatic approximation. The electrostatic results are linearly connected with the SCF ones and are sufficient to get an ordering of the protonation energies in different chemical sites and to obtain reliable representations of the proton approaching paths.

Key words: Protonation process – Three-membered ring

In the present paper it will be shown to what extent it is possible, in a given family of chemical compounds, to obtain from the wavefunction of molecule A only the essential information about the protonation process:



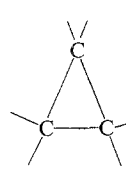
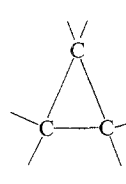
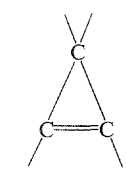
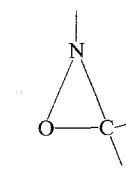
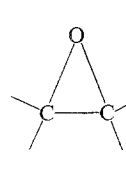
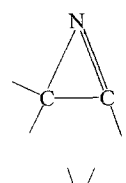
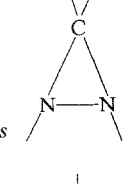
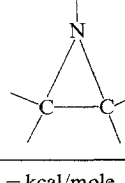
i.e. an ordering of the proton affinities (P.A.'s) along the family, and also more detailed information about the protonation paths and protonation sites.

Such a possibility arises from a first order treatment of the perturbation induced by the proton on molecule A. At the first order the interaction energy is given, at every stage of the proton approach process, by the value of the electrostatic potential $V(r)$ ¹ of molecule A, calculated at the point r where the proton is located. The electrostatic potential, already introduced [1], depends only on the charge distribution of the unperturbed A molecule, and from its spatial maps one can get the minima, i.e. the geometry of AH^+ and the value of the protonation energy, and also the favoured paths leading to the minima, i.e. the protonation channels.

Such a simple electrostatic picture is as valid as the first order treatment. It is evident that the relatively great perturbation produced by the proton cannot be sufficiently represented by its first order approximation: the $V(r)$ values are very far from the true P.A.'s. A typical example is given by NH_3 : its experimental P.A. is about 200 kcal/mole, while the $V(r)$ minimum, even with a good wavefunction, will hardly exceed 100 kcal/mole [2].

¹ Here-after we shall call $V(r)$ both the electrostatic potential and the interaction energy with $a + 1$ point charge placed at position r .

Table 1. SCF energies for neutral molecules and numerical values of protonation energies in different approximations

Molecule		Neutral molecule SCF energy ^a	Protonation site	Protonation energy ^b		
				ΔE (SCF)	V	ΔE (pol)
Cyclopropane		-116.46366	C-C	- 64.69	-15.13	- 28.484
Cyclopropene		-115.26787	C-C	- 62.239	-13.6	- 27.197
			C=C	- 76.930	-12.0	- 22.321
Oxaziridine		-168.09006	O	-134.883	-43.3	- 66.58
			N	-164.82	-65.1	- 89.34
Oxirane		-152.17361	O	-141.039	-44.8	- 70.705
1-Azirine		-131.16796	N	-163.787	-62.0	- 96.270
Diaziridine, <i>cis</i> Diaziridine, <i>trans</i>		-148.31973 -148.33048	N	-178.59	-75.5	-101.27
			N	-174.94	-66.8	- 91.15
Aziridine		-132.39751	N	-186.58	-76.9	-103.07
			C-C	- 56.522	-10.1	- 22.315

^a = a.u.^b = kcal/mole.

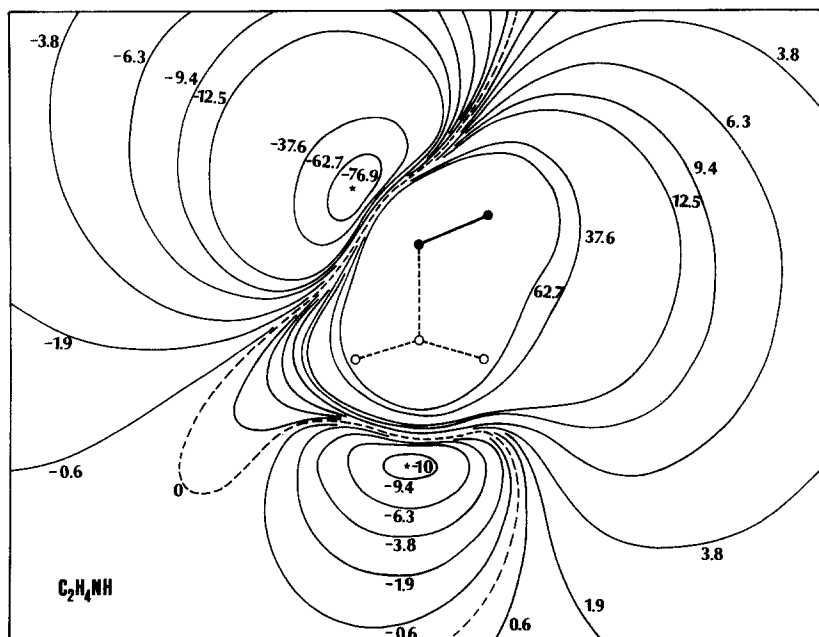


Fig. 1. Electrostatic potential energy map for the aziridine molecule in the plane perpendicular to the ring and containing the N-H nuclei. The energies are expressed in kcal/mole

Some effects not included in the first order treatment give in fact contributions to the interaction energy of the same order as the electrostatic one: polarization of the charge distribution of A and charge transfer to the proton. Other effects, such as exchange or overlap energy terms, which play an important role in other molecular interaction processes, give rise, in the present case, to contributions of lesser weight. Finally, the changes in geometry of A are surely important, but they depend extensively on the particular family of molecules considered; other comments on this point will be made later.

The main point is that effects like polarization, charge transfer and exchange, seem to be relatively constant at the $V(r)$ minima in a given chemical family and that also their variations when the distance of H^+ from the molecule is changed are not too different in passing from a molecule to another (of the same family).

The evidence of such empirical finding will be shown here by comparing the electrostatic potentials of some three-membered cyclic molecules (see Table 1) and the SCF protonation energies and protonation paths for the same molecules.

In all cases a gaussian basis set [3] ($(7s, 3p/3s)$ contracted to $[2s, 1p/1s]$) was employed. SCF calculations have been performed with the IBMOL programme. SCF wavefunctions employing either gaussian basis sets (GTO) or Slater-type orbitals (STO) have been previously calculated for all the neutral molecules here considered [4-27] as well as for some protonated species [11, 12, 28-30]. The

energies obtained in the present calculations (reported in Table 1 for neutral species) range intermediately in accuracy among the above quoted results.

For all the molecules of Table 1 the electrostatic potential $V(r)$ was calculated according to the procedure outlined in Ref. [31]. In every case the shape of $V(r)$ is similar to that already found with STO wavefunctions [19, 20]. This is a gratifying finding, because it confirms once more that qualitative interpretations of chemical behaviour relying on the electrostatic potential do not depend too heavily on the wavefunction employed. The shape is similar, but the absolute values are not the same. An example may suffice: Fig. 1 reports the $V(r)$ map for the aziridine molecule in a plane perpendicular to the ring and containing the N–H nuclei, the same map is reported in Fig. 8 of Ref. [19] for the STO wavefunction. The outstanding features, the minima corresponding to the N lone pair and the C–C bent bond, are nearly in the same position, but the values are different (-92.6 kcal/mole and -17.2 kcal/mole respectively, for the w.f. of Ref. [19]). A good linear relation between STO and gaussian values of the potential minima in the overall set of molecules was found. For the molecules here considered the most probable protonation sites correspond to the heteroatom lone pairs and to the C–C bonds of the rings, each of these sites being characterized by a minimum for the electrostatic potential in a neighbouring position of the outer molecular space.

The SCF wavefunctions of protonated species were calculated keeping the geometry of A unaltered and placing the additional proton at one of the potential minima. The effect of changes in geometry has been in this way completely neglected. Some considerations must be made on this subject. It is well known that for almost all triatomic rings protonation is followed by ring opening, and that in some cases different opening channels leading to different molecular reorganization processes are possible (see, e.g. Ref. [30]). On the other hand a ring is a somewhat rigid structure, where deformations from the equilibrium position are not easy. A partial optimization of geometry for the loosest groups (e.g. $-\text{NH}_2^+$) was however performed (the results are not reported here), but the corresponding changes in protonation energy have been found to be unessential with respect to the main topic of this paper. In conclusion, the difference $\Delta E = E(\text{AH}^+) - E(\text{A})$ cannot be considered as an approximation of the proton affinity, which should be made at the true energy minimum, but can be considered to represent the interaction energy at the end of the primary protonation process, which may be eventually followed by a molecular reorganization process. The values of ΔE (Table 1) are compared in Fig. 2 (curve *a*) with the corresponding $V(r)$ values. A linear relationship is evident (the correlation value for regression line *a* is 0.985). The electrostatic potential seems to be sufficient to get a prediction of the ordering of the various protonation energies.

As a second point in the present investigation it has been controlled how realistic is the first order description of the reaction channels. It is evident that the electrostatic approximation will be better at the former stages of the interaction process, when the proton is at large distances from the molecule A. Polarization, charge transfer and the other terms discarded in the first order treatment will have a different R -dependence with respect to the electrostatic one.

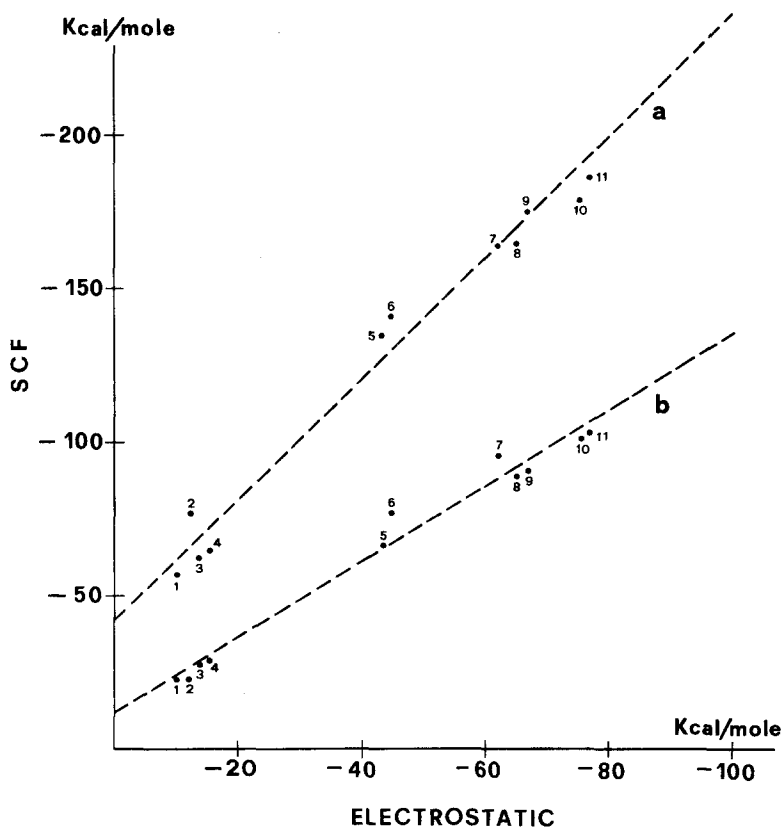


Fig. 2. Comparison between $V(r)$ values in the minima and ΔE . Curve *a* correlation with ΔE *ab initio* SCF; curve *b* correlation with ΔE electrostatic + polarization. The molecules considered and the protonation sites are respectively: 1 aziridine (C-C); 2 cyclopropene (C=C); 3 cyclopropene (C-C); 4 cyclopropane (C-C); 5 oxaziridine (O); 6 oxirane (O); 7 1-azirine (N); 8 oxaziridine (N); 9 *trans*-diaziridine (N); 10 *cis*-diaziridine (N); 11 aziridine (N)

Figure 3 depicts the situation for the favoured (on electrostatic grounds) approaching path of the proton to the N lone pair of aziridine (practically a straight line passing across the minimum of Fig. 1). Curve *a* gives the values of $V(r)$, curve *c* the SCF value of the interaction energy. At great distances the interaction is practically only electrostatic. As long as the proton approaches, the non-electrostatic terms become gradually of more weight, but it is important to point out that the minimum of the SCF curve lies at a R -value next to the electrostatic one (1.12 Å and 1.20 Å respectively).

When an approaching path is investigated, care must be taken to ensure the right convergency behaviour as well as to have sufficient flexibility in the basis to describe correctly the charge transfer to the proton. Some controls have been made, examining some characteristics of the wavefunction at large distances (populations, etc.) and repeating all the calculations without the constraint of

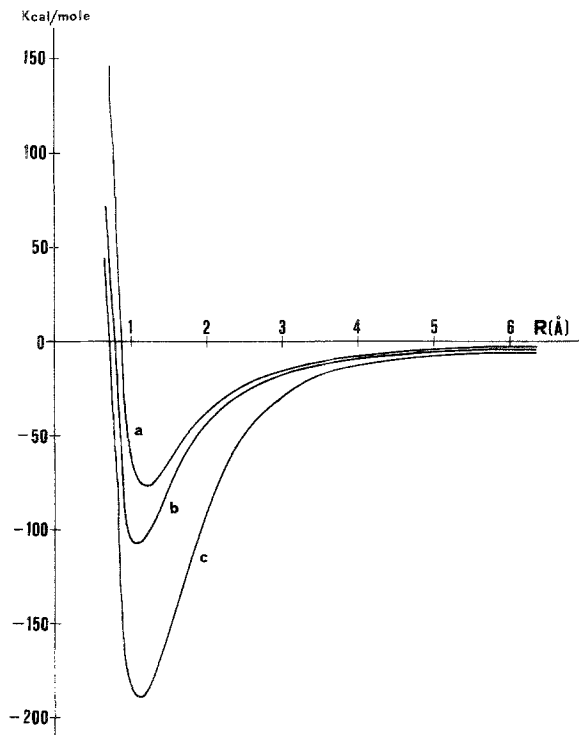


Fig. 3. The favoured approaching path of the proton to the N lone-pair of aziridine. Curve *a* gives the electrostatic term, curve *b* gives the electrostatic + polarization term, curve *c* gives the SCF value of the interaction energy

contraction on the three gaussian orbitals centered on the proton. The results are practically the same as those of Fig. 3 and are not reported here.

For obvious reasons of space, other comparisons between electrostatic and SCF previsions are not reported, but one may state that the example given in Fig. 3 is typical insofar as it concerns both other protonation sites and less favoured reaction paths.

A question concerning the practical application of simplified methods to calculate the energetics of the protonation process, may be posed at this point. Is it possible to add in a simple manner other terms to the first order ones and to improve the precision of the results? One of the first conceivable effects is the polarization one: it is the first in a logical sequence (the approaching proton is bare and produces a considerable field) and at the same time may be treated easily in a perturbative scheme.

We have calculated this effect, to all the orders, simply repeating the SCF calculations with the constraint that no basis functions are placed on the proton.

Some results are reported in Figs. 2 and 3. The straight line *b* of Fig. 2 shows that a linear relationship between V and the polarization is present. The

corresponding points relate the $V(r)$ values at the minima to the values $\Delta E_{\text{pol}} = W(\text{AH}^+) - E(\text{A})$ where $W(\text{AH}^+)$ is the SCF energy (with the proton placed at the V minimum) obtained with the above introduced constraint. ΔE_{pol} gives altogether the electrostatic and polarization terms as approximated by the minimal basis set employed in the present calculations.

Curve *b* of Fig. 3 reports the electrostatic plus polarization energy variation for the considered trajectory. The polarization terms (difference between curve *b* and curve *a*) are decidedly lower than the charge transfer and others (difference between curve *c* and curve *b*) and, in addition, the minimum of curve *b* differs from the SCF one by practically the same amount as the electrostatic curve. (For a similar analysis on CNDO wavefunctions see Ref. [32]).

Although the introduction of polarization, reduces the difference between approximate and SCF calculation, it does not improve the precision of the results substantially.

In conclusion linear relationships among electrostatic, polarization, and other terms have been found, at least near the end of the primary protonation process. The minima along the reaction paths are given reasonably well by the electrostatic approximation which on the whole gives a representation of the proton interaction hypersurface sufficient to permit the $V(r)$ maps to be viewed as a useful tool for qualitative comparisons on the proton reactivity in different sites of chemically related molecules.

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Dr. J. Tomasi
Laboratorio di Chimica
Quantistica ed Energetica
Molecolare del CNR
Via Risorgimento 35
I-56100 Pisa, Italy