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Molecular SCF Calculations for the Ground State of Some Three-Membered Ring Molecules: *Cis* and *Trans* Diaziridine, Oxaziridine and the Corresponding Imminium Ions

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LCAO SCF MO calculations with minimal basis sets of Slater-type orbitals are performed for some three-membered heterocycles. A reinterpretation of the resulting wavefunctions in terms of localized (exclusive) orbitals is employed to show the bending of the ring bonds and to measure the degree of transferability of some groups among chemically different yet related molecules. The electrostatic potentials produced in the neighbouring space by the nuclear and electronic charge distributions are evaluated and employed to indicate the molecular sites most likely subject to electrophilic attack. Some features of the electrostatic potential may be easily related to the entities employed in the usual intuitive description of chemical binding (lone pairs, etc.).

LCAO SCF-MO-Berechnungen mit minimalen Basissätzen von Slater-Orbitalen werden für einige dreigliedrige Heterozyklen durchgeführt. Eine Darstellung der resultierenden Wellenfunktionen mit Hilfe lokalisierter ("Exclusive") Orbitale wird benutzt, um die Biegung der Ringbindungen zu zeigen, und um den Grad der möglichen Übertragbarkeit einiger Gruppen zwischen chemisch verschiedenen, aber noch ähnlichen Molekülen zu erfassen. Die elektrostatischen Potentiale, die durch Kern- und Elektronenverteilung entstehen, werden dazu verwendet, diejenigen Stellen im Molekül anzugeben, die am meisten für einen elektrophilen Angriff zugänglich sind. Einige Eigenschaften des elektrostatischen Potentials können leicht solchen Größen zugeordnet werden, die bei der üblichen intuitiven Beschreibung der chemischen Bindung eine Rolle spielen (einsame Elektronenpaare usw.).

On a effectué des calculs de fonction d'onde, selon la méthode SCF MO LCAO, pour quelques molécules cycliques à trois atomes. On a trasformé les orbitales SCF en orbitales localisées pour mettre en évidence que les liaisons du cycle sont courbées vers l'extérieur et pour mesurer le degré de transferibilité des groupements chimiques.

On a calculé le potentiel électrostatique engendré par les charges électroniques et nucléaires de la molécule et on l'a employé pour mettre in évidence les parties de la molécule plus facilement disponibles aux attaques électrophiles.

1. Introduction and SCF Results

In a preceding paper [1] (hereafter called I) were reported some results of LCAO MO SCF calculations for a set of three-membered ring molecules. The discussion of the results has given particular emphasis to the characterization of the electronic description of the ground state and to extract from the corresponding wavefunctions some information on the chemical reactivity.

Such a discussion was made possible by the fairly large variety of functional groups treated in the set of molecules considered. In this paper, we extended the number of cases considered by taking into account also diaziridine, $CH_2(NH)_2$, and oxaziridine, CH_2NHO, which are formed by a different combination of the functional groups which were present in the set examined in I.

Both molecules were the subject of preceding studies with *ab initio* methods: diaziridine by Basch *et al.* [2], oxaziridine by Robb and Csizmadia [3] and by Lehn *et al.* [4]. In these three papers Gaussian orbitals were employed; the present treatment, to our knowledge, is the first using Slater-type basis sets.

As in paper I, we have employed a minimal basis set (best atom zetas [5]): some justifications for using such a type of basis are reported in I.

In the lack of experimental data, we have chosen for both molecules "reasonable" geometries. The internal parameters and the coordinates in a suitable reference system are reported in Table 1; the coordinates will be useful later.

Both *trans* and *cis* conformations for diaziridine and also the protonated species, $CN_2H_5^+$ and $CNOH_4^+$, were considered.Table 1 reports the geometry for the *trans* $CH_2(NH)_2$; in our calculations the *cis* conformer is obtained by changing the sign of the y coordinate of the H attached to N^2 and the ion by appending a second proton to N^2. Also the extra proton of $CNOH_4^+$ is placed in a symmetrical position with respect to the proton already present in the NH group.

Table 2 reports the total (E_{tot}), electronic (E_{el}), kinetic (T) and orbital (ε) energies for all the species considered. The *trans* conformation of diazirine results in a more stable conformation than the *cis* ($\Delta E = 7.1$ Kcal/mole). The changes in the order of orbital energy levels between the two conformations is more apparent than real and is due in part to a change of orbital labels since the symmetry group has changed. The proton affinities we found are 234.3 Kcal/mole for $CH_2(NH)_2$ and 220.6 Kcal/mole for CH_2ONH. A comparison with experimental

Table 1. *Nuclear coordinates*[a] *and geometry*

Atom	x	y	z		
Diaziridine					
N^1	0	0	−1.371010	R(N–N) = 1.451 Å	< HCH = 116°18′
H^4	−0.376488	1.839740	−2.011923	R(C–N) = 1.490 Å	< NCN = 58°16′30″
N^2	0	0	1.371010	R(N–H) = 1.050 Å	< HNN = 149°34′
H^7	−0.376488	−1.839740	2.011923	R(C–H) = 1.083 Å	< (NH, NNC) = 68°
C^3	2.459393	0	0		
H^8	3.539381	1.738438	0		
H^9	3.539381	1.738438	0		
Oxaziridine					
O^1	0	0	−1.149514	R(C–O) = 1.435 Å	< HCH = 116°18′
C^2	0	0	1.562270	R(C–N) = 1.490 Å	< OCN = 56°18′
H^4	−0.509517	1.738438	2.514517	R(O–N) = 1.381 Å	< NOC = 63°52′
H^5	−0.509517	−1.738438	2.514517	R(N–H) = 1.050 Å	< (HCH, CN) = 151°51′
N^3	2.342540	0	0	R(C–H) = 1.083 Å	< HNO = 149°24′
H^6	3.083580	−1.839740	−0.058020		< (NH, CNO) = 68°

[a] Atomic units.

values is at present not possible, but the present ones seem of the right order of magnitude.

A comparison of mean values of observables with experiment not being possible, detailed results are not reported here. Table 3 reports only the values of the dipole and quadrupole moments, together with results of other calculations. The non-invariant moments are referred to the center of mass.

Table 2. *Energy values and orbital energies*[a]

	$CH_2(NH)_2$	$CH_2(NH)_2$	$CH_2NHNH_2^+$	CH_2ONH	$CH_2ONH_2^+$
	trans	*cis*			
E_{tot}	−148.5708	−148.5594	−148.9328	−168.2672	−168.6187
E_{el}	−223.8458	−223.8996	−231.9939	−243.3438	−251.5518
T	147.2965	147.2927	146.8397	167.0119	166.4526
$-2T/V$	0.9957	0.9957	0.9929	0.9963	0.9935
ε_1	−15.6458 (1a)	−15.6546 (1a)	−16.0832 (1a)	−20.6873 (1a)	−21.0431 (1a)
ε_2	−15.6457 (1b)	−15.6546 (1b)	−15.9757 (2a)	−15.6837 (2a)	−16.1245 (2a)
ε_3	−11.3813 (2a)	−11.3858 (2a)	−11.6986 (3a)	−11.4164 (3a)	−11.7491 (3a)
ε_4	− 1.3217 (3a)	− 1.3336 (3a)	− 1.6719 (4a)	− 1.4760 (4a)	− 1.8183 (4a)
ε_5	− 0.9542 (2b)	− 0.9544 (2b)	− 1.3025 (5a)	− 1.0130 (5a)	− 1.3874 (5a)
ε_6	− 0.8685 (4a)	− 0.8771 (4a)	− 1.1654 (6a)	− 0.8999 (6a)	− 1.2049 (6a)
ε_7	− 0.6641 (3b)	− 0.7094 (5a)	− 1.0732 (7a)	− 0.7064 (7a)	− 1.1059 (1b)
ε_8	− 0.6353 (5a)	− 0.6052 (6a)	− 0.9512 (8a)	− 0.6290 (8a)	− 0.9652 (7a)
ε_9	− 0.5116 (4b)	− 0.5005 (7a)	− 0.8599 (9a)	− 0.5500 (9a)	− 0.8855 (2b)
ε_{10}	− 0.4922 (6a)	− 0.4838 (3b)	− 0.8269 (10a)	− 0.4837 (10a)	− 0.8732 (8a)
ε_{11}	− 0.3929 (5b)	− 0.4340 (8a)	− 0.7708 (11a)	− 0.4397 (11a)	− 0.7753 (9a)
ε_{12}	− 0.3590 (7a)	− 0.3457 (4b)	− 0.6768 (12a)	− 0.3702 (12a)	− 0.7411 (3b)
Symmetry	C_s	C_2	C_1	C_1	C_s

[a] Atomic units.

Table 3. *Dipole and quadrupole moments*[a]

	$CH_2(NH)_2$	$CH_2(NH)_2$	CH_2ONH
	trans	*cis*	
μ_x	0.674	0.781	−0.052
μ_y	0	3.362	1.733
μ_z	0	0	1.208
μ_{tot}	0.67[b]	3.45	2.11[c]
θ_{xx}	−0.280	−0.034	−1.429
θ_{xy}	0	−3.613	3.359
θ_{xz}	0	3.529	−4.691
θ_{yy}	3.181	2.807	1.818
θ_{yz}	−5.878	0	−0.410
θ_{zz}	−2.901	−2.773	−0.389

[a] Dipole moments in Debye and quadrupole moments in Buckinghams. The non invariant moments are referred to the mass center point.

[b] According to Ref. [2], $\mu_{tot} = 1.41\ D$.

[c] According to Ref. [4], $\mu_{tot} = 3.37\ D$.

2. A Description of the Electronic Structure

As in paper I, this section relies principally on the reformulation of the SCF density function in terms of localized orbitals (LO). The objection that such an analysis is not founded on physical observables, may be tempered by recalling the correspondence found in I between the exclusive orbital description and the picture obtained from the electrostatic molecular potential which is a physical observable. Furthermore, this analysis has as its purpose to compare variations of local properties among chemically related molecules and is strengthened by the *intrinsic* method adopted for the localization, which does not require *ad hoc* stipulations.

For details on the localization method and on the definition of the numerical quantities employed in this section, we refer the reader to preceding papers [1, 6, 7].

The first column of Table 4 reports a measure of the degree of localization, which is not unlike that already found in other molecules [6, 7] and in paper I. Columns 2 and 3 report the modulus of the parallel ($\mu_{\|}$) and perpendicular ($\mu_{\perp}$) components of the orbital dipole moment (O.D.M.). More detailed information on the direction of the ODM's may be obtained from the charge centroids reported in columns labeled $\langle x \rangle$, $\langle y \rangle$, $\langle z \rangle$.

The ODM is defined as the resulting moment of a charge system consisting of two positive point charges placed on the nuclei pertinent to the considered bond or lone pair, and the negative charge accounted for by the corresponding LO. For the bonds, the direction of the parallel component is defined by the line joining together the two nuclei; for lone pairs only the absolute value of the ODM is given. This partitioning of the total dipole moment is quite arbitrary and it may be of some interest to recall the discussion about the sign and value of the C–H bond moment. Recently Rothemberg [8] and Pritchard and Kern [9] made an analysis of dipole moments obtained through *ab initio* calculations. However, their respective definitions of the C–H bond moment differ, Pritchard and Kern having chosen the presently defined convention. In our opinion it is only a matter of convenience and, at least for our purposes, the present definition seems adeguate.

The $\mu_{\perp}$ values give a measure of the bending of the ring bonds, the situation being similar to that found in paper I. The parallel component is related to the electronegativity difference between the two atoms involved and hence, the trend of the ODM may be compared with the atomic gross populations reported in Table 5. The $\mu_{\|}$ values of the protonated species show that the protonation should produce a heterolytic ring opening in both molecules through the C–N bonds (compare the $\mu_{\|}$ values of $b_{\mathrm{C-N}}$ in neutral and protonated species; for diaziridine $\Delta\mu_{\|}\,(\mathrm{CN}) = 1.05\,D$ and for oxaziridine $\Delta\mu_{\|}\,(\mathrm{CN}) = 1.11\,D$).

The C–H bond orbitals may be employed to ascertain the degree of transferability of the LO's. The ODM values are nearly equal for neutral species (mean value, comprising also the C–H bonds of paper I: 1.83 D) and for cations (mean value: 1.57 D). This last value is in accord with the charge transferred in the protonation process which may be obtained from the data of Table 5 (remember that the polarity is $\mathrm{C^{+}{-}H^{-}}$). On the other hand, the orbital kinetic energies (T_i),

Table 4. *Summary of numerical quantities relative to localized orbitals*[a]

Molecule	Orbital[b]	$2(1-\langle\lambda\|\mu\rangle)$	$\mu_{\parallel}$	$\mu_{\perp}$	$\langle x\rangle$	$\langle y\rangle$	$\langle z\rangle$	T_i	E_i	E_i°
$CH_2(NH)_2$ *cis*	$i\mathrm{N}^1$	0.0001	—	—	0.0005	0.0010	−1.3703	22.7153	−45.9224	−44.5979
	$i\mathrm{C}$	0.0008	—	—	2.4591	0.0000	0.0000	16.2553	−35.7540	−32.3030
	$b\mathrm{CN}^1$	0.0191	0.41	1.83	1.3348	0.0038	−1.0385	1.3231	−11.6686	−13.8080
	$b\mathrm{N}^1\mathrm{N}^2$	0.0253	—	1.32	−0.2593	0.0221	0.0000	1.5474	−12.3911	−15.8243
	$b\mathrm{N}^1\mathrm{H}^4$	0.0282	1.09	0.04	−0.2264	1.1225	−1.7541	1.2298	−10.3835	− 9.3069
	$b\mathrm{CH}^8$	0.0258	1.92	0.01	3.1992	1.1887	0.0000	0.8983	− 9.2279	− 7.1146
	$b\mathrm{CH}^9$	0.0226	1.83	0.04	3.1958	−1.1703	0.0000	0.9042	− 9.1506	− 7.1498
	$l\mathrm{N}^1$	0.0565	3.47	—	−0.2126	−0.5584	−1.7021	1.7522	−10.7135	− 9.1096
$CH_2(NH)_2$ *trans*	$i\mathrm{N}^1$	0.0001	—	—	0.0005	0.0010	−1.3703	22.7147	−45.9126	−44.5972
	$i\mathrm{C}$	0.0008	—	—	2.4591	0.0000	0.0000	16.2551	−35.7494	−32.3030
	$b\mathrm{CN}^1$	0.0193	0.39	1.83	1.3369	0.0096	−1.0374	1.3229	−11.6610	−13.8034
	$b\mathrm{N}^1\mathrm{N}^2$	0.0216	—	1.24	−0.2574	0.0000	0.0000	1.5421	−12.3813	−15.8241
	$b\mathrm{N}^1\mathrm{H}^4$	0.0275	1.03	0.06	−0.2278	1.1108	−1.7449	1.2412	−10.3537	− 9.3420
	$b\mathrm{CH}$	0.0241	1.88	0.03	3.1992	1.1808	0.0061	0.9008	− 9.1822	− 7.1293
	$l\mathrm{N}^1$	0.0556	3.47	—	−0.2054	−0.5606	−1.7040	1.7458	−10.7479	− 9.1180
$CH_2NHNH_2^+$	$i\mathrm{N}^1$	0.0001	—	—	0.0005	0.0010	−1.3705	22.7253	−46.5006	−44.5962
	$i\mathrm{N}^2$	0.0005	—	—	0.0002	0.0000	1.3707	22.5678	−46.8888	−44.6399
	$i\mathrm{C}$	0.0008	—	—	2.4590	0.0000	0.0001	16.2631	−36.3206	−32.3022
	$b\mathrm{CN}^1$	0.0288	0.56	1.82	1.3077	−0.0014	−1.0524	1.3506	−12.2296	−13.8364
	$b\mathrm{CN}^2$	0.0178	1.44	1.73	1.1482	−0.0023	1.1215	1.3985	−12.5376	−14.0184
	$b\mathrm{N}^1\mathrm{N}^2$	0.0197	0.93	1.27	−0.2495	0.0177	0.1825	1.5511	−13.1197	−15.8142
	$b\mathrm{N}^1\mathrm{H}^4$	0.0322	0.78	0.13	−0.2282	1.0687	−1.7184	1.2863	−11.0317	− 9.4841
	$b\mathrm{N}^2\mathrm{H}^6$	0.0313	0.49	0.43	−0.2504	0.9775	1.7873	1.3262	−11.2507	− 9.6211
	$b\mathrm{N}^2\mathrm{H}^7$	0.0314	0.40	0.44	−0.2561	−0.9611	1.7791	1.3429	−11.2350	− 9.6655
	$b\mathrm{CH}^8$	0.0260	1.61	0.15	3.1532	1.1477	0.0238	0.9248	− 9.8133	− 7.2259
	$b\mathrm{CH}^9$	0.0244	1.56	0.13	3.1514	−1.1367	0.0219	0.9284	− 9.7742	− 7.2442
	$l\mathrm{N}^1$	0.0588	3.48	—	−0.2417	−0.5777	−1.6474	1.7546	−11.2921	− 9.1197

Table 4 (continued)

Molecule	Orbital[b]	$2(1-\langle\lambda\|\mu\rangle)$	$\mu_\parallel$	$\mu_\perp$	$\langle x\rangle$	$\langle y\rangle$	$\langle z\rangle$	T_i	E_i	E_i°
CH_2ONH	*i*O	0.0000	—	—	0.0001	0.0000	−1.1493	30.3160	−58.0437	−58.8254
	*i*C	0.0008	—	—	0.0001	0.0000	1.5619	16.2547	−35.9948	−32.3034
	*i*N	0.0001	—	—	2.3417	0.0010	0.0001	22.7183	−46.2058	−44.5981
	*b*OC	0.0121	0.90	1.55	−0.3054	−0.0012	0.0293	1.6045	−12.6706	−16.1410
	*b*CN	0.0163	0.39	1.96	1.4485	0.0050	1.0593	1.3205	−11.8250	−13.7384
	*b*NO	0.0167	0.47	1.05	1.1783	0.0119	−0.8013	1.8088	−13.4195	−18.2286
	*b*CH^4	0.0255	1.89	0.06	−0.3571	1.1856	2.2037	0.9070	− 9.3389	− 7.1155
	*b*CH^5	0.0239	1.84	0.04	−0.3523	−1.1751	2.2068	0.9091	− 9.2989	− 7.1361
	*b*NH^6	0.0277	1.07	0.07	2.7798	1.1207	−0.0415	1.2450	−10.5502	− 9.3176
	*l*O	0.0405	2.95	—	−0.1211	0.5331	−1.3429	2.3270	−12.5478	−12.1739
	*l*O	0.0406	2.94	—	−0.1098	−0.5348	−1.3396	2.3298	−12.5159	−12.1625
	*l*N	0.0561	3.53	—	2.7385	−0.5673	−0.0499	1.7652	−10.9325	− 9.1036
$CH_2ONH_2^+$	*i*O	0.0000	—	—	0.0000	0.0000	−1.1494	30.3329	−58.6646	−58.8232
	*i*C	0.0007	—	—	0.0002	0.0000	1.5619	16.2641	−36.5810	−32.3025
	*i*N	0.0005	—	—	2.3422	0.0000	−0.0001	22.5721	−47.1836	−44.6392
	*b*OC	0.0211	1.20	1.53	−0.3021	0.0000	−0.0289	1.6636	−13.3199	−16.2720
	*b*CN	0.0157	1.50	1.87	1.6213	0.0000	0.9225	1.3997	−12.7154	−13.9594
	*b*NO	0.0135	0.30	1.04	1.3146	0.0000	−0.7318	1.7490	−14.0385	−18.0169
	*b*CH^4	0.0257	1.56	0.12	−0.3127	1.1405	2.1719	0.9360	− 9.9495	− 7.2371
	*b*NH^6	0.0318	0.43	0.43	2.8192	0.9666	−0.0551	1.3482	−11.4451	− 9.6498
	*l*O	0.0448	2.96	—	−0.0774	0.5410	−1.3480	2.3382	−13.1297	−12.1801

[a] Columns contain: 2, orbital identification, 3 mean-square deviation between the localized orbital and its relevant (normalized) part; 4–5 parallel and perpendicular components of the ODM; 6–8 coordinates of the charge centers; 9, kinetic energy; 10 electronic energy; 11, "proper" electronic energy. All the quantities are expressed in atomic units, with exception of the ODM's which are in Debyes.

[b] *i* stands for *k* inner shell, *l* for lone pair and *b* for bond orbital.

Table 5. *Gross populations*[a]

Molecule	Atom	Gross pop.	Molecule	Atom	Gross pop.
trans $CH_2(NH)_2$	N	7.2596	$CH_2NHNH_2^+$	N^1	7.1443
	$H^{4,7}$	0.7557		H^4	0.6820
	C	6.3137		N^2	7.2944
	$H^{8,9}$	0.8279		H^6	0.6075
cis $CH_2(NH)_2$	N	7.2430		H^7	0.5827
	$H^{4,6}$	0.7756		C^3	6.2213
	C	6.3126		H^8	0.7420
	H^8	0.8394		H^9	0.7258
	H^9	0.8108			
CH_2ONH	O	8.1148	$CH_2ONH_2^+$	O	7.9832
	C	6.2713		C	6.1560
	H^4	0.8268		H	0.7196
	H^5	0.8118		N	7.2550
	N	7.2128		H	0.5834
	H^6	0.7625			

[a] Numerations of the atoms according to Table 1.

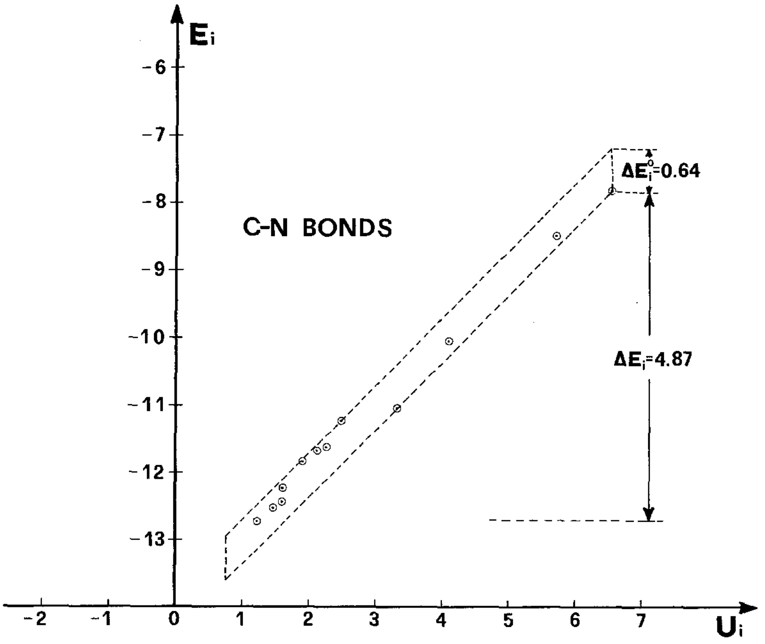

Fig. 1. Variations of E_i and U_i for C–N bonds (a.u.). From left to right the values refer to: oxaziridinium, diaziridinium (NH_2), diaziridinium (NH), aziridinium, oxaziridine, diaziridine (*cis* and *trans* values coincident in the drawing), aziridine, diazirine, isocyanic acid, cyanate ion, hydrocyanic acid, cyanide ion

which are particularly sensitive to the degree of hybridisation show that the protonation does not affect markedly the shape of the C–H orbital.

Form an energetic point of view, the columns of Table 4 headed E_i and E_i° show that the variations in the electronic energy pertinent to the C–H are due principally to variations in the interaction energy with the other parts of the molecule. The values of the present paper fit perfectly into the range found in I (see, in this Ref., Fig. 7); the variation of the E_i° values is less than 7% of the corresponding E_i variation.

The results for C–N bond orbitals may be supplemented by those of Ref. [6] with regard to a completely different set of chemical compounds (pseudohalide acids and their anions). The C–N bond orbitals of these last compounds refer to single components of multiple bonds and experience completely different molecular fields. The interaction energy of such an orbital with the remainder of the molecule ($U_i = E_i - E_i^\circ$) is decidedly different from that of a single bond C–N orbital. In spite of this difference in environment the "internal" energies (E_i°) of such types of localized orbitals remain nearly constant.

The degree of constancy may be observed in Fig. 1, where the E_i values of C–N LO's are reported *versus* their U_i values. The constancy of E_i° should require a rectilinear plot with unit slope, while actually one finds a maximum variation of the corresponding E_i° values of 0.73 a.u., i.e. nearly 13% of the corresponding E_i variation (4.87 a.u.). As stated above, the U_i values for the cyclic compounds span the range 1–2.5 a.u. while for the pseudohalide acid set the range is 3–6.5 a.u.

3. The Electrostatic Molecular Potentials

As was shown in I, some useful information may be obtained by the values of the electrostatic potential, $V(\boldsymbol{x}_i)$ produced in the neighbouring space by the electronic and nuclear charges of the molecule. $V(\boldsymbol{x}_i)$ is a physical observable, whose value for every point of the space, may be easily obtained once the first order density function $\varrho(\boldsymbol{x}_1)$ is known.

$$V(x_i) = \int d\tau_1 \left[\varrho(\boldsymbol{x}_1) - \sum_{\alpha} Z_\alpha \delta(\boldsymbol{x}_1 - \boldsymbol{x}_\alpha)\right] \cdot \frac{1}{|\boldsymbol{x}_1 - \boldsymbol{x}_i|}$$

nucl

where $\sum_{\alpha} Z_\alpha \delta(\boldsymbol{x}_1 - \boldsymbol{x}_\alpha)$ is the distribution of nuclear charges.

From the $V(\boldsymbol{x}_i)$ function one can immediately arrive at the electrostatic interaction energy $W(\boldsymbol{x}_i) = q \cdot V(\boldsymbol{x}_i)$ between the molecular charge distribution, considered rigid, and an external point charge q. The electrostatic energy $W(\boldsymbol{x}_i)$ is the first order value of the perturbation energy of the molecule when a point charge q is placed at the point $\boldsymbol{x}_i$ of the "outer" space.

Some maps of the electrostatic energy for unit point charge are displaced in Figs. 2–5 to show the electrostatic potential may be used as an auxiliary tool in the analysis of chemical properties of the considered molecule. Fig. 2 reports how the map for the ring plane of *trans*-diaziridine. The regions most subject to electrophilic attack surround the two nitrogen atoms. The minimum of potential energy is not in the ring plane, this being due to the out of plane position of the corresponding hydrogens and to hybridisation of the nitrogen atomic orbitals. In fact, the shape of the electrostatic potentials shows a clear correspondence between an empirical

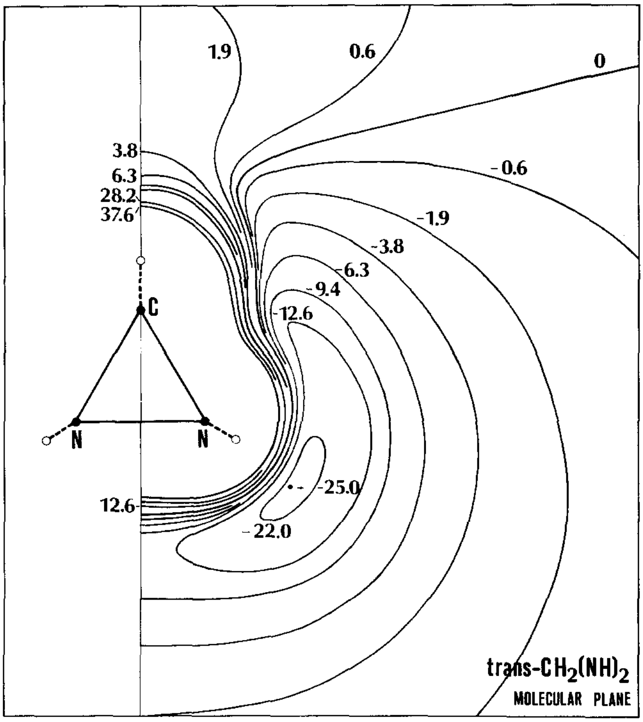

Fig. 2. Electrostatic potential energy map for the ring plane of *trans*-diaziridine (energies in Kcal/mole)

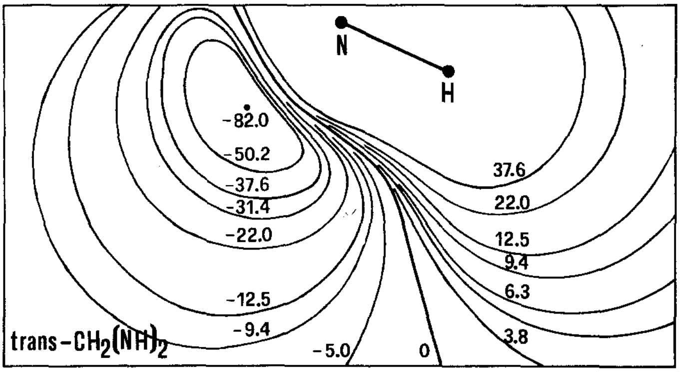

Fig. 3. Electrostatic potential energy map for the plane containing the N–H bond of *trans*-diaziridine and perpendicular to the ring plane

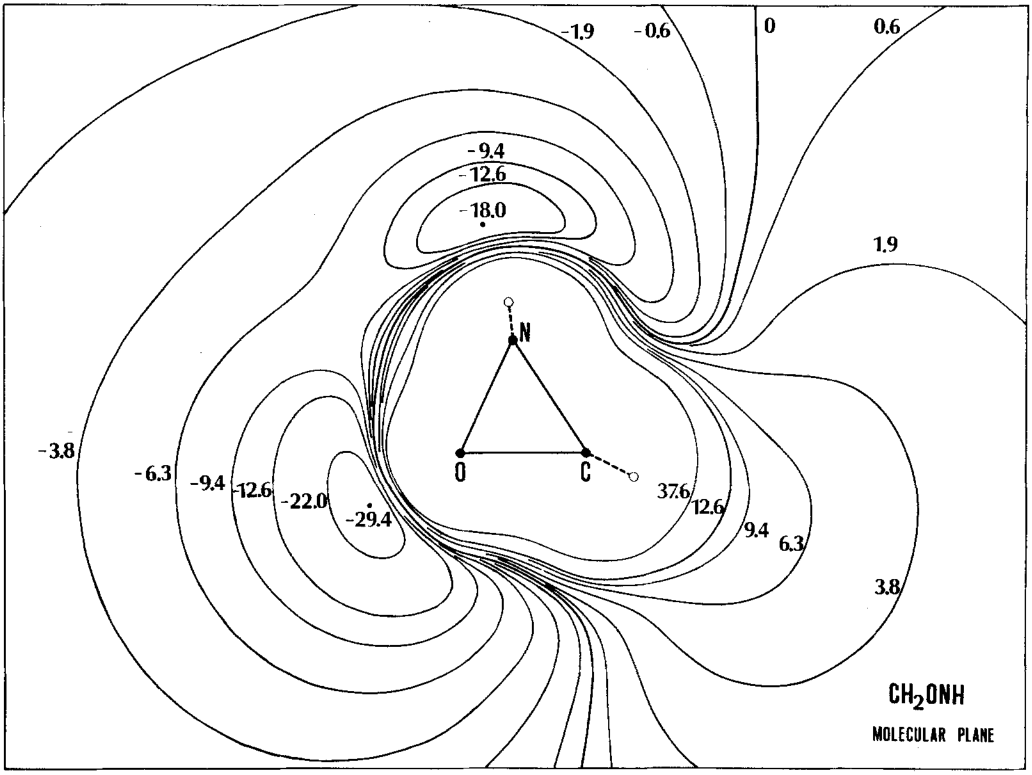

Fig. 4. Electrostatic potential energy map for the ring plane of oxaziridine

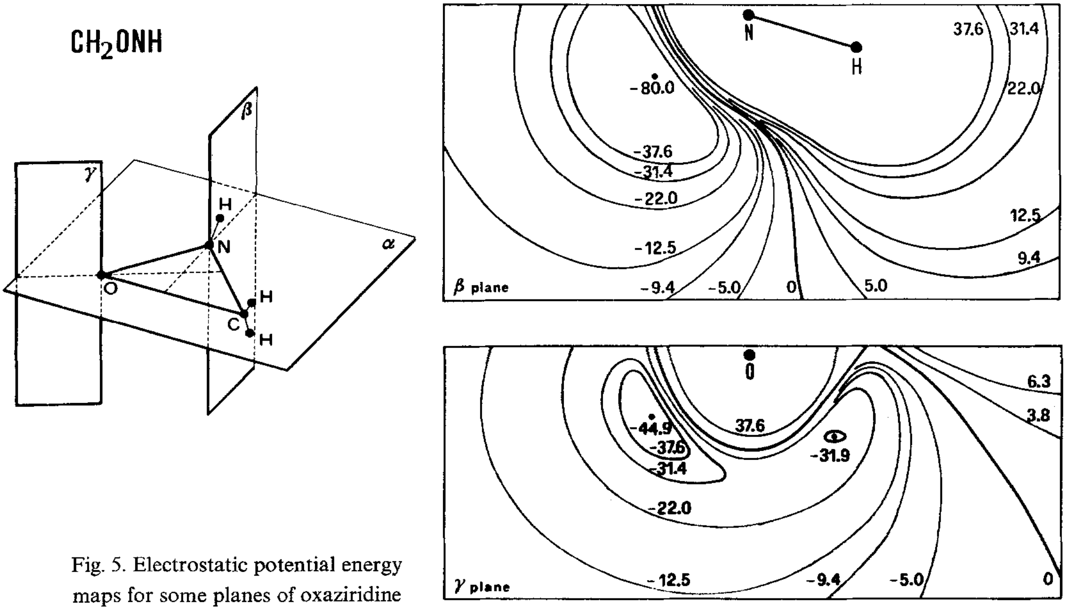

Fig. 5. Electrostatic potential energy maps for some planes of oxaziridine

concept like "*atomic hybridisation*" and the values of a physical observable as $V(\boldsymbol{x}_i)$. In the case of *trans*-diaziridine this fact may be evidenced through Fig. 3 which refers to a plane perpendicular to the ring plane containing the N and H nuclei.

The position of the minimum of $W(\boldsymbol{x}_i)$ (-82.0 Kcal/mole) may be related to the direct influence of the nitrogen lone pair. The *cis*-diaziridine maps are not reported but the main difference with respect to the *trans* case is in the value of the minimum: -92.2 Kcal/mole (the location of the minimum is the same as in the *trans* conformer). This difference in the value of the two minima ($\Delta V_{\min} = 9.8$ Kcal/mole) may be compared with the difference in the proton affinity of the two conformers ($\Delta(P.A.) = 7.1$ Kcal/mole). According to what has been previously said in this section, the $\Delta V_{\min}$ value can in fact be considered as a first order value for $\Delta(P.A.)$.

The map of $W(\boldsymbol{x}_i)$ for the ring plane of oxaziridine is reported in Fig. 4. In this case, again the CH_2 group is surrounded by a zone of positive $W(\boldsymbol{x}_i)$ values while the two heteroatoms are surrounded by deep minima which are more exactly identified in Fig. 5. In this figure the β plane is to be compared with Fig. 3. The two minima are nearly in the same direction and the difference in their absolute value may be related in the difference in the protonation energies reported above. The γ plane contains two minima; the correspondence with the two lone pairs of oxygen is clear (see also Table 4). The ring plane not being a symmetry plane, the two minima are not equivalent. The values of the nitrogen and oxygen minima are to be compared with those of aziridine and oxirane of paper I; a relation with the nucleophilic character of the corresponding heteroatoms may be seen.

It is perhaps unnecessary to emphasize again that the $W(\boldsymbol{x}_i)$ values employed in this discussion give only a crude picture of the energies involved in the protonation process (the $W(\boldsymbol{x}_i)$ are only first order energies). It may, however, give an idea of the favoured approach paths of the proton (or other electrophilic reagents) in a hypothetical gas-phase reaction.

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References

1. Bonaccorsi, R., Scrocco, E., Tomasi, J.: J. chem. Physics **52**, 5270 (1970).
2. Basch, H., Robin, M. B., Kuebler, N. A., Baker, C., Turner, D. W.: J. chem. Physics **51**, 52 (1969).
3. Robb, M. A., Csizdmadia, I. G.: J. chem. Physics **50**, 1819 (1969).
4. Lehn, J. M., Munsch, B., Millie, P., Veillard, A.: Theoret. chim. Acta (Berl.) **13**, 313 (1969).
5. Clementi, E., Raimondi, D. L.: J. chem. Physics **38**, 2686 (1963).
6. Bonaccorsi, R., Petrongolo, C., Scrocco, E., Tomasi, J.: J. chem. Physics **48**, 1500 (1968).
7. — Scrocco, E., Tomasi, J.: J. chem. Physics **50**, 2940 (1969).
8. Rothemberg, S.: J. chem. Physics **51**, 3389 (1969).
9. Pritchard, R. H., Kern, C. W.: J. Amer. chem. Soc. **91**, 1631 (1969).

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