

Non Empirical LCAO-MO-SCF Calculations with Gaussian Type Functions on Some Three Membered Ring Heterocycles

II. Energies and Population Analysis

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Non empirical molecular quantum chemical calculations have been performed on the three membered ring heterocyclic molecules, aziridine, oxirane and thiirane and the as yet unknown 1 azirene, 2 azirene, oxirene and thiirene. For the nitrogen compounds the corresponding protonated species have been investigated and for comparison the isoelectronic saturated and unsaturated hydrocarbon molecules, cyclopropane and cyclopropene. A discussion is given of total energies, eigenvalues, and gross atomic populations.

An den folgenden Dreiring-Heterocyclen werden nicht-empirische quantenmechanische Rechnungen ausgeführt: Aziridin, Oxiran und Thiiran sowie an den bis heute unbekanntten Verbindungen 1-Aziren, 2-Aziren, Oxiren und Thiiren. Die zu den Stickstoffverbindungen gehörenden protonierten Verbindungen werden untersucht und vergleichshalber die gesättigten und ungesättigten Kohlenwasserstoffe Cyclopropan und Cyclopropen. Gesamtenergien, Eigenwerte und Atombesetzungszahlen werden diskutiert.

Calculs non empiriques sur les hétérocycles à 3 atomes: aziridine, oxirane, thiirane, et les molécules encore inconnues de 1 azirene, 2 azirene, oxirene et thiirene. On a étudié les espèces protonées des composés azotés et, à titre de comparaison, les hydrocarbures saturés et non saturés isoelectroniques: cyclopropane et cyclopropene. Discussion des énergies totales, des valeurs propres et des populations atomiques totales.

1. Introduction

For the most part the non-empirical calculations that have been performed, have been on molecules of known structure [1] so that direct comparison could be made between calculated and experimentally observable properties. There has been much less attention to using such calculations in a predictive role for molecules which are as yet unknown, or for calculating reaction co-ordinates. However the first "ab initio" calculation of an organic reaction co-ordinate has recently been completed [2] and a discussion of some aspects of the chemistry of some three membered ring heterocycles, which are as yet unknown, has been presented [3]¹. The heterocyclic compounds studied in this work are shown in

¹ Clark, D. T.: Proc. Israel Academy of Science and Humanities (in press) (this is considered as part I).

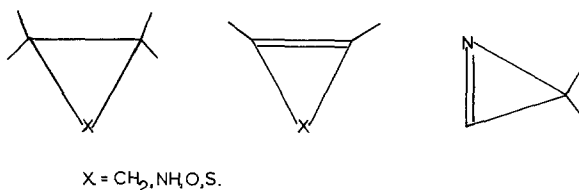


Fig. 1. Three membered ring saturated and unsaturated heterocyclic compounds

Fig. 1, the as yet unknown, 1 azirene, 2 azirene, oxirene and thiirene, and for comparison purposes, their saturated derivatives aziridine, oxirane, thiirane and also cyclopropane and cyclopropene. In part I [3] a discussion was given of, barriers to inversion, antiaromaticity, enthalpies of formation, decomposition, isomerization, hydrogenation and basicities and acidities. In this paper we report the total energies, eigenvalues and population analysis for those compounds. For the saturated molecules, cyclopropane, aziridine, protonated aziridine, oxirane and cyclopropene, Scrocco and co-workers [4] have independently carried out calculations using a minimal Slater basis set and so it is of interest to compare the results of the two investigations for these compounds.

2. Method of Calculation

The calculations performed in this work were carried out using the POLYATOM system [5] tailored to make use of the extensive disc handling facilities of the Northumbrian Universities IBM/360/67 Multiple Access Computer (NUMAC). The structures of the saturated compounds and cyclopropene have all been investigated by microwave spectroscopy and the bond lengths derived from these investigations have been used in the calculations [6]. For 2 azirene, oxirene and thiirene the C=C bond length was fixed at 1.28 Å as in cyclopropene [6]. The C-X bond lengths were then derived from those for the saturated compounds by reducing the bond lengths in direct proportion to the C-C bond length in going from cyclopropane to cyclopropene. For 1 azirene the C=N bond length was taken from acetone oxime [6] with a reduction of 0.05 Å for being in the ring, the C-C and C-N bond lengths were then taken as those in cyclopropane and aziridine respectively [6]. To enable a reasonably comprehensive treatment of the chemistry of these compounds to be discussed, a large number of calculations were carried out and this dictated that a medium size basis set be used. This consisted of 5s and 6p (2 each for p_x , p_y , p_z orbitals) GTF for each C, N, O and S atom and 2s for each hydrogen. For the sulphur compounds of course the basis set is minimal since the 5s GTF have to accommodate the 1s, 2s and 3s orbitals and the 2p GTF the 2p and 3p orbitals. The s and p GTF exponents for carbon, nitrogen and oxygen are those reported in Ref. [7] while the exponents of s GTF on the hydrogen atoms were taken from Ref. [8]. The exponents for sulphur are those of Ref. [9]. The d orbitals were not taken into consideration since the "ab initio" work carried out on divalent sulphur compounds [9] indicate that inclusion of the latter has a very small effect.

3. Results and Discussion

3.1. Eigenvalues and Total Energies

Table 1 contains the occupied orbital energies, and total energies for the saturated molecules cyclopropane, aziridine, oxirane and thiirane, together with the results where applicable from Scrocco's minimal Slater basis set calculations [4]. For aziridine, calculations were performed corresponding to out of plane angles of H 5 about nitrogen of 0° , 15° , 45° , 60° , 75° and 90° . The potential energy curve for this inversion process has previously been described [3] and a barrier to inversion of 15.50 kcal/mole and out of plane angle of 61° obtained. This is in good agreement with the experimental values of 10.0 kcal/mole, (for 1-methyl-2, 2-dimethyl aziridine [10], that for aziridine itself would be expected to be somewhat larger), and 68° [6] respectively. Veillard and co-workers [11] have carried out calculations using a contracted Gaussian basis set on planar aziridine and with an out of plane angle of 68° . The calculated barrier to inversion 18.0 kcal/mole is in good agreement with that reported here. It is of interest to compare the barrier to inversion with that calculated for the isoelectronic cyclopropyl anion (20 kcal/mole) [12]. As for the corresponding unsaturated species [3, 13] the anion has the higher inversion barrier. The minimal Slater basis set gives a slightly lower energy than the uncontracted 5.2.2.2 Gaussian basis set. For aziridine the contracted 9.5.5.5.4 basis set of Veillard gives a total energy of -132.9487 a.u. for the equilibrium geometry. Cyclopropane has also been treated with Gaussian basis set by Preuss and Dierksen [14]. For comparison their total energy calculated for a C-C bond length of 2.91 a.u. (exptl.) 2.88 a.u. is -116.0200 a.u. The energy difference between aziridine and its protonated species is essentially the same for both basis sets 242.90 kcal/mole (Gaussian) 240.01 kcal/mole (Slater).

Table 2 contains the occupied orbital energies and total energies for the unsaturated molecules cyclopropene, 1 azirene, 2 azirene and their conjugate acids, and for oxirene and thiirene. With the exception of cyclopropene these molecules are as yet unknown and their likely chemistry has been discussed in part I [3]. For 2 azirene, calculations were performed corresponding to out of plane angles of H 3 about nitrogen of 0° , 15° , 45° , 60° , 75° and 90° . The potential energy curve for this inversion process has previously been described [3] and a barrier to inversion of 35.14 kcal/mole and out of plane angle of 68° obtained. The activation barrier is substantially higher than for the saturated analogue, aziridine. This reflects the anti-aromatic character of planar 2 azirene. This is also clearly evident in the protonation energy for 2 azirene 243.01 kcal/mole, almost identical to that for aziridine. This contrasts sharply with the behaviour of the 5 membered ring aromatic pyrrole and its saturated derivative pyrrolidine, where the 6π system is destroyed on protonation and consequently the basicity is orders of magnitude less than for the saturated compound [15]. The protonation of nitrogen in 1 azirene (221.50 kcal/mole) still leaves the 2π electron system intact and the compound is predicted to be markedly less basic than 2 azirene. In both cases the effect of protonation shows up in the marked lowering in energy of the carbon and nitrogen 1s orbitals.

Table 1. Orbital energies, total energies, ionization potentials and dipole moments for unsaturated three membered ring heterocycles

	Cyclopropane		Aziridine $\theta = 60^\circ$		Aziridine protonated		Oxirane		Thiirane	
	This work	Ref. [4]	This work	Ref. [4]	This work	Ref. [4]	This work	Ref. [4]	This work	Ref. [4]
	E_{total} (a.u.)	-115.9978	-116.7516	-131.8049 ^a	-132.6582	-132.1920	-133.0407	-151.3951	-152.3688	-456.0016
$I_{\text{calc.}}$ (eV)	11.04	11.68	9.74	10.00	19.40	20.27	11.19	11.18	4.18	
$I_{\text{exp.}}$ (eV) [16]	10.53	10.53	9.94	9.94	—	—	10.65	10.65	8.87	
$\mu_{\text{calc.}}$ (D)	0	0	2.10	1.77	—	—	2.35	1.19	5.17	
$\mu_{\text{exp.}}$ (D) [17]	0	0	1.89	1.89	—	—	1.88	1.88	1.66	

^a Total energy is the minimum for 61° out of plane angle obtained from the potential energy curve.

It is of interest to compare the energetics in the transformation of 2 azirene to 1 azirene and for their corresponding conjugate acids. Both reactions are kinetically facile simply involving a prototropic rearrangement. For the neutral molecules, the isomerization of the 2 azirene ring system to the 1 azirene system involves an energy change of -26.98 kcal/mole and this forms the basis for the prediction [3] that it will be extremely difficult to isolate the parent 2 azirene ring system. The effect of protonation is to considerably lower the energetic preference for the 1 azirene ring system, the energy change in going from protonated 2 azirene to protonated 1 azirene being only -5.46 kcal/mole.

The first ionization potentials approximated to the energy of the highest occupied orbitals are in reasonable agreement with the experimentally determined values, with the Gaussian basis calculation giving slightly better correlation.

For protonated aziridine the first ionization potential 19.40 eV (Gaussian), 20.27 eV (Slater) [4], would appear to be entirely reasonable and are in accord with the marked lowering in energy of both the carbon and nitrogen $1s$ orbitals on protonation. The low ionization potential calculated for the sulphur compound emphasizes the fact that in this case the 5.2.2.2 basis set on sulphur is minimal. The calculated dipole moments are also in reasonable agreement with the experimentally determined quantities with the minimal Slater basis set tending to underestimate and the Gaussian basis set to overestimate the dipole moments. The contracted Gaussian basis set [11] calculation gives a dipole moment of $2.31 D$ for aziridine. The dipole moment for thiirane is considerably overestimated once again pointing to the limitations of the basis set employed for sulphur and we are currently investigating thiirane and thiirene and their 1.1 dioxides with larger basis sets and for the latter, the inclusion of d orbitals.

The first ionization potentials for cyclopropene, 2 azirene, 1 azirene and oxirene form an interesting series. For cyclopropene the calculated first ionization potential is in good agreement with experiment [16] as is the dipole moment [17], the ionization being from a π type orbital. For oxirene and thiirene the ionizations are from π type orbitals but for the sulphur compound the orbital is almost completely localized on the heteroatom. In the case of 1 azirene the ionization is from the nitrogen lone pair (σ) which is extensively delocalized onto C 1 and to a lesser extent C 2. The low ionization potentials of oxirene and 2 azirene emphasize again the anti-aromatic character of these species [3]; the ionization potential for the nitrogen heterocycle being much higher with respect to the oxygen compound, than would be expected, since the anti-aromaticity for the former can be relieved to some extent by the out of plane bending of the hydrogen attached to nitrogen.

As expected the effect of protonation is to increase the ionization potentials of both 1 and 2 azirene; ionization now being from π type orbitals in both cases.

3.2. Population Analysis

Table 3 shows the gross atomic populations for cyclopropane, aziridine, protonated aziridine, oxirane and thiirane, and where relevant the corresponding figures for the minimal Slater basis set. The populations on hydrogen are uni-

Table 3. Gross atomic populations for saturated three membered ring heterocycles

<i>Cyclopropane</i>	C 1	C 2	C 3	H 1	H 2	H 3	H 4		
This work	6.484	6.484	6.484	0.758	0.758	0.758	0.758		
Ref. [4]	6.370	6.370	6.370	0.815	0.815	0.815	0.815		
<i>Aziridine</i>	N	C 1	C 2	H 1	H 2	H 3	H 4	H 5	
(Planar) $\theta = 0^\circ$. This work	7.675	6.316	6.316	0.768	0.768	0.768	0.768	0.62	
$\theta = 60^\circ$. This work	7.514	6.390	6.390	0.740	0.766	0.740	0.766	0.694	
$\theta = 68^\circ$. Ref. [4]	7.278	6.338	6.338	0.813	0.828	0.813	0.828	0.764	
<i>Aziridine</i>	N	C 1	C 2	H 1	H 2	H 3	H 4	H 5	H 6
(protonated). This work	7.680	6.351	6.351	0.639	0.639	0.639	0.639	0.531	0.531
Ref. [4]	7.328	6.264	6.264	0.736	0.736	0.736	0.736	0.600	0.600
<i>Oxirane</i>	O	C 1	C 2	H 1	H 2	H 3	H 4		
This work	8.310	6.337	6.337	0.754	0.754	0.754	0.754		
Ref. [4]	8.138	6.297	6.297	0.817	0.817	0.817	0.817		
<i>Thiirane</i>	S	C 1	C 2	H 1	H 2	H 3	H 4		
	14.928	6.908	6.908	0.814	0.814	0.814	0.814		

formly lower for the Gaussian basis set as compared to the minimal Slater. There are several points of interest in comparing the two basis sets. For non planar aziridine for example the hydrogen attached to nitrogen is considerably more positive than those attached to carbon, and for the latter those cis to H 5 are the least positive and this appears in both calculations. The population difference between hydrogen attached to nitrogen and carbon respectively becomes even more marked in planar aziridine. The effect of protonation is a net migration of electrons to nitrogen from the carbon and hydrogen atoms and the overall positive charge is extensively delocalized.

The effect of replacing a CH_2 group by oxygen in going from cyclopropane to oxirane is of some interest. As expected the population on carbon decreases on introduction of the electronegative oxygen atom, however the population on the hydrogens remains remarkably constant, showing a slight decrease for the Gaussian basis calculation and a slight increase for the Slater basis set. For thiirane there is a substantial positive charge on sulphur and the population on hydrogen is considerably higher than in cyclopropane.

Table 4 shows the gross atomic populations for cyclopropene, 2 azirene, oxirene and thiirene. Both calculations show that the population on the methylene carbon (C 1) in cyclopropene is higher than for the vinylic carbons (C 2, C 3). For 2 azirene ($\theta = 60^\circ$) there is an interesting comparison to be drawn with aziridine. For the former the population on the hydrogen (H 3) attached to nitrogen is *larger* than for hydrogen (H 1, H 2) attached to carbon this is the reverse of the situation for aziridine. Bending H 3 into the plane of the ring ($\theta = 0$) causes a substantial reorganization of the electrons and the H 3 now has a lower population than for H 1 and H 2, mainly due to the larger decrease in population at H 3. This parallels the behaviour of aziridine. The effect of protonation of 2 azirene

Table 4. Gross atomic populations for unsaturated three membered ring heterocycles

<i>Cyclopropene</i>	C 1	C 2	C 3	H 1	H 2	H 3	H 4
This work	6.412	6.326	6.326	0.702	0.702	0.766	0.766
Reference	6.354	6.204	6.204	0.790	0.790	0.829	0.829
<i>2 Azirene</i>	N	C 1	C 2	H 1	H 2	H 3	
$\theta = 0^\circ$	7.670	6.157	6.157	0.701	0.701	0.614	
$\theta = 60^\circ$	7.454	6.226	6.226	0.690	0.690	0.714	
<i>2 Azirene</i>	N	C 1	C 2	H 1	H 2	H 3	H 4
<i>protonated</i>	7.650	6.081	6.081	0.566	0.566	0.528	0.528
<i>1 Azirene</i>		7.263	6.410	6.135	0.755	0.755	0.682
<i>1 Azirene</i>							
<i>protonated</i>	7.588	6.272	5.828	0.635	0.635	0.554	0.488
<i>Oxirene</i>	O	C 1	C 2	H 1	H 2		
	8.296	6.174	6.174	0.678	0.678		
<i>Thiirene</i>	S	C 1	C 2	H 1	H 2		
	14.906	6.769	6.769	0.778	0.778		

is to reduce the population on C 1, C 2 and the hydrogens and increase that on nitrogen. The positive charge is again extensively delocalized. The population on nitrogen in 1 azirene is considerably smaller than for 2 azirene and as in cyclopropene the population is highest on the methylene (C 1) carbon atom. It is interesting to note that the population on the vinylic hydrogen H 3 is lower than that of hydrogen (H 3) attached to nitrogen in nonplanar 2 azirene. Protonation of 1 azirene causes a net migration of electrons to nitrogen and the vinylic carbon (C 2) actually carries a small positive charge and again the overall positive charge is extensively delocalized.

As in the saturated case, the replacement of the methylene group of cyclopropene by oxygen to produce oxirene causes an overall drift of electrons to the oxygen atom, however the population on the latter and the carbon atoms is lower than for the saturated derivative, and this also applies to the sulphur analogues.

It is clear from Tables 1 and 2 that the carbon 1s orbitals span a considerable energy range from -11.208 a.u. in thiirane to -11.370 a.u. in 1 azirene, a total of 4.41 eV. The gross atomic populations on carbon also cover a considerable range, from 6.135 (vinylic carbon in 1 azirene) to 6.908 for the carbon atoms in thiirane. It has previously been noted [2, 18], that inner shell orbital energies are a sensitive function of the electronic environment of the atom and in Fig. 2 a plot is shown of carbon 1s orbital energies versus gross atomic populations. For this particular series of closely related compounds it would appear that there is a clear relationship between orbital energy and gross atomic population. In this respect the charged species (protonated aziridine, 1 and 2 azirene) must be considered separately since inspection of Tables 2, 3, 4 and 5, shows clearly that these molecules do not fit the correlation in Fig. 2. Fig. 3 shows a similar plot for nitrogen (neutral molecules) and again there is a reasonable correlation. Comparison of the oxygen 1s orbital energies in oxirane and oxirene show that these are almost

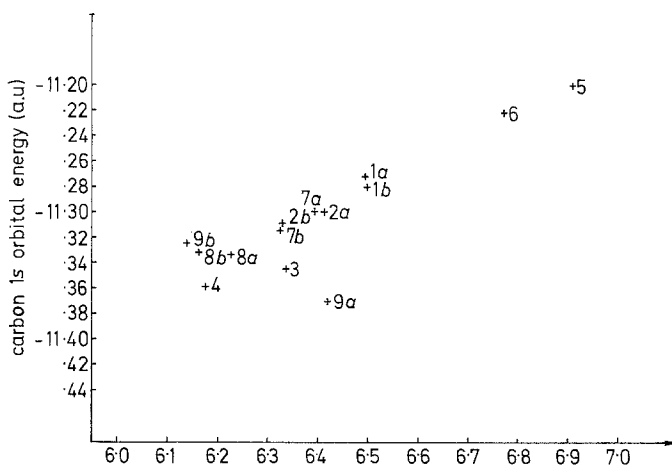


Fig. 2. Plot of calculated carbon 1s orbital energies (in a.u.) versus gross atomic populations. Key: 1a, 1b. Cyclopropane; 2a, 2b. Cyclopropene; 3. Oxirane; 4. Oxirene; 5. Thiirane; 6. Thiirene; 7a. Aziridine ($\theta = 60^\circ$); 7b. Aziridine ($\theta = 0^\circ$); 8a. 2 Azirene ($\theta = 60^\circ$); 8b. 2 Azirene ($\theta = 0^\circ$); 9a, 9b. 1 Azirene

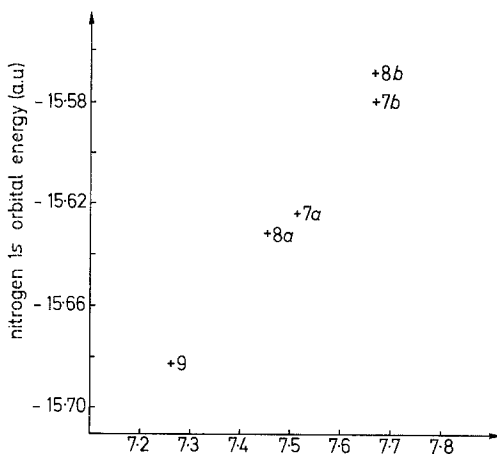


Fig. 3. Plot of calculated nitrogen 1s orbital energies (in a.u.) versus gross atomic populations. (Key as for Fig. 2)

identical, and the gross atomic populations are also very similar. The difference in electron population between the sulphur atoms in thiirane and thiirene is almost double the corresponding difference for the oxygen compounds and this is reflected in the lower energy of the sulphur 1s orbital in thiirene.

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