Theoretical Studies on the Formation, Electronic Structures, and Electrophilic Reactivity of the Pyrazole Cation System

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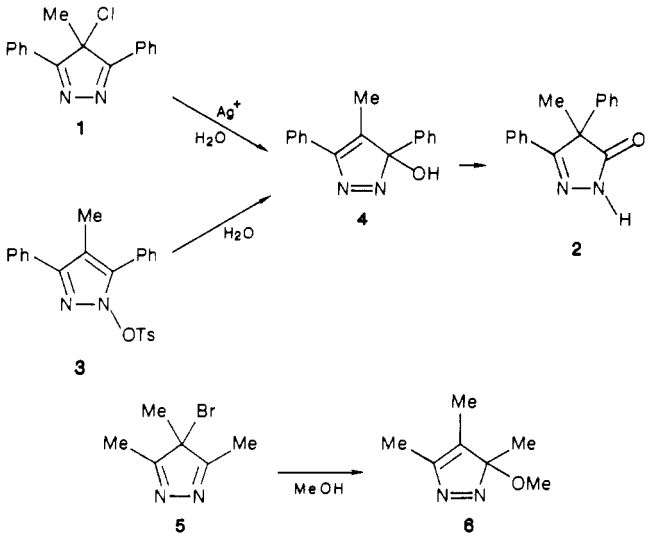
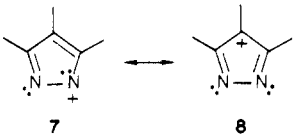
The solvolysis of 1- and 4-substituted pyrazoles has been reported to produce an intermediate cation that undergoes nucleophilic attack only at the 3 (and 5) position. Molecular orbital calculations have been carried out on the various singlet and triplet electronic configurations of the pyrazole cation in order to characterize the structure of the intermediate cation and the factor(s) controlling the regioselectivity in the reactions of the cation with nucleophiles. The lowest energy singlet, closed-shell configuration is a four π-electron structure having a $1b_1^2,2b_1^2$ π configuration. The LUMO of this state is the $1a_2$ π MO in which the largest coefficients are at C3 and C5, indicating that the attack by a nucleophile on the cation is controlled by HOMO–LUMO interactions. The second lowest energy state is the four π-electron structure having the $1b_1^2,1a_2^1$ π configuration. The six π-electron structure lies >50 kcal/mol above the $1b_1^2,2b_1^2$ four π-electron state. The energy gained by occuping the lower lying sp-hybrid nonbonding orbitals on the nitrogen atoms and the decrease in π-electron repulsion more than offset the aromatic stabilization energy of the six π-electron system. The four and five π-electron, open-shell singlet and triplet states are predicted to be lower in energy that the four π-electron $1b_1^2,2b_1^2$ state. Calculations have also been carried out on O-protonated 1-hydroxypyrazole at stretched N–O bond distances to simulate the loss of a leaving group. These calculations indicate that the OH_2 group departs in an out-of-plane manner to directly form the four π-electron $1b_1^2,2b_1^2$ cation.

Introduction

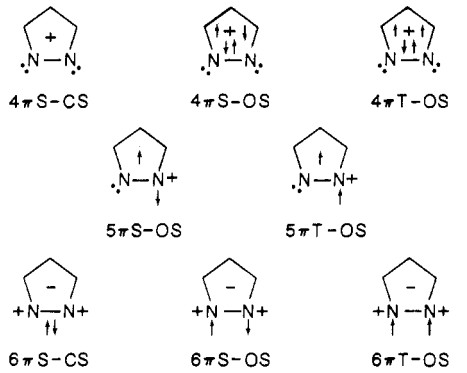
The hydrolysis of the 4-chloropyrazole **1** has been reported to produce the structurally rearranged pyrazolone **2**.[1] Pyrazolone **2** is also formed in the hydrolysis of the *N*-(tosyloxy)pyrazole **3**.[1] Carbinol **4** was assumed to be



the intermediate on the basis of the prior observation that the methanolysis of **5** produced the rearranged pyrazole **6**.[2] It was suggested that the ionization of **1** and **3** results in the formation of a cation represented by the resonance structures **7** and **8** which reacts with nucleophiles only at



the 3 (and 5) position.[3] It was not obvious why the cation preferred to react with nucleophiles at only the 3 (and 5) position. Molecular orbital calculations have been carried out on the various electronic states of the pyrazole cation shown below in which the number indicates the number of electrons in the π system, S and T indicate singlet or triplet state, and CS and OS indicate closed-shell and open-shell systems in order to gain an understanding of this phenomenon. HF calculations on the closed-shell and UHF calculations on the open-shell triplet systems have been carried out by using the GAUSSIAN80 package of programs.[4] ROHF and GVB calculations on the open-shell triplet and singlet systems have been carried out by using the GAMESS package of programs.[5]



Results and Discussion

The cation formed in the solvolysis reactions of **1** and **3** must be formed in a singlet electronic state, even though this state may not be the lowest in energy of all of the possible electronic states for the pyrazole cation. It is also reasonable to expect that attack by a nucleophile will occur on a singlet state of the cation. The cations formally derived from **1** and **3**, however, do not possess the same electronic configurations, the cation derived from **1** being a four π-electron system with two nonbonded pairs of electrons on the nitrogen atoms, while the cation derived from **3** will have an aromatic, six π-electron configuration. The four π-electron cation can exist in two different singlet closed-shell π electronic configurations designated as

(1) Freeman, J. P.; Janiga, E. R.; Lorenc, J. F. *J. Org. Chem.* **1977**, *42*, 3721.
(2) Closs, G. L.; Heyn, H. *Tetrahedron* **1966**, *22*, 463.
(3) Freeman, J. P.; Janiga, E. R. *J. Org. Chem.* **1974**, *39*, 2663.
(4) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. QPCE Catalog 13, Program 406. Indiana University, Bloomington, IN, 1981.
(5) Dupuis, M.; Spangler, D.; Wendolski, J. J. NRCC Software Catalog 1, Prog. NO. QG01 (GAMESS), Lawrence Berkeley Laboratories, University of California, Berkeley, CA, 1980.

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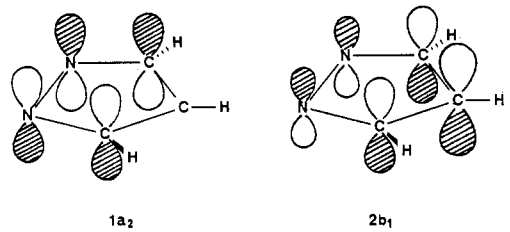

$1a_2$ $2b_1$

Figure 1. $^2b_1$ and $^1a_2$ π MO's of the pyrazole cation system.

Table I. Energies (au) of the 4πS-CSb_1, 4πS-CSa_2, and 6πS-CS Pyrazole Cations at Different Basis Levels

basis set	4πS-CSb_1	4πS-CSa_2	6πS-CS
3-21G[a]	-222.51644	-222.50591	-222.43145
6-31G[a]	-223.67940	-223.66337	-223.49314
6-31G*[a]	-223.81513	-223.79149	-223.71571
CID/6-31G[b]	-224.16464	-224.15395	-224.12725
CID/6-31G*[b]	-224.50173	-224.48095	-224.44761

[a] The structures were fully geometry optimized. [b] Single-point calculations on the 6-31G and 6-31G* optimized geometries.

$1b_1^2,2b_1^2$ and $1b_1^2,1a_2^2$. In the pyrazole cation the C_{2v} symmetry of the system breaks the degeneracy of the $2b_1$ and $1a_2$ MO's (see Figure 1). This is in contrast to that observed in the cyclopentadienyl cation of higher D_{5h} symmetry.[6] The $1b_1^2,2b_1^2$ and $1b_1^2,1a_2^2$ cations possess significantly different geometries as will be pointed out in later discussions. The four π-electron cations will be referred to as 4πS-CSb_1 and 4πS-CSa_2 and the six π-electron cation as 6πS-CS.

Complete geometry optimization calculations have been carried out on the two, four, and six π-electron singlet closed-shell systems at the 3-21G, 6-31G, and 6-31G* levels, with single point calculations also being carried out at the CID/6-31G and CID/6-31G* frozen core levels including all single and double excitations. The total energies are given in Table I and the π and nonbonded MO energies and LUMO coefficients are given in Table II. The STO-3G calculated structural parameters are given in the structures in Figure 2 and the 6-31G and 6-31G* structural parameters are given in Table 1 of the supplementary material.

At all levels the 4πS-CSb_1 configuration is lowest in energy, with the 4πS-CSa_2 state 6.6–14.8 kcal/mol higher in energy and the 6πS-CS state 53.3–62.4 kcal/mol at the non-CI level and 34.0 kcal/mol higher in energy than the 4πS-CSb_1 state at the CI/6-31G* level.

The structures of the 4πS-CSb_1 and 4πS-CSa_2 cations differ significantly, and are also highly basis set dependent. A calculation of the $1b_1^2,2b_1^2$ π configuration at the optimized geometry of the $1b_1^2,1a_2^2$ configuration gave a much higher energy (116.2 kcal/mol), indicating that the two states have little interaction with each other. In the 4πS-CSb_1 cation the C–N distances are very long, commensurate with the antibonding characteristics of the $2b_1$ MO between the carbon and nitrogen atoms. At the 3-21G level the C–N distance is unrealistically long (1.558 Å). On improving the quality of the basis set, particularly on adding d functions, the C–N distance decreases to 1.488 Å at the 6-31G* level. The other structural parameters are much less sensitive to the quality of the basis set. The structure of the 4πS-CSb_1 cation contains an essentially isolated allyl cation system, with C–C distances of 1.37 Å which are very similar to the C–C distances in the allyl cation of 1.385 Å.[7] The N–N distance of 1.224 Å is slightly shorter than that calculated for *cis*-diazene of 1.254 Å.[8] The cation is best represented by the two resonances structures shown as 9. The LUMO of this cation is the

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$^1a_2$ π MO in which the coefficient of the 2p AO on C3 and C5 is significantly greater than that on the nitrogen atoms (0.62 vs. 0.27 at the 3-21G level). Reaction of this cation with nucleophiles is thus expected to occur at C3 (or C5), which is consistent with what is observed experimentally.

In the 4πS-CSa_2 cation the $1a_2$ MO is highly bonding between the carbon and nitrogen atoms resulting in an almost pure C–N double bond and highly antibonding between the two nitrogen atoms resulting in a rather long N–N bond distance. At the 3-21G level the N–N distance is unrealistically long (1.613 Å), but it decreases markedly with improvement in the basis set of 1.483 Å at the 6-31G* level. The other structural parameters are much less sensitive to the quality of the basis set. This cation is best represented by the single resonance structure **10**.

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The LUMO of this cation is the $2b_1$ π MO in which the coefficient of the 2p AO on C4 is dominant (0.73 vs. 0.08 on C3(5) and 0.42 on N). Nucleophilic attack on this cation is expected to occur at C4 which is not consistent with the experimental observations.

Table II. π and Nonbonded MO Energies (eV) of the 4πS-CSb_1, 4πS-CSa_2, and 6πS-CS Pyrazole Cations

MO's LUMO c_is[a]	basis set 3-21G	6-31G	6-31G*
	4πS-CSb_1		
$1b_1$	-22.518	-22.578	-22.656
$9a_1$ (n + n)	-21.654	-21.709	-21.835
$2b_1$ (π HOMO)	-18.318	-18.125	-18.006
$6b_2$ (n - n)	-17.803	-17.985	-17.894
$1a_2$ (π LUMO)	-8.145	-8.228	-7.812
C_4	0.00, 0.00	0.00, 0.00	0.00, 0.00
$C_{3,5}$	0.30, 0.45	0.35, 0.38	0.35, 0.37
N	0.14, 0.18	0.19, 0.17	0.19, 0.17
	4πS-CSa_2		
$8a_1$ (n + n)	-23.983	-24.098	-24.276
$1b_1$	-22.008	-21.986	-22.038
$6b_2$ (n - n)	-20.153	-19.963	-19.439
$1a_2$ (π HOMO)	-18.317	-18.144	-17.811
$2b_1$ (π LUMO)	-8.648	-8.687	-8.369
C_4	0.35, 0.53	0.42, 0.46	0.42, 0.46
$C_{3,5}$	0.06, 0.04	0.05, 0.07	0.08, 0.06
N	0.21, 0.29	0.26, 0.25	0.24, 0.23
	6πS-CS		
$1b_1$	-26.673	-26.545	-26.432
$9a_1$ (n + n)	-22.060	-21.806	-21.638
$2b_1$	-17.757	-17.548	-17.309
$1a_2$ (HOMO)	17.046	17.135	16.848
$6b_2$ (n - n LUMO)	-8.916	-9.966	-8.628
$2a_2$ (π LUMO)	-2.849	-2.899	-2.278
C_4	0.00, 0.00	0.00, 0.00	0.00, 0.00
$C_{3,5}$	0.24, 0.42	0.29, 0.43	0.27, 0.43
N	0.33, 0.57	0.40, 0.57	0.39, 0.58

[a] The first coefficient is for the inner set, the second for the outer set.

(6) Bordon, W. T.; Davidson, E. R. *J. Am. Chem Soc.* **1979**, *101*, 3771.
(7) Radom, L.; Hariharan, P. C.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 6531.
(8) Pasto, D. J. *J. Am. Chem. Soc.* **1979**, *101*, 6852.

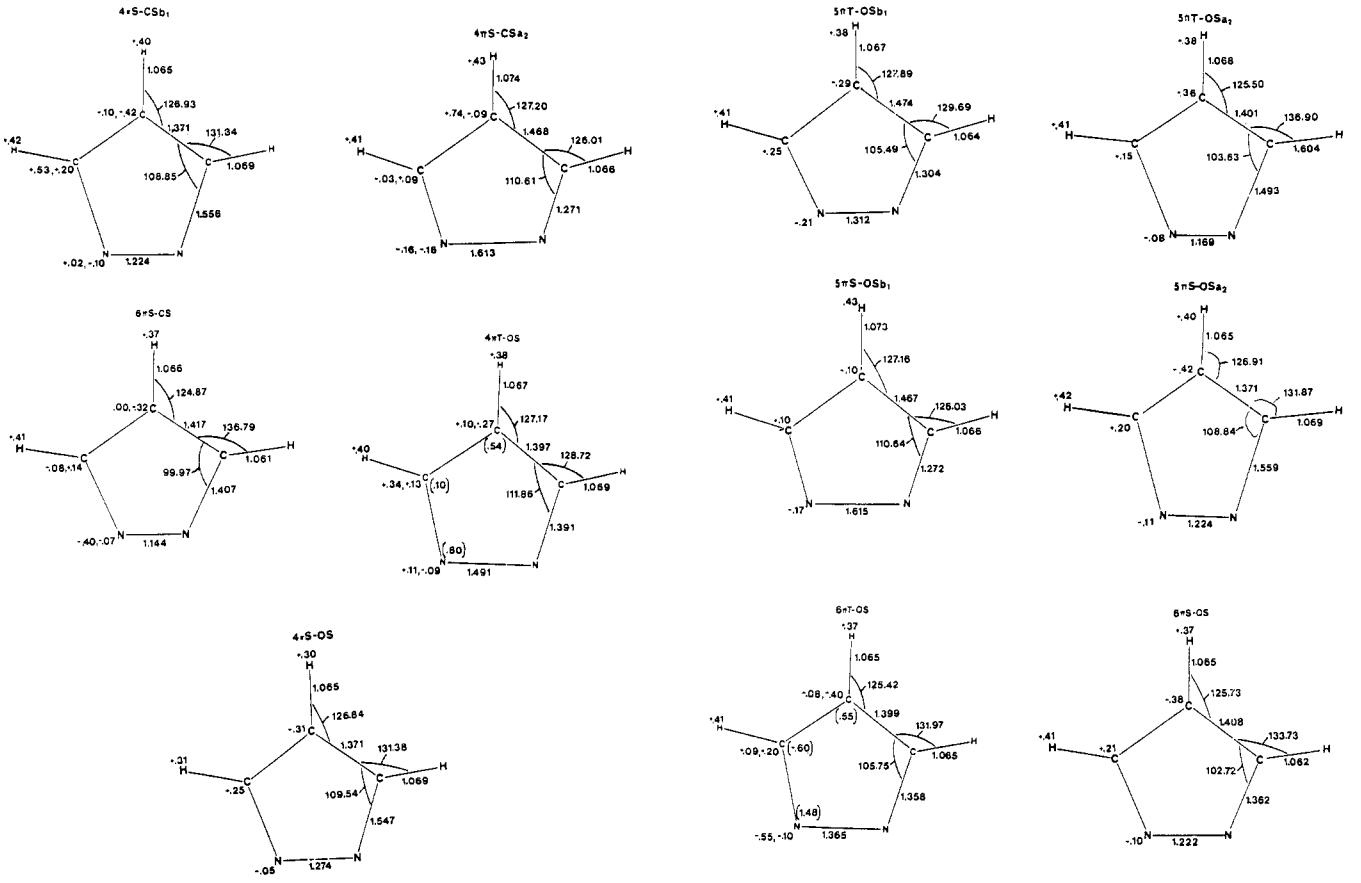
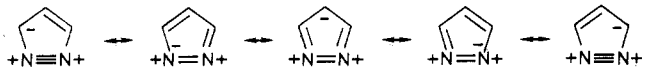


Figure 2. 3-21G optimized structural parameters and π (left) and total (right) atomic charges in the pyrazole cation systems. Spin densities of open-shell systems from UHF calculations are given in parentheses. Only total atomic charges are given for the singlet open-shell systems.

The structure of the 6πS-CS cation is predicted to have a very short N–N distance, intermediate between that of a N=N and N≡N. The structural parameters are not very sensitive to the quality of the basis set. The negative π charge is concentrated on the two nitrogen atoms and C4 with some negative charge appearing on C3 and C5. This cation is best represented by the resonance contributing structures shown in **11** in which the major contributors are the three center structures. This cation is expected to react with a nucleophile at one of the nitrogen atoms where the electron deficiency is in the σ MO's.



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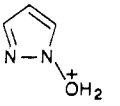
The energy of the 6πS-CS cation is higher than either of the four π-electron cations. At first glance this relative energy sequence may seem surprising because of the presence of the six π-electron, aromatic system in the 6πS-CS cation and the presence of nonbonded four-electron repulsion in the four π-electron systems when the $9a_1$ and $6b_2$ nonbonded pair MO's are both doubly occupied. The energy gained by occupying the much lower energy sp-hybrid nonbonded MO's on the nitrogen atoms more than offsets the aromatic stabilization energy of the six π-electron cation and the increased electron repulsion in the two nonbonding-pair MO's in the four π-electron cations.

Mechanism of Ionization. The ionization of a 4-substituted pyrazole would be expected to produce the 4πS-CSa_2 cation (based on a comparison of the C–N bond lengths in the pyrazole and the two possible four π-electron cations), which would rapidly relax to the lower energy 4πS-CSb_1 cation. The ionization of a 1-substituted pyrazole via an in-plane departure of the leaving group would formally produce the very high energy 6πS-CS cation. An out-of-plane departure would lead directly to the 4πS-CSb_1 cation.

Model calculations have been carried out to determine the lowest energy mode of departure of a leaving group for the 1-substituted pyrazole system. Geometry optimization calculations at the 3-21G level have been carried out on the O-protonated *N*-hydroxypyrazole (**12**). The N–O



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distance in **12** was increased from its equilibrium value to 1.60 and 1.75 Å and geometry optimization calculations were carried out for both in-plane and out-of-plane departures of the water molecule. At both distances the out-of-plane departure was lower in energy. At the N–O distance of 1.75 Å the optimized ring plane–N–O angle was calculated to be 130.5°. These calculations suggest that the ionization of a 1-substituted pyrazole proceeds with an out-of-plane departure of the leaving group to give directly the 4πS-CSb_1 cation.

Four π-Electron, Open-Shell Cations. The calculations on the 6πS-CS cation indicated that the $2b_1$ and $1a_2$ MO's are nearly degenerate when both are doubly occupied (see Table II). In the $2b_1$ MO maximum electron density resides on C4 with little density residing on C3 and C5. In contrast, in the $1a_2$ MO there is no electron density on C4. The combination of near degeneracy and the difference in electron distributions suggested that open-shell

Table III. Total Energies of the Four, Five, and Six π-Electron Open-Shell Pyrazole Cations

structure	basis set 3-21G	6-31G
4πT-OS (UHF)	-222.52801	[a]
(ROHF)	-222.52318	-223.68822
4πS-OS	-222.56483	-223.72807
5πT-OSb$_1$ (UHF)	-222.52999	-223.69578
(ROHF)	-222.51136	-223.67611
5πT-OSa$_2$ (UHF)	-222.54664	-223.70856
(ROHF)	-222.52305	-223.68429
5πS-OSb$_1$ (GVB)	-222.50749	-223.66487
5πS-OSa$_2$ (GVB)	-222.52278	-223.68560
6πT-OS (UHF)	-222.50487	-223.66647
(ROHF)	-222.49279	-223.65272
6πS-OS (GVB)	-222.50669	-223.67021

[a] Convergence could not be achieved.

configurations might be more favorable than the four π-electron, closed-shell configurations due to a reduction in π-electron repulsion. Accordingly, calculations were carried out at the 3-21G and 6-31G levels with full geometry optimization on the triplet (4πT-OS) and singlet (4πS-OS) four π-electron, open-shell cations. The UHF calculation on the triplet state indicated considerable contamination of the wave function by higher spin states ($\langle S \rangle_2 = 2.023$), and ROHF calculations were also carried out. GVB calculations were carried out on the open-shell, singlet state. The total energies of the triplet and singlet, open-shell four π-electron cations are given in Table III and the energies of the π and nonbonded-pair MO's derived from the UHF and ROHF calculations are given in Table IV. The 3-21G optimized structural parameters are shown in the structures in Figure 2 and are also given in Table 2 of the supplementary material along with the 6-31G UHF and ROHF optimized structural parameters. The π (left) and total charge densities (right), and the spin densities (in parentheses), calculated for the 4πT-OS cation are shown with the structure in Figure 2. Total charge densities only are shown for the 4πS-OS cation.

The UHF and ROHF optimized structures for the 4πT-OS cation are very similar. The structures of the 4πT-OS and 4πS-OS cations, however, are significantly different, particularly when comparing the C–N and N–N distances. The 4πT-OS cation is best represented by the resonance structures shown as **13** in which positive charge appears only at the 3 and 5 positions, with the unpaired spin densities being concentrated on the nitrogen atoms.

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Both the singlet and triplet four π-electron open-shell cations are predicted to be lower in energy than the 4πS-CSb$_1$ cation; however, absolute comparisons cannot be made because of the different calculational methods used. The calculations do suggest that the four π-electron open-shell cations are relatively close in energy with the four π-electron closed-shell cations.

Five π-Electron Cations. Calculations have also been carried out on the triplet and singlet five π-electron cations to assess the relative importance of occupying a σ nonbonding MO vs. a π MO. Again, there are two possible five π-electron configurations; $1b^2<<bvw1,1a_2^2,2b_1^1$, designated as 5πT-OSb$_1$, and $1b_1^2,2b_1^2,1a_2^1$ designated as 5πT-OSa$_2$. UHF calculations on the triplet states indicated extensive contamination of the ground-state triplet wave function by higher spin-state wave functions ($\langle S \rangle_2 = 2.393$ for the 5πT-OSb$_1$ cation and 2.216 for the 5πT-OSa$_2$ cation) and ROHF calculations on the pure triplet states were carried out. GVB calculations were carried out on the five π-electron, singlet, open-shell cations (5πT-OSa$_2$ and 5πT-OSb$_1$). The total energies are given in Table III and the energies of the π and nonbonded MO's derived from the UHF and ROHF calculations are given in Table IV. The calculated structural parameters and total charge densities are given in the structures in Figure 2. The UHF and ROHF optimized structures are very similar. The 5πT-OSb$_1$ and 5πT-OSa$_2$ structures differ significantly and are also significantly different from their open-shell singlet counterparts. In all cases the $1b_1^2,2b_1^2,1a_2^1$ configurations are lower in energy than the $1b_1^2,1a_2^2,2b_1^1$ configurations. The ROHF 5πT-OSa$_2$ and GVB 5πS-OSa$_2$ cations are indicated to be slightly lower in energy (only a few kcal/mol)

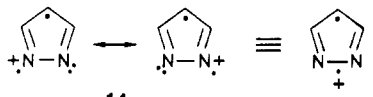
Table IV. UHF and ROHF Energies (eV) of π and Nonbonded MO's in the Four, Five, and Six π-Electron, Open-Shell Pyrazole Cations

MO	basis set 3-21G α	3-21G β	6-31G α	6-31G β
	4πT-OS (UHF)[a]			
1b$_1$	-25.035	-19.286		
9a$_1$ (n + n)	-20.409	-19.734		
6b$_2$ (n - n)	-20.313	-19.233		
1a$_2$ (SOMO)	-19.516			
2b$_1$ (SOMO)	-18.837			
	4πT-OS (ROHF)			
1b$_1$	-21.244		-22.332	
9a$_1$	-20.180		-20.768	
6b$_2$	-19.883		-18.655	
2b$_1$	-20.389		-19.072	
1a$_2$	-19.550		-18.314	
	5πT-OSb$_1$ (UHF)			
1b$_1$	-26.430	-22.223	-26.500	-22.143
9a$_1$	-22.467	-17.722	-22.543	-17.743
6b$_2$ (n - n, SOMO)	-21.413		-21.324	
1a$_2$	-19.633	-17.893	-19.495	-17.752
2b$_1$ (SOMO)	-18.931		-18.877	
	5πT-OSb$_1$ (ROHF)			
1b$_1$	-24.345		-24.288	
9a$_1$	-20.430		-20.469	
6b$_2$	-20.981		-20.873	
1a$_2$	-17.869		-17.702	
2b$_1$	-18.722		-18.690	
	5πT-OSa$_2$ (UHF)			
1b$_1$	-25.845	-23.618	-25.819	-23.606
9a$_1$	-24.559	-20.491	-24.605	-20.512
6b$_2$ (n - n, SOMO)	-20.241		-20.168	
2b$_1$	-18.847	-18.211	-18.790	-18.113
1a$_2$ (SOMO)	-18.301		-18.253	
	5πT-OSa$_2$ (ROHF)			
1b$_1$	-24.674		-24.627	
9a$_1$	-22.319		-22.130	
6b$_2$	-20.386		-20.577	
2b$_1$	-18.167		-17.895	
1a$_2$	-17.338		17.459	
	6πT-OS (UHF)			
1b$_1$	-26.304	-23.757	-26.476	-23.696
9a$_1$ (n + n, SOMO)	-22.815		-22.708	
6b$_2$ (n - n, SOMO)	-22.526		-22.319	
1a$_2$	-19.939	-17.809	-19.851	-17.718
2b$_1$	-17.421	-16.315	-17.324	-16.202
	6πT-OS (ROHF)			
1b$_1$	-24.881		-24.949	
9a$_1$	-25.548		-25.701	
6b$_2$	-24.655		-24.533	
1a$_2$	-18.547		-18.374	
2b$_1$	-16.830		-16.717	

[a] Convergence could not be achieved at the 6-31G level.

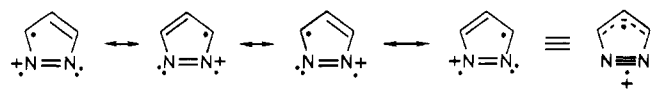
than the 4πS-CSb_1 cation; however, only qualitative comparisons can be made.

In the 5πT-OSb_1 cation the maximum π-spin density resides on C4. The slightly longer N–N distance than a normal N=N distance is accommodated by the resonance-contributing structures shown as **14** which is



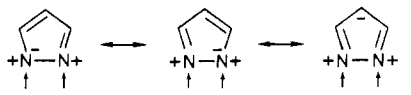
14 **15**

equivalent to the MO description in **15** in which the (n + n) MO is doubly occupied in the (n − n) MO is singly occupied. In the 5πT-OSa_2 cation the π-electron spin density resides predominantly on C3 and C5. The N–N distance is intermediate between that of N=N and N≡N. This cation is best represented by the resonance-contributing structures shown as **16**, of the MO description shown in **17**.



16 **17**

Six π-Electron, Open-Shell Cations. Calculations have also been carried on the six π-electron, σ-triplet, and singlet open-shell cationic systems. The total energies are given in Table III, and the π and nonbonded MO energies are given in Table IV. The 3-21G optimized structural parameters, π and total charge densities, and spin densities are given in the structure in Figure 2. The 6-31G optimized structural parameters are given in Table 2 of the supplementary material. The structure and π charge distribution of the 6πT-OS cation suggest that the structure is best represented by the resonance structures shown as **18**. The



18

structure of the 6πS-OS cation is quite similar to that of the triplet structure except for a slightly longer N–N distance. Its overall electronic structure is similar to that shown as the hybrid **18**. Both the triplet and singlet structures are slightly higher in energy that the 4πS-CSb_1 cation.

Summary

Of the closed-shell singlet cationic structures, the 4πS-OBb_1 cation is the lowest in energy. The electronic properties predicted from the calculations correspond to those observed experimentally. The calculations indicate that several other singlet and triplet electronic configurations lie close in energy. The highest lying configuration appear to be the aromatic six π-electron closed-shell system.

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Supplementary Material Available: Tables of calculated structural parameters for the pyrazole cations studied (7 pages). Ordering information is given on any current masthead page.

Stereoselective Intramolecular Iodoetherification of 4-Pentene-1,3-diols: Synthesis of *cis*-2-(Iodomethyl)-3-hydroxytetrahydrofurans

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Intramolecular iodoetherification of 4-pentene-1,3-diol and its monosubstituted derivatives, irrespective of the substitution pattern, provides *cis*-2-(iodomethyl)-3-hydroxytetrahydrofurans in high yields. The cis selectivity generally exceeds 95%. Some of the disubstituted 4-pentene-1,3-diols similarly undergo the selective cyclization; however, the others show anomalies on regio- and/or stereoselectivities, providing either tetrahydropyrans or *trans*-2-(iodomethyl)-3-hydroxytetrahydrofurans as main products. A mechanism that may reconcile all of these results is proposed.

The control of stereochemistry in an acyclic system is an important consideration in the synthesis of many complex molecules.[1] However, despite the great advances that have been made in cyclic systems, the control of stereochemistry in acyclic systems remains a challenge. The hydroxy group of allylic alcohols often provides a moderate to strong stereo-directing effect during addition to double bonds (epoxidation,[2] glycolation,[3] halogenation,[4] etc.[5]). Katzenellenbogen,[6] Chamberlin,[7] and we[8] have demonstrated that the hydroxyl group of 3-hydroxy-4-penten-

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