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Theoretical Studies on the Diazacyclopentadienylidenes: An Analysis of Aromatic Versus Nonaromatic Systems and Singlet Versus Triplet Reactivity*

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ABSTRACT

Ab initio *molecular orbital calculations have been carried out on the various electronic states of 2,3-* (**6**), *2,4-* (**7**), *2,5-* (**8**), *and 3,4-diazacyclopentadienylidene* (**9**) *at the fully geometry optimized 6-31G* level, with single point calculations being carried out at the MP2/6-31G* level. The calculated geometries are interpreted in terms of the degree of occupancy and the nature of the π and σ-nonbonded MO's. At the 6-31G* level the five π-electron, π,σ-triplet states were calculated to be considerably lower in energy. At the MP2/6-31G* level, however, with* **7** *the six π-electron singlet state is calculated to lie only slightly above the five π-electron triplet (0.4 kcal mole^{-1}), whereas with* **8** *and* **9** *the aromatic six π-electron singlet states are calculated to be lower in energy (9.0 and 8.1 kcal mole^{-1}). With* **3** *and* **9** *the aromatic six π-electron σ-triplet states lie only 3.6 and 5.5 kcal mole^{-1} above the lowest energy states. It is concluded that, in general, the energy gained by having an electron in a lower energy σ-type MO instead of a higher energy π MO effectively offsets the energy gained by having an aromatic π system. The results are discussed in terms of the observed chemistry of* **6–9** *and their substituted systems.*

Dedicated to Professor Ernest E. Eliel on the occasion of his seventieth birthday.

INTRODUCTION

The azocyclopentadienylidenes (azoylidenes), in which one or more of the C–H units in cyclopentadienylidene (**1**) has been replaced by a nitrogen atom, represent a very interesting class of reactive intermediates in organic chemistry. A number of substituted azoylidenes have been generated by the thermolysis and photolysis of the corresponding diazo compounds, and their chemical properties have been studied. [1–7]. The azoylidenes are very reactive, undergoing electrophilic addition reactions with substituted aromatic compounds and hydrogen atom abstraction with hydrogen atom donors, suggesting their ability to react either as a closed-shell, singlet (electrophilic species), or as an open-shell, triplet (diradical) species.

1

A number of different representations have been used to describe the electronic states of these intermediates. In addition to their reacting as an electrophilic or diradical species, certain of the azoylidenes undergo ring opening reactions as exemplified by the ring opening of **2** to produce **3** [7]. Because of an interest in better understanding the theoretical aspects of reactions of reactive intermediates [8], an ab initio theoretical study was undertaken of the azoylidenes. The result of preliminary calculations at the 3-21G level on a number

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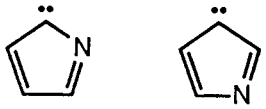
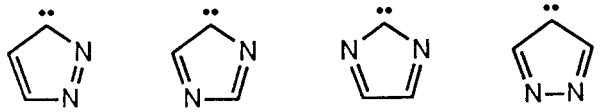
of azoylidenes revealed the requirements for the ring-opening process. The ring-opening process was indicated to occur, with apparently no activation energy barrier, from the 6 π-electron, closed-shell, singlet states when there are at least two nitrogen atoms at the 2- and 3-positions [8]. The results of a subsequent detailed theoretical study of the 2- and 3-azoylidenes **4** and **5** at the 6-31G* level provided interesting insights on the effects of aromatic and nonaromatic π systems versus nonbonded-pair orbital occupancy interactions [9]. The results of the calculations correlated well with the known chemistry of the substituted derivatives of **4** and **5** reported in the literature [9]. The present paper describes the results of high-level ab initio calculations on the unsubstituted diazoylidenes **6–9**.

2 **3**

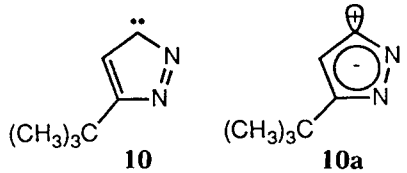


4 **5**



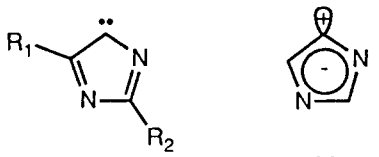
6 **7** **8** **9**

Only a few derivatives of this class of intermediates have been studied experimentally. Diazoylidene **10** undergoes electrophilic substitution and addition reactions with aromatic compounds, but is not reported to undergo hydrogen atom abstraction reactions typical of a diradical species [2]. This azoylidene has been described as an unusually unselective and energetic singlet electrophile whose electronic structure is best represented as **10a**. Other substituted azoylidenes related to **10** show similar characteristics.



10 **10a**

Azoylidene **11a** has been described as a highly reactive, indiscriminate electrophile in reactions with substituted benzenes, and was observed not to undergo hydrogen atom abstraction reactions, or C–H bond insertion reactions [3]. The electronic structure of **11a** was represented as shown in **12** [4]. No ESR signal was detected for the parent **11a**. Very interestingly, **11b** and **11c** do undergo hydrogen atom abstraction and C–H bond insertion reactions [4], and do give rise to an ESR signal [5], both suggestive of the presence of a low lying triplet diradical state. Azoylidene **8** shows both electrophilic and radical characteristics [6]. Azoylidene **9** or its derivatives appear not to have been studied experimentally.



11a $R_1 = H, R_2 = H$ **12**

b $R_1 = CONH_2, R_2 = H$

c $R_1 = R_2 = -C_6H_5$

In the present study ab initio MO calculations have been carried out on the various electronic configurations of **6–9** to determine the effect of the second nitrogen atom on relative energies of the various electronic configurations of **6–9**. The calculations have been carried out at the 6-31G* level with full geometry optimization, with single point calculations being carried out at the MP2/6-31G* and UMP2/6-31G* levels using the GAUSSIAN86 package of programs [10].

In order to facilitate the discussion of the orbital occupancy of the various electronic states of **6–9**, the orbital symmetries will be referred to in the C_{2v} point group. Although **6** and **7** belong to the C_s point group and not the C_{2v} point group, the MO's of **6** and **7** show pseudo-C_{2v} properties, the pseudo-C_2 axes being oriented as shown in Figure 1. (The pseudo C_2 axis resides in the molecular plane coincident with the nodal plane of the π MO's.) Diazoylidenes **5** and **6** do belong to the C_{2v} point group. The π MO's of **6–9** are referred to as b_1 (symmetric in the yz plane) and a_2 (antisymmetric in the yz plane). The nonbonded combination MO's will be indicated according to their dominant contributions; i.e., the nonbonded orbital on the carbenic carbon atom as C, and the two linear combinations of the nonbonded orbitals on the two nitrogen atoms as N_+ and N_-. These are illustrated in Figure 1 for each of the systems.

The following convention will be used to specify the system and the electronic states as done in our earlier publication [9]. The positions of the two nitrogen atoms in the ring will be indicated by two numbers followed by **N**. Next, the number of electrons in the π system will be indicated by a number followed by **P**. When appropriate, the orbital occupancy will be indicated with **B** for b_1 and **A** for a_2, with doubly occupied orbitals being indicated

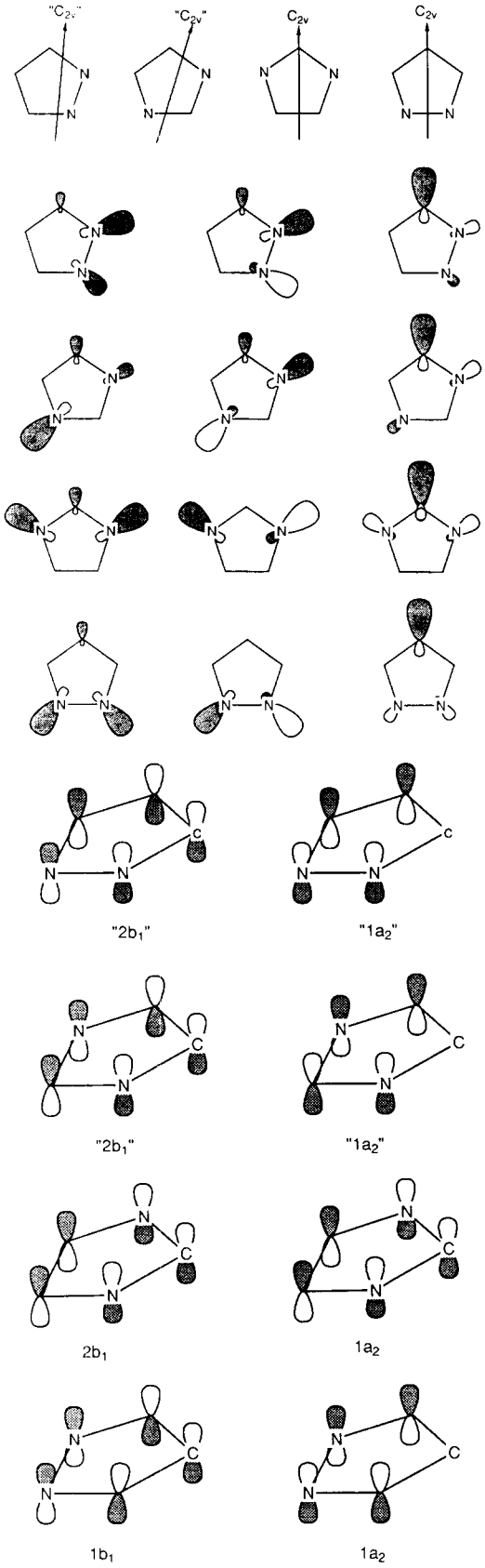


FIGURE 1 Illustrations of the π and σ MO's of **6–9**.

first and any singly occupied orbitals following. Finally, the multiplicity will be indicated as **S** (singlet) or **T** (triplet). For example, the four π-electron $1b_1^2, 1a_2^2$ singlet and five π-electron $1b_1^2, 2b_1^2, 1a_2^1$ triplet states of **6** will be designated as **34N4PBAS** and **34N5PBBAT** respectively. (The $1b_1$ MO is always lowest in energy; however, the relative energies of the $2b_1$ and $1a_2$ MO's vary.) This convention will greatly facilitate the discussion of the comparison of the relative energies of the different systems. The prior studies on **4** and **5** showed that of the two possible configurations available for the **4P** singlet and the **5P** triplet states, one of the configurations either does not represent an energy minimum structure, or if it does, it is very much higher in energy [9]. In this study, attempts have been made only to locate the lowest-energy **4P** singlet and **5P** triplet states. Attempts to calculate the open-shell singlet states have not been made; it is assumed that the corresponding singlet states would be higher in energy than the triplet states (shown to be true with the five π-electron states of the 2,3-diazolylidene system).

RESULTS AND DISCUSSION

The 2,3-Diazacyclopentadienylidene System (**6**)

The calculated geometries for the various electronic states of **6** are shown in Figure 2. The calculated structures for the various electronic states of **6** differ substantially, in particular the N_2–N_3 and C_4–C_5 bond lengths, and reflect primarily the bonding properties of the occupied π MO's. For example, in **23N4PBAS** both the $1b_1$ and $1a_2$ MO's are bonding between N_2 and N_3 and C_5 and C_4. This results in rather short calculated bond lengths compared to those in **23N4PBAS** and **23N4PT** in which one electron has been removed from the $1a_2$ MO and placed in the $2b_1$ MO, which is antibonding between N_2 and N_3, and C_5 and C_4. This change in occupancy also results in a substantial decrease in the N_3–C_4 bond length as a result of the bonding characteristics of the $2b_1$ MO between these two atoms. There is little change in the N_2–N_3 and C_4–C_5 bond lengths on going from **23N4PT** to **23N5PBBAT** because of the similarity in the number of net bonding and antibonding interactions. Finally, on going from **23N5PBBAT** to **23N6PT**, in which an electron has been added to the $1a_2$ MO, which is bonding between N_2 and N_3, a substantial decrease in the N_2–N_3 distance is observed. A similar analysis of the somewhat smaller effects on the C_1–N_2 and C_1–C_5 bond lengths can also be made. In **23N4PBAS**, the $1b_1$ MO is bonding between C_1 and N_2, and C_1 and C_5, while the $1a_2$ MO is nonbonding between these sets of atoms. Adding electrons to the $2b_1$ MO, which is bonding between C_1 and N_2, and C_1 and C_5, on going to the **23N4PT** and **23N5PBBAT** configurations re-

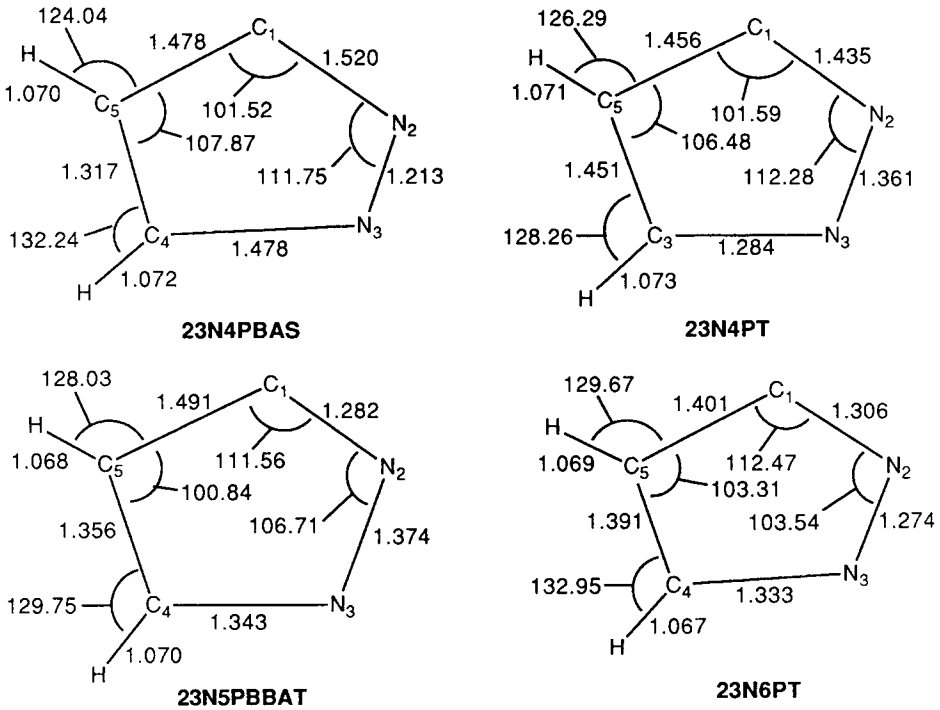


FIGURE 2 Calculated structural parameters for the various electronic states of **6**.

sults in a shortening of these bond lengths. The only apparent effect that the occupancy of the nonbonded MO's has on the geometries of the various electronic configurations of **3** is on the C_5–C_1–N_2 bond angle. In the **4P** systems the C MO is doubly occupied and the C_5–C_1–N_2 angles are 101.52° and 101.59°. Removal of one electron from the C MO results in an increase in the C_5–C_1–N_2 angle by approximately 10°.

The total energies of the various configurations of **6** are given in Table 1, and the energies of the π and σ nonbonded MO's are given in Table 2. The lowest energy configuration at both the 6-31G* and UMP2/6-31G* levels is the five π-electron triplet **23N5PBBAT**. At the UMP2/6-31G* level **23N6PT** is slightly higher in energy (3.5 kcal mole^{-1}), while the four π-electron singlet state is calculated to be considerably higher in energy (17.7 kcal per mole). The **6PT** configuration lies only slightly higher in energy than the **23N5PBBAT** state (3.6 kcal mole^{-1}). A single point calculation was carried out on the open-shell singlet having the structure calculated

TABLE 1 Total and Relative[a] Energies and $< S^2 >$ Values of the Various Electronic States of the Diazoylidenes

State	*6-31G* E_{tot} (au)*	$< S^2 >$	*E_{rel} (kcal mole^{-1})*	*$E_{MP2/6\text{-}31G^*}$ (au)*	*E_{rel} (kcal mole^{-1})*
23N4PBAS	−233.43734		49.5	−224.09283	17.7
23N4PT	−233.43610	2.0009	50.3	−224.06287	39.8
23N5PBBAT	−233.51622	2.0007	0.0	−224.12638	0.0
23N6PT	−233.47115	2.0064	28.3	−224.12072	3.6
24N4PBAS	−233.48560		46.1	−224.13808	27.9
24N6PS	−223.47920		50.1	−224.18183	0.4
24N4PT	−223.46275	2.0010	60.5	−224.08143	63.4
24N5PBBAT	−223.55910	2.0239	0.0	−224.18254	0.0
24N6PT	−223.48776	2.0069	44.8	−224.13334	30.9
25N4PBAS	−223.48397		46.3	−224.14008	35.8
25N6PS	−223.50202		35.0	−224.19707	0.0
25N4PBABT	−223.44975	2.0002	67.8	−224.07496	76.7
25N5PBABT	−223.55775	2.0181	0.0	−224.18280	9.0
25N6PT	−223.47450	2.0003	52.2	−224.15722	25.0
34N4PBAS	−223.44102		45.3	−224.10087	23.8
34N6PS	−223.42373	2.0010	56.2	−224.13883	0.0
34N5PBABT	−223.51328	2.0619	0.0	−224.12591	8.1
34N6PT	−223.46783	2.0304	28.5	−224.13007	5.5

[a] Relative energies are given individually for each series of configurations.

TABLE 2 π and σ Nonbonded MO Energies (eV) of the Electronic States of the Diazoylidenes **6–9**

MO	*4PS*	*6PS*	*4PT*	*5PT*	*6PT*
			6		
$1b_1$	−16.076		−15.938	−16.445	−17.654
$1a_2$	−11.323		−12.776	−12.607	−10.264
$2b_1$	−0.599		−11.177	−10.865	−10.147
$2a_2$	+5.522		+4.866	+6.243	+6.449
$3b_1$	+5.924		+4.743	+6.007	+6.449
C	−10.551		−10.314	−12.057	−12.458
N	−11.539		−12.415	−12.340	−13.749
N_+	−15.557		−14.244	−14.368	−17.052
			7		
$1b_1$	−15.858	−17.403	−15.832	−16.374	−17.004
$1a_2$	−0.468	−9.521	−10.895	−10.763	−9.219
$2b_1$	−11.852	−11.285	−13.658	−11.695	−11.489
$2a_2$	+5.546	−5.439	+5.620	+6.575	+5.933
$3b_1$	+6.042	+5.653	+5.977	+5.502	+6.126
C	−10.160	+0.728	−10.296	−12.068	−11.841
N	−12.520	−11.839	−12.904	−12.418	−13.456
N_+	−13.693	−14.863	−13.980	−14.759	−14.011
			8		
$1b_1$	−15.593	−15.332	−16.352	−17.798	−17.071
$1a_2$	−12.052	−13.965	−11.580	−11.210	−11.401
$2b_1$	−0.320	−10.384	−10.885	−9.971	−9.548
$2a_2$	+7.036	+5.560	+5.719	+5.058	+5.520
$3b_1$	+5.819	+5.962	+6.344	+6.159	+6.018
C	−10.484	−10.232	−12.424	+1.402	−13.024
N	−12.266	−12.464	−12.631	−13.812	−14.206
N_+	−12.881	−14.244	−13.420	−14.658	−15.689
			9		
$1b_1$	−15.769	−16.886		−16.002	−17.712
$1a_2$	−11.512	−10.310		−11.361	−10.181
$2b_1$	−0.864	−10.202		−12.160	−10.344
$2a_2$	+5.438	+5.198		+5.697	+5.697
$3b_1$	+6.133	+5.572		+6.491	+6.491
C	−10.907	+0.228		−12.526	−12.901
N	−12.963	−10.965		−12.513	−13.568
N_+	−14.074	−16.886		−13.881	−14.463

for **23N5PBBAT**, giving an energy 23.2 kcal mole^{-1} higher than that of the triplet as expected. Optimization calculations on the singlet open-shell species were not pursued. The results of these calculations suggest that **6** should exhibit triplet diradical reactivity. However, this is not in agreement with the observed chemistry of **10**, which is reported to possess a high degree of electrophilic reactivity. The results of the calculations suggest that **10** should show triplet diradical properties (it is doubtful that the *t*-butyl group would cause such a structural change that a different electronic configuration would be favored). The electronic configuration implied in **10a** would be a six π-electron singlet configuration that would be expected to exhibit electrophilic reactivity. However, previously published calculations have indicated that the **34N6PS** configuration apparently does not represent a minimum energy structure, instead undergoing spontaneous ring opening by cleavage of the N–N bond [8]. The triple configurations **23N5PBBAT** and **23N6PT** possess very low-lying singly occupied π(+0.790 eV) and nonbonded σ MO's (+0.700 eV), which will impart electrophilic character to the triplet diradical states. Whether these states react both as radical and electrophilic species cannot be assessed. It should also be noted that the **23N4PBAS** singlet state poessesses and extremely low-lying unoccupied π MO (−0.599 eV) indicating a high degree of π electrophilicity. However, this state lies so much higher in energy that formation and observation of its chemistry is improbable.

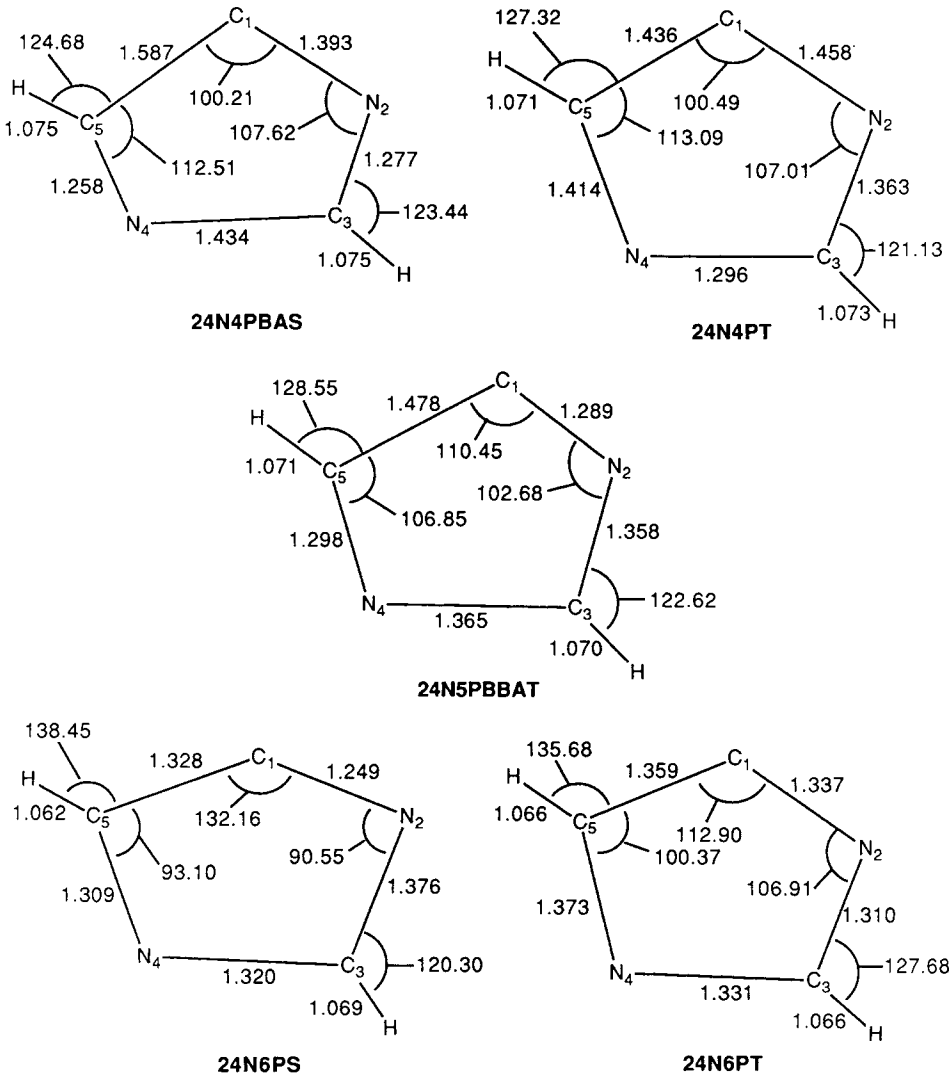


FIGURE 3 Calculated structural parameters for the various electronic states of **7**.

The 2,4-Diazacyclopentadienylidene System (**7**)

The calculated geometries for the various electronic states of **7** are shown in Figure 3. The calculated geometries of the various electronic states of **7** reflect the occupancy of the π MO's as observed with **6**. The effect of the occupancy of the C MO on the C_5–C_1–N_2 bond angle is even more pronounced than with **6**. In the **4P** states, in which the C MO is doubly occupied, the C_5–C_1–N_2 bond angles are 100.21° and 100.49°. In the **5PT** and **6PT** states, in which the C MO is singly occupied, the C_5–C_1–N_2 angles are 110.45° and 112.90°, while in the **6PS** configuration, in which the C MO is vacant, the angle has increased dramatically to 132.16°. This reflects the increasing carbocationic character of C_1, which increasingly prefers larger C_5–C_1–N_2 bond angles.

The total energies of the various electronic configurations of the **24N** system are given in Table 3, and the energies of the π and nonbonded orbitals are given in Table 1. At the 6-31G* level the **24N5PBBAT** configuration is considerably lower in energy than the other states. However, at the MP2/6-31G* level **24N5PBBAT** is only slightly lower in energy (0.4 kcal mole^{-1}) than the **24N6PS** configuration. As there is extensive contamination of the UHF wave function of **24N5PBBAT** by higher spin states (as indicated by the values of $< S^2 >$ it is entirely possible that the six π-electron singlet species might actually be lower in energy than **24N5PBBAT**. Regardless, the calculations indicate that the five π-electron, π,σ-triplet, and the aromatic six π-electron singlet are close in energy, and are possibly capable of coexistence under experimental conditions resulting in reactivity consistent with both triplet diradical and singlet electrophilic species. In addition, the unoccupied C MO of the six π-electron singlet lies very low in energy (+0.728 eV, see Table 2), which will impart highly reactive electrophilic character at C_1. In this case the **6PT** configuration lies considerably above the **6PS** state by 30.9 kcal mole^{-1} in contrast to that with **6**.

TABLE 3 Total (au) and Relative (kcal mole^{-1}) MP2/6-31G* Energies of the **5PT** and **6PS** States of **6–9**

System	**5PT**	**6PS**
23N (6)	**−224.12638** (35.4)	—
24N (7)	**−224.18254** (0.2)	−224.18183 (9.6)
25N (8)	−224.18280 (0.0)	**−224.19707** (0.0)
34N (9)	−224.12591 (35.7)	**−224.13883** (36.5)

The 2,5-Diazoylidene System (**8**)

The calculated geometrical parameters for the various electronic states of **8** are given in Figure 4. In this system the bond lengths and the N_5–C_1–N_2 bond angles are quite sensitive to both the occupancy of the π and the σ nonbonded pair MO's. The length of the N_2–C_3 bond (and the symmetry related N_5–C_4 bond) increases as the occupancy of the $2b_1$ MO increases and as the occupancy of the $1a_2$ MO decreases, as observed in the various electronic states of **6** and **7**. The lengths of the C_1–N_2 (C_1–N_5) bonds decrease substantially as the occupancy of the predominantly C MO decreases. In this system the predominantly C nonbonded MO is antibonding between C_1 and N_2 and N_5 (see Figure 1). In addition, there is an even greater increase in the N_5–C_1–N_2 bond angle as the occupancy of the C nonbonded MO decreases; the N_5–C_1–N_2 bond angle in the **25N6PS** configuration is calculated to be an amazing 143.53°, which is compensated for by a dramatic decrease in the C_1–N_2–C_3 and C_1–N_5–C_4 bond angles to 88.46°. This increase in the N_5–C_1–N_2 bond angle appears to be the result of an increased electron deficiency on C_1 that stems from the increased inductive withdrawing effects of two nitrogen atoms attached to C_1.

The total energies of the various electronic states of **8** are given in Table 1. The energies of the π and σ nonbonded MO's are given in Table 2. At the 6-31G* level the five π-electron, π,σ-triplet configuration **25N5PBABT** is calculated to be substantially lower in energy than the other electronic states. At the MP2/6-31G* level, however, the aromatic six π-electron singlet states **25N6PS** is calculated to be

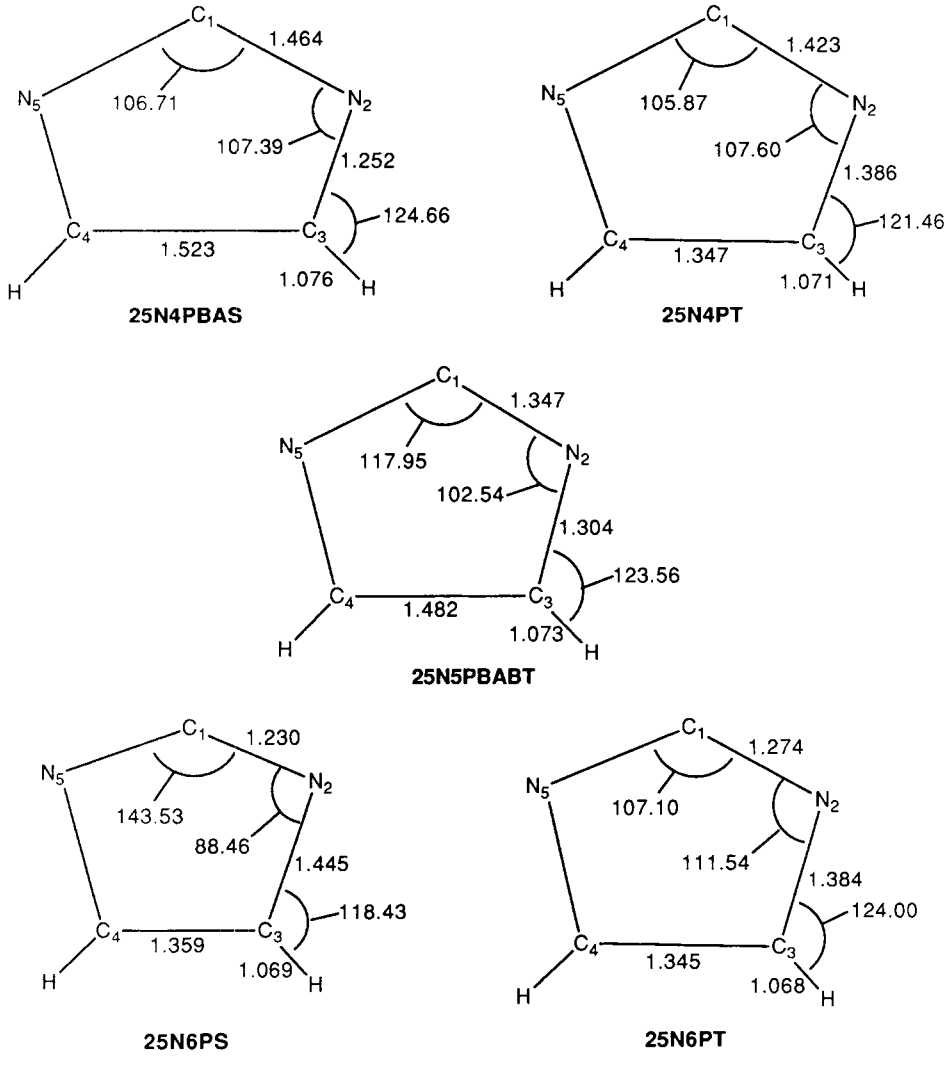


FIGURE 4 Calculated structural parameters for the various electronic states of **8**.

lower in energy than the **25N5PBABT** state by 9.0 kcal mole^{-1}. The **6PT** configuration lies considerably above the **6PS** state by 25.0 kcal mole^{-1}. These results suggest that the **25N6PS** configuration is the lowest energy state for **8**. Diazoylidene **8** does show electrophilic characteristics, but it also displays triplet diradical characteristics. The relatively reduced electrophilic reactivity might be attributed to the higher energy of the predominantly C MO LUMO (+1.402 eV, Table 2) compared to the six π-electron singlet states of **7**.

The 3,4-Diazoylidene System

The calculated geometrical parameters for the various electronic states of **9** are given in Figure 5. (A local minimum-energy structure could not be located for the four π-electron triplet state.) The calculated structures for the various states of **9** show the same dependence of C_2–N_3 (C_5–N_4) bond lengths on the type and occupancy of the π MO's and the C_5–C_1–C_2 bond angles on the degree of occupancy of the C MO as observed with **6–8**.

The total energies of the various electronic states of **9** are given in Table 1, and the energies of the π and σ nonbonding MO's are given in Table 2. At the 6-31G* level the five π-electron, π,σ-triplet configuration is calculated to be much lower in energy than the other electronic states. At the MP2/6-31G* level, however, the aromatic six π-electron configuration **34N6PS** is calculated to be lower in energy than the **5PT** configuration by 8.1 kcal mole^{-1}. Considering also that the unoccupied C MO of **34N6PS** lies very low in energy (+0.228 eV) strongly suggests that **6** and its derivatives should exhibit highly electrophilic characteristics. Very interestingly, in this system the **6PT** state is calculated to lie only 5.5 kcal mole^{-1} above the **6PS** state. It is also interesting to note that the **34N4PBAS** configuration has an exceedingly low-lying π MO (−0.864 eV, Table 2) and should show high π electrophilicity. However, considering that it lies considerably higher in energy above the **34N6PS** and **34N5PBAS** states, its chemistry probably would not be observable.

SUMMARY

Comparison of the Total Energies of the Lowest-Energy Electronic States of **6–9**

Table 3 summarizes the total and relative energies of the **5PT** and **6PS** states of **6–9**. The lowest energy

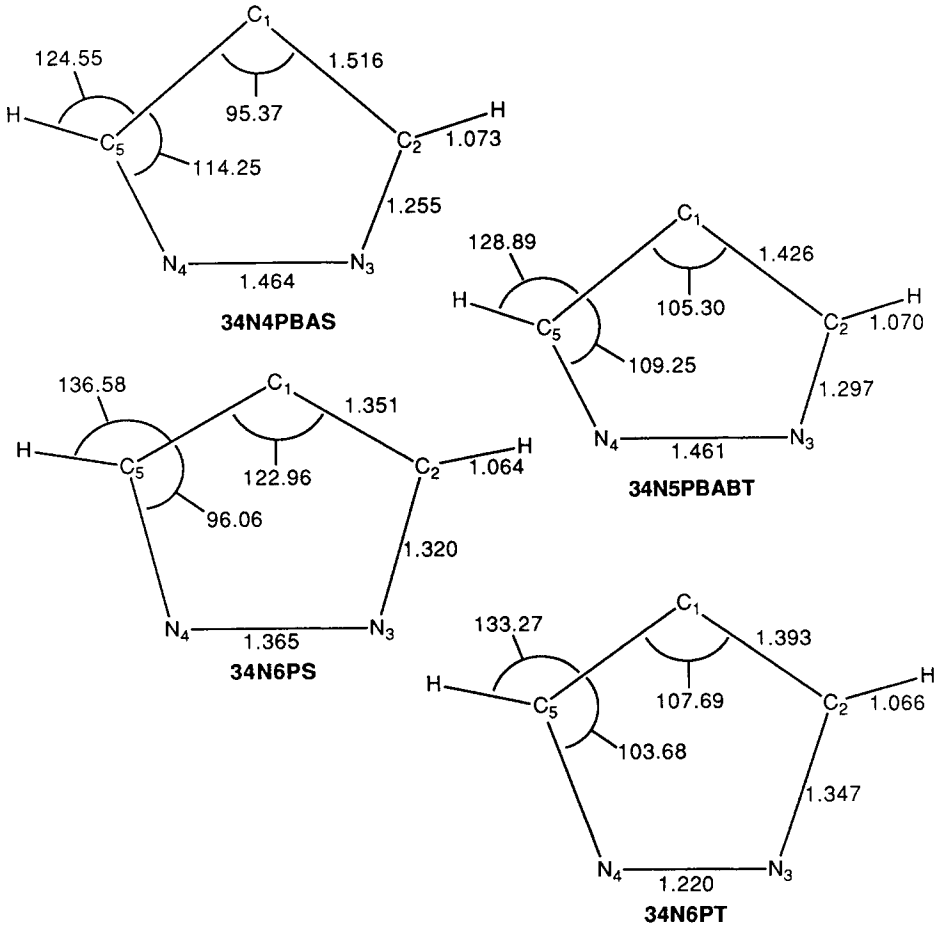


FIGURE 5 Calculated structural parameters for the various electronic states of **9**.

configuration for each system is indicated in boldface numbers, while the relative energies for each type of configuration are given in parentheses. In both the **5PT** and **6PS** states, the **24N** and **25N** systems, in which the nitrogen atoms are not directly bonded to each other, are quite similar in energy and are considerably lower in energy than the **23N** and **34N** systems in which the two nitrogens are directly bonded to each other. This would appear to be due to greater nonbonded pair repulsion when the two nitrogen atoms are directly bonded to each other.

In the **24N** system the five π-electron π,σ-triplet state is only very slightly lower in energy than the aromatic, six π-electron singlet, while in the **25N** and **34N** systems the aromatic six π-electron singlet states are lower in energy by 9.0 and 8.1 kcal mole^{-1}. In the former it appears that the extra stabilization gained by having an aromatic π-system in the **6PS** and **6PT** states is comparable to that gained by placing an electron in a lower-lying σ MO relative to being in a π MO, whereas in the latter there appears to be a slight energetic advantage in having an aromatic π-system.

Comparison of the Relative Energies of the σ Nonbonded MO's

One of the objectives of this study was to determine the effect of the position in the ring of the two nitrogens atoms on the relative energies of the σ nonbonded MO's, particularly on the C MO when doubly occupied and when vacant, and on the splitting of the N_+ and N_- MO's. For this purpose a comparison is made of the energies of the σ nonbonded MO's in the **4PS** and **6PS** states of **6–9**. These energies are summarized in Table 4. When the two nitrogen atoms are directly bonded to each other there is a considerably larger splitting of the N_+ and N_- MO's than when 1,3-situated as expected.

In the **4PS** states the lowest-lying C MO is observed in the **34N** system where there is very little mixing of the N_+ MO with the C MO. The highest-lying C MO occurs in the **24N** system in which the C MO mixes with only one nitrogen nonbonding MO. In the **23N** and **25N** systems, which have allyl-type σ MO's, the energy of the C MO is intermediate between the C MO's of the **34N** and **24N** systems. A priori, one might have guessed that the mixing of the C MO with both the N_+ and N_- MO's would have elevated the C MO above the energy of the C MO in the **24N** system. The lowering of the energy of the C MO's in the **23N** and **25N** systems must be because of the effect of the greater electronegativity (nuclear potential) by the two nitrogen atoms in the allyl-type σ MO's.

TABLE 4 Energies of the σ Nonbonding MO's in the **4PS** and **6PS** States of **6–9**

MO	**6**	**7**	**8**	**9**
		4PS state		
C	−10.551	−10.907	−10.160	−10.484
N_-	−11.539	−12.963	−12.520	−12.266
N_+	−15.557	−14.074	−13.693	−12.881
		6PS state		
C	—	+0.228	+0.728	+1.402
N_-	—	−10.965	−11.839	−13.812
N_+	—	−16.886	−14.963	−14.658

Similar trends are observed in the **6PS** states. In particular, as the number of the nitrogen nonbonding MO's that mix with the C MO increases, the energy of the unoccupied C MO becomes more positive. This would suggest that adjacent substitution of C–H by N in cyclopentadienylidene lowers the electrophilic reactivity of the species.

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