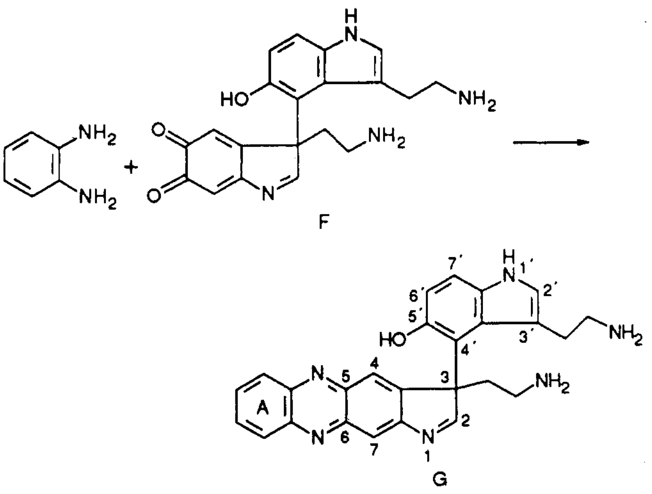
Scheme I



electrochemical oxidation at 0.30 V in 0.01 M HCl.

3-(2-Aminoethyl)-3-[3′-(2-aminoethyl)-5′-hydroxyindol-4′-yl]indolenine-5,6-dione (F). In 0.01 M HCl this bright orange compound shows absorption bands at λ_{max} = 458, 282, 215 nm. FAB-MS (thioglycerol matrix) showed intense ions at m/e 367.1770 ($C_{20}H_{23}N_4O_3$, calcd m/e 367.1770) and at m/e = 365.1614 ($C_{20}H_{21}N_4O_3$, calcd m/e = 365.1614). These results indicate that under the FAB-MS conditions employed F is partially reduced. Similar effects with other easily reducible compounds have been noted by other workers.[6,7] The FAB-MS results show that F is a dimer consisting of one residue of 5-HT and a second residue that contains an additional oxygen atom.

Compound F was not stable in either Me$_2$SO-d_6 or D_2O as evidenced by the gradual disappearance of ^{1}H NMR peaks and the appearance of many new peaks with the result that a very complex spectrum was ultimately obtained. The mass and UV-visible spectra of F along with partial interpretation of the NMR spectrum suggested that this compound possessed an *o*-quinone residue. This was confirmed by reacting F with *o*-phenylenediamine using a procedure described elsewhere.[2] After purification of the resulting product by chromatography on Sephadex LH-20[2] a stable, golden product (λ_{max} in 0.01 M HCl: 530 sh, 498, 390, 316 sh, 280, 231 nm) was obtained. FAB-MS (glycerol matrix) on this compound showed an intense pseudomolecular ion (MH$^+$) at m/e 437.2090 ($C_{26}H_{25}N_6O_1$, calcd m/e 437.2090). ^{1}H NMR (Me$_2$SO-d_6): δ 2.68 (m, 1 H, CH$_2$), 2.90 (m, 3 H, CH$_2$), 3.61 (m, 4 H, CH$_2$CH$_2$), 6.48 (s, 1 H, C(2)-H), 6.71 (d, $J_{6',7'}$ = 8.7 Hz, 1 H, C(6′)-H), 7.01 (s, 1 H, C(4)-H), 7.26 (d, $J_{6',7'}$ = 8.7 Hz, 1 H, C(7′)-H), 7.48 (s, 1 H, C(2′)-H), 7.76 (m, 1 H, ring A), 7.86 (m, 1 H, ring A), 7.95 (s, 1 H, C(7)-H), 8.10 (m, 2 H, ring A), 8.32 (s, 3 H, NH$_3^+$), 8.45 (s, 3 H, NH$_3^+$), 9.28 (s, 1 H, OH), 11.37 (d, $J_{1',2'}$ = 2.4 Hz, N(1′)-H). Addition of D_2O caused the resonances at 8.32, 8.45, 9.28, and 11.37 to disappear. These spectral data indicate that this compound has the structure G (Scheme I). Such a structure can only be formed by condensation of *o*-phenylenediamine with dimer F, which contains a 5,6-dione residue, as illustrated in Scheme I. The ^{1}H NMR spectrum of G had two important features in common with that of A. Thus, in Me$_2$SO-d_6, the C(2) proton of G (δ 6.48) and A (δ 6.08) both show a high-field shift compared to that of 5-HT (δ 7.13). The high-field region of the ^{1}H NMR spectrum of A and G show an unresolved multiplet centered at δ 3.52 and δ 3.61, respectively, corresponding to the ethylamino side chain of a 5-HT residue. In addition, both compounds show complex systems for the other side chain. For A these appear as δ 2.42 (m, 1 H) and 2.70 (m, 3 H) and for B δ 2.68 (m, 1 H) and 2.90 (m, 3 H). These systems are consistent with the presence of chiral centers at the C(3)-positions in both compounds.

The structures A–G described above are based upon spectral methods of analysis. Establishment of these structures beyond any doubt would require independent synthesis.

Acknowledgment. This work was supported by Grant No. GM-32367 from the National Institutes of Health.

Theoretical Studies on 2- and 3-Azacyclopentadienylidene. An Analysis of Aromatic versus Nonaromatic π-Systems and Nonbonded-Pair Interactions

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Received July 12, 1988

High-level ab initio calculations have been carried out on the various electronic configurations of the 2- and 3-azacyclopentadienylidenes **4** and **5**. 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* level. In each system the lowest energy configuration is calculated to be the five π-electron, σ,π triplet state having a $1b_1^2,2b_1^2,1a_2^1$ π configuration. The six π-electron, closed-shell states are very close in energy and, in fact, may be lower in energy than the pure triplet states. The LUMO's of the six π-electron, closed-shell species have a dominant contribution from the vacant σ orbital on the carbene carbon atom and are very low in energy ($\sim$+1.1 eV). The results of these calculations suggest that the lowest energy derivatives of **4** and **5** should exhibit chemistry typical of either, or both, triplet diradical and highly reactive electrophilic closed-shell singlet species. This is consistent with various experimental observations. The four π-electron, closed-shell singlet states are considerably higher in energy than the six π-electron, closed-shell singlet states. The highest-energy states are calculated to be the four and six π-electron, open-shell triplets states which are the triplet excited states of the four and six π-electron closed-shell singlet states. In the lowest energy states, the configurations of **4** are calculated to be lower in energy, while in the higher energy states, the configurations of **5** are calculated to be lower in energy. These energy differences are interpreted in terms of stabilizing delocalization effects and destablilzing electron repulsion effects.

Introduction

Cyclic π carbenes such as **1**-**3** have received considerable attention both theoretically and experimentally. The lowest member of the series, cyclopropenylidene (**1**), has been subjected to a number of theoretical infestigations. High-level ab initio calculations on the closed-shell singlet and open-shell triplet states of **1** using the Huzinaga-


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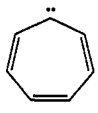
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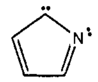
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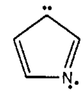
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Dunning double-ζ (DZ) and double-ζ plus polarization (DZ + P) basis sets indicated that the $\pi^2\sigma^2$ singlet $^1A_1$ state lies

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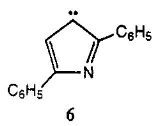
~70 kcal per mole lower in energy than the two $\pi^3\sigma^1$ triplet $^3B_1$ and $^3A_2$ states which lie close in energy.[1a] More recent ab initio calculations also considered the various open-shell singlet states.[1b] At the CISD/6-31G* level, the closed-shell singlet $^1A_1$ state was calculated to be lowest in energy, followed by the $^3A_2$ (66.4 kcal per mole), the triplet $^3B_1$ (69.9), the open-shell $\pi^3\sigma^1$ singlet $^1A_2$ (70.1), the open-shell $\pi^3\sigma^1$ singlet $^1B_1$ (119.0), the open-shell $\pi^3\sigma^1$ singlet $^1B_2$ (198.1), and the $\pi^4\sigma^0$ singlet 2^1A_1 (235.7) state.[1b] The 1^1A_1 state is stabilized by the presence of an aromatic, two π-electron system, and the occupying of the lower lying sp²-type σ MO (relative to a π MO). The $^1A_2$ and $^1B_1$ represent singly excited states of the $^1A_1$ state, while the 2^1A_1 state is a doubly excited, singlet state. In contrast to the results of extended Hückel[1c] and INDO[1d] calculations, which predicted that **1** should be a highly nucleophilic carbene (consistent with the observed properties of the diphenyl derivative),[2] the results of the ab initio calculations indicated that **1** should possess only weakly nucleophilic properties.

High-level ab initio calculations on cycloheptatrienylidene, **3**, also indicate that the $\pi^6\sigma^2$ singlet state lies lower in energy that the $\pi^7\sigma^1$ triplet state.[3] In this case, however, the singlet–triplet energy gap is much smaller than with **1**, being calculated to be 1.8 kcal per mole at the fully optimized (DZ + P) [C(9s5p1d/4s2p1d, H(4s/2s)] basis level, with the triplet described at the single-configuration SCF level and the singlet at the two-configuration SCF level.[3] Low-temperature ESR studies on **3** have produced strong ESR signals leading to the suggestion that the triplet state is possibly lower in energy than the singlet, or if higher in energy, it must be reasonably close in energy to the singlet.[4]

In contrast to **1** and **3**, in which the aromatic π structures represent the lowest energy singlet states, calculations at the MNDO[5a] and ab initio MCSCF[5b] levels indicate that the lowest energy closed-shell singlet state of cyclopentadienylidene, **2**, possesses the nonaromatic $\pi^4\sigma^2$ configuration; the stabilization gained by having an aromatic $\pi^6\sigma^0$ configuration apparently being less than the energy required to promote the two electrons from the lower lying sp²-type σ MO to the π system. Extended Hückel calculations indicate that the triplet state is lowest in energy.[1c] Very recent high-level ab initio calculations indicate that the lowest energy state is the $^3B_1$ triplet, with the lowest energy closed-shell singlet 12.2 kcal/mol higher in energy (CISD/6-31G*).[1b] The photolysis of diazocyclopentadiene at 77 or 4 K produces a triplet ESR spectrum,[6] although in solution the photolysis of diazocyclopentadiene produces products characteristic of a singlet carbene.[6b]

The substitution of one or more CH units in **2** by one or more nitrogen atoms produces a class of compounds referred to as azoylidenes, examples being **4** and **5**. 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. Azoylidene **6**[7] undergoes electrophilic substitution and addition reactions with substituted benzenes, and hydrogen atom abstraction and C–H bond insertion reactions with toluene, cumene, and cyclohexane.[8] These observations have been interpreted in terms of **6** reacting via both singlet (**6s**) and triplet (**6t**) states.[8b,9]



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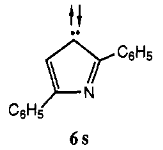
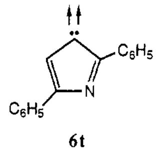
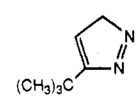


6s



6t

Azoylidene **7** undergoes electrophilic substitution and addition reactions with substituted benzenes but does not undergo hydrogen atom abstraction reactions.[10] Azoylidene **7** has been described as an unusually unselective and energetic singlet electrophile whose electronic structure is best represented as **7a**. Other substituted azoylidenes related to **7** show similar characteristics.



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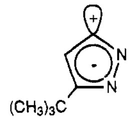
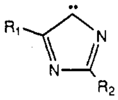
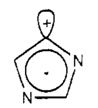


7a

Azoylidene **8a** has been described as a highly reactive, indiscriminate electrophile in reactions with substituted benzenes and was observed not to undergo hydrogen atom abstraction or C–H bond insertion reactions.[11] No ESR signals were detected for **8a**. The electronic structure of **8a** was represented as shown in **9**.[11] Very interestingly, azoylidenes **8b** and **8c** undergo hydrogen atom abstraction and C–H bond insertion reactions[12] and do give rise to an ESR signal,[13] both suggestive of the presence of a low lying triplet diradical state. Azoylidene **10**[7] shows both electrophilic and diradical characteristics.[14] Finally, azoylidene **11**[7] undergoes electrophilic substitution reactions with substituted benzenes, but apparently no hydrogen atom abstraction or insertion reactions, and has been represented by the electronic configuration shown as **11a**.[15] Interestingly, **11** undergoes ring opening to form **12**, a process which preliminary calculations carried out by the author indicate the ring-opening process to occur sponta-



8a $R_1 = H, R_2 = H$
b $R_1 = \text{-CONH}_2, R_2 = H$
c $R_1 = R_2 = \text{-C}_6H_5$



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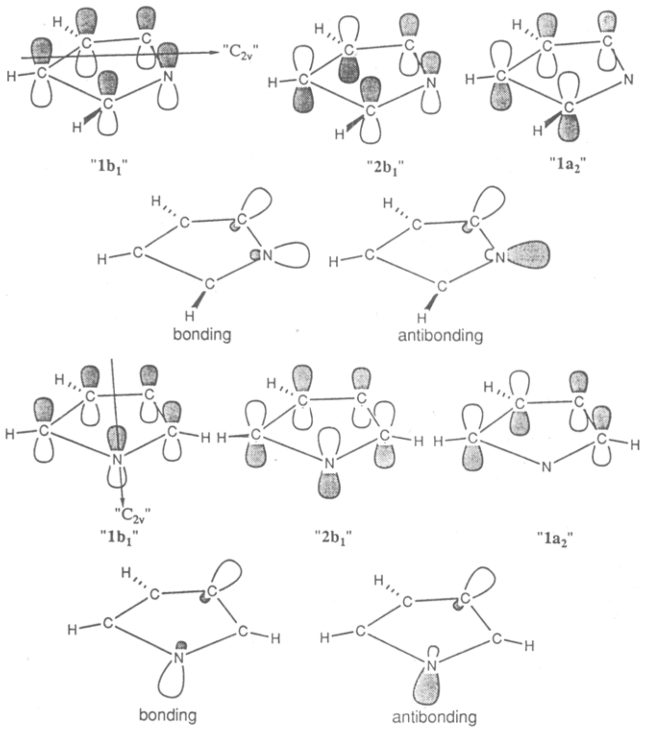
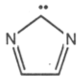


Figure 1. General respresentation of the π and σ nonbonded MO's of **4** and **5**.

neously from the six π-electron, singlet state represented in **11a**.[16]



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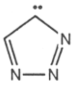
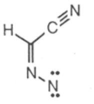


11

11a



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Overall, it appears that azoylidenes react via both singlet and triplet states and that the electronic structure of the ground state is dependent on the degree and position of nitrogen substitution, as well as on the nature of the substituents attached to the ring.

The azoylidene systems provide for an interesting analysis of several electronic effects on the relative energies of the various possible electronic configurations. In this article, attention will be focused on the two monoazacyclopentadienylidenes **4** and **5**. The substitution of CH in **2** by N reduces the symmetry of the system, which destroys the degeneracy of the second and third π MO's in **2**. In **4** and **5** this provides for two different $\pi^4\sigma^2$ closed-shell, singlet states and two different $\pi^5\sigma^1$ open-shell, singlet and triplet states in contrast to the single states with **2**. The substitution of CH by N also introduces other effects. The presence of the nitrogen atom in **4** and **5** will lower the energies of the σ-type MO's to a greater extent than the π MO's, which will in turn increase the promotion energies for the elevation of an electron from the sp^2-type σ MO's to a π MO. This should result in a relative stabilization of the nonaromatic $\pi^4\sigma^2$ states. However, the nonbonding pair orbitals on the nitrogen atoms will form symmetric (bonding) and antisymmetric (antibonding) combination MO's with the σ-type nonbonding orbital on the carbene carbon, which in the $\pi^4\sigma^2$ states requires occupancy of the antisymmetric (antibonding) combination.[17] This will result in the relative destabilization of these states. Thus, there are countering effects which will affect the relative energies of the various electronic states. Herein we report the results of a theoretical study on the various closed-shell singlet and open-shell triplet electronic states of **4** and **5**. Calculations have not been carried out on the open-shell singlet states which should be intermediate in energy between the $\pi^4\sigma^2$ and $\pi^6\sigma^0$ closed-shell singlet states, the main objective being to determine whether the ground state will be the singlet or the triplet, and if the singlet, what its electronic configuration is.

Table I. Total Energies (Hartrees) of the 2N6PS and 2N4PBBS States as a Function of Basis Set

basis set	2N6PS	2N4PBBS	ΔE, kcal/mol
3-21G	−206.297 51	−206.300 82	+2.08
6-31G	−207.377 61	−207.379 88	+1.42
6-31G*	−207.484 72	−207.484 44	−0.18
MP2/6-31G*	−208.149 88	−208.107 76	−26.43

In order to facilitate the discussion of the orbital occupancy of the various configurations of **4** and **5**, the orbital symmetries will be referred to in the C_{2v} point group. Although **4** and **5** belong to the C_s point group, the MO's show pseudo-C_{2v} properties, the pseudo-C_2 axes being oriented as shown in Figure 1. (The "pseudo-C_{2v}" axes do not intersect the nitrogen atom, but are displaced slightly toward the more electronegative carbene carbon atom). The π MO's will be 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 referred to simply as *bonding* or *antibonding* nonbonded MO's. Initial geometry optimization calculations were carried out at the 3-21G level with the GAUSSIAN82[18a] and -86[18b] packages of programs. Subsequent geometry optimization calculations were carried out at the 6-31G* level, with final single point energies being calculated at the MP2/6-31G* level.

Results and Discussion

2-Azacyclopentadienylidene System. The various electronic configurations for **4** will be designated by **2N**, followed by the number of π electrons **NP**, the π MO occupancy when appropriate, and finally by the multiplicity (**S** for single and **T** for triplet). The seven possible configurations considered in this study are thus designated as **2N6PS** having a π MO configuration of $1b_1{}^2,2b_1{}^2,1a_2{}^2$ with the σ bonding MO doubly occupied, **2N6PT** with the σ bonding and antibonding MO's singly occupied, **2N5PBBAT**, having a π MO configuration of $1b_1{}^2,2b_1{}^2,1a_2{}^1$ with the σ bonding MO doubly occupied and the antibonding MO singly occupied, **2N5PBABT** having a π MO configuration of $1b_1{}^2,1a_2{}^2,2b_1{}^1$ with the σ bonding MO doubly occupied and the antibonding MO singly occupied, **2N4PBBS** having a π MO configuration of $1b_1{}^2,2b_1{}^2$ with the σ bonding and antibonding MO's both doubly occupied, **2N4PBAS** having a π MO configuration of $1b_1{}^2,1a_2{}^2$, and **2N4PT** having a π MO configuration of $1b_1{}^2,1b_1{}^1,1a_2{}^1$. The **2N6PS** and **2N6PT** configurations are aromatic π systems, the others configurations having nonaromatic π systems.

Initial calculations were carried out on the **2N4PBBS** and **2N6PS** systems. At the fully geometry optimized

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Table II. Total Energies (Hartrees) of the Various Electronic Configurations of 4 at the 6-31G* and MP2/6-31G* Levels

configuration	6.31G*	ΔE^a	MP2/6-31G*	ΔE^a
2N5PBBAT	−207.556 64	0.0	−208.155 46	0.0
2N6PS	−207.484 72	+45.1	−208.149 88	+3.5
2N4PBBS	−207.484 44	+45.3	−208.107 76	+29.9
2N6PT	−207.479 17	+48.6	−208.076 10	+49.8
2N4PT	−207.469 60	+54.6	−208.063 67	+57.6

[a] Relative energies in kilocalories per mole.

3-21G level the **2N4PBBS** configuration was calculated to be lower in energy by 2.08 kcal per mole. On going to higher level basis sets and the inclusion of polarization functions, however, the **2N6PS** configuration is calculated to be lower in energy (see Table I). For example, at the fully geometry optimized 6-31G* level the **2N6PS** configuration is calculated to be lower in energy by 0.18 kcal per mole. The inclusion of electron correlation at the MP2/6-31G* level on the 6-31G* optimized structures increased this difference significantly to 26.43 kcal per mole. Optimization at the MP2 level, or carrying out electron correlation calculations to the MP3 or MP4 levels, is expected to further increase this difference in energy in favor of the **2N6PS** configuration. Accordingly, it was not felt necessary to carry out calculations at these levels for this reason, and also because of the computer time required. In view of these findings, initial geometry optimization calculations were carried out at the 3-21G level to economically locate minimum energy structures, with the final geometry optimization calculations being carried out at the 6-31G* level with single point calculations then being carried out at the MP2/6-31G* or UMP2/6-31G* level. Attempts to locate local minima for the **2N5PBABT** and **2N4PBAS** configurations failed. Beginning with a reasonable geometry for the **2N5PBABT** configuration optimization was accomplished at the 3-21G level, giving an energy 5.64 kcal per mole higher than that for the **2N5PBBAT** configuration. Optimization at the 6-31G* level, however, could not be accomplished, and resulted in a slow conversion to the **2N5PBBAT** configuration. The 3-21G optimization calculations on the **2N5PBBAT** configuration suggested a rather flat energy surface around the 3-21G minimum for this configuration. Optimization calculations on geometries having a starting **2N4PBAS** configuration also resulted in conversion and optimization to the **2N4PBBS** configuration. The calculations on structures having the **2N4PBAS** configuration gave energies approximately 0.05 au higher in energy than the **2N4PBBS** configuration. Apparently the **2N4PBAS** configuration does not represent a local minimum energy structure. Calculations have not been carried out on the five π-electron open-shell singlet states; their energies expected to lie intermediate between the four and six π-electron closed-shell singlet states. The total energies of the **2N** species are given in Table II. The energies of the π and σ nonbonding MO's and the π MO coefficients are given in Tables V and VI of the supplementary material.

The calculated geometries of the five configurations for which local minima were found are given in Figure 2. The calculated geometries are quite sensitive to the electronic configuration and, for the most part, reflect the orbital characteristics of the π and σ nonbonding MO's that are occupied, the σ effects being fairly constant in the series. This is illustrated with the structures of the **2N4PS** and **2N6PS** configurations whose occupied π wave functions and π Mulliken populations are shown in Figure 3. In **2N4PS** the high degree of π bonding between C_4 and C_5 in both the $1b_1$ and the $2b_1$ MO's results in a short bond length, while the antibonding interactions in the $2b_1$ MO between C_1 and C_4, and C_3 and C_5, results in rather long

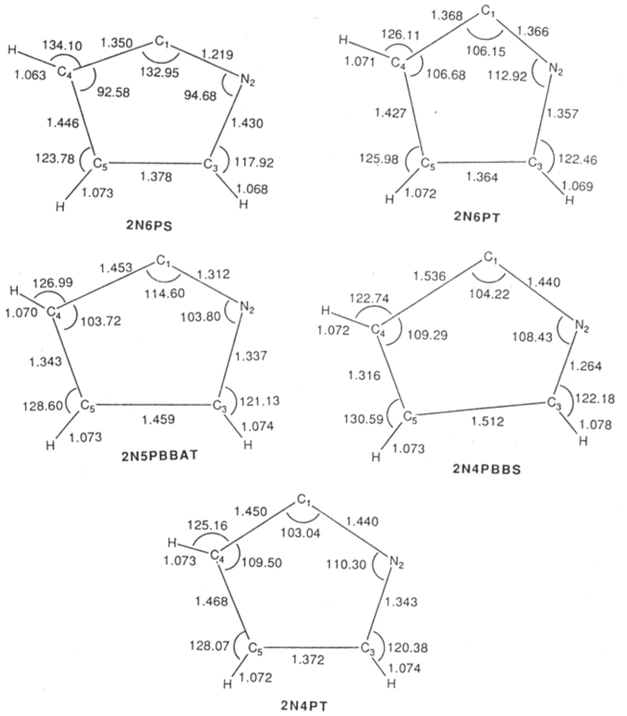


Figure 2. Calculated structural parameters for the various electronic configurations of **4**.

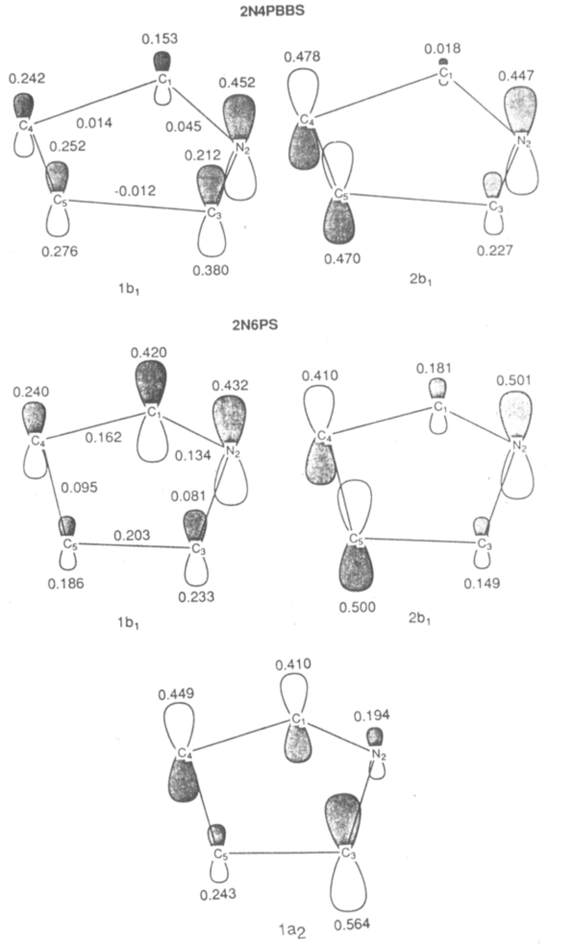
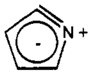


Figure 3. π Wave functions and π Mulliken populations (given inside rings) for the **2N4PS** and **2N6PS** configurations of **4**.

bonds. In **2N6PS** the blending of the bonding and antibonding characteristics of the three π MO's results in more similar bond lengths. The C_1–N_2 distances are very sensitive to the degree of occupancy of the bonding and antibonding σ nonbonding MO's. In **2N6PS** only the bonding combination MO is occupied, resulting in a very short bond length, and suggests than the structure should be more accurately respresented as an "yne" structure **13**.



13

In **2N4PS** both the bonding and the antibonding MO's are doubly occupied, the occupancy of the antibonding MO resulting in a substantial lengthening of the C_1–N_2 distance. The σ and σ,π triplet structures have intermediate C_1–N_2 distances commensurate with the single occupancy of the antibonding MO.

The lowest energy structure is the five π-electron triplet having the **2N5PBBAT** configuration (see Table 2). However, the UHF wave function is contaminated by higher spin state wave functions ($\langle S^2 \rangle = 2.0047$) which lowers the UHF energy below that of the pure triplet. At the MP2 level the six π-electron aromatic **2N6PS** is calculated to be only slightly higher in energy than the **2N5PBBAT** configuration (3.5 kcal per mole); however, due to the comtamination of the UHF wave function, the **2N6PS** state may actually be lower in energy than the pure triplet. It is obvious that these two states are very close in energy, and chemistry characteristic of either the singlet or triplet state might be anticipated. Although the chemistry of substituted 2-azacyclopentdienylidenes does not appear to have been studied, the diaza system **8**, which should be similar to **4**, has been studied and, depending on the nature of the substituents, displays chemical characteristics of both singlet and triplet states.[11–13]

Of the two closed-shell singlet states, the six π-electron system **2N6PS** is calculated to be lower in energy than the four π-electron system **2N4PBBS** at the MP2/6-31G* level by 26.4 kcal per mole. The gain in energy by having an aromatic π system and the reduction of the σ four-electron repulsion due to the occupancy of both the bonding and the antibonding σ MO's in the **2N4PBBS** configuration more than offsets the expected gain in energy by occupying a lower lying σ MO (−9.699 eV in **2N4PBBS** versus −8.673 eV for the $1a_2$ π MO in **2N6PS**) and increased π-space electron repulsion. The LUMO of **2N6PS** is the antibonding σ MO with dominant contributions from the AO's on the carbene carbon. The LUMO lies rather low in energy (+1.065 eV), which will result in a high degree of electrophilic reactivity. This is consistent with the observed reactions of the related system **8**, which has been described as a highly reactive, indiscriminate electrophile.[11]

3-Azacyclopentadienylidene System. The various electronic configurations for **5** are designated by 3N followed by an indication of the number of electrons in the π system, the occupancy of the π MO's, and the multiplicity as described above for **4**. Two five π-electron triplets were located, both having well-defined minima. As in the case with **4** the **3N4PBAS** configuration does not appear to represent a local minimum energy structure, calculations on reasonable geometries for the **3N4PBAS** configuration being much higher in energy (0.05 au), and attempted optimization resulting in the slow cross over to the **3N4PBBS** geometry and configuration. The energies of the π and σ nonbonded MO's and π coefficients are given in Tables V and VI of the supplementary material.

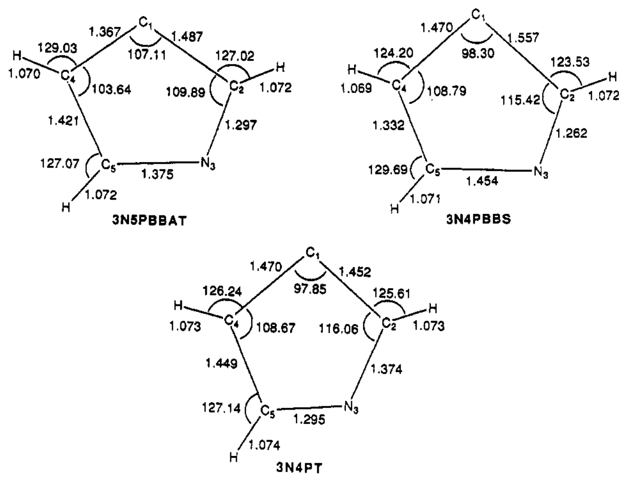


Figure 4. Calculated structural parameters for the various electronic configurations of **5**.

Table III. Total Energies (Hartrees) of the Various Electronic Configurations of 5

configuration	6-31G*	ΔE^a	MP2/6-31G*	ΔE^a
3N5PBBAT	−207.55093	0.0	−208.13877	0.0
3N6PS	−207.46067	+56.6	−208.13842	+0.2
2N5PBABT	−207.53828	+7.9	−208.11717	+13.6
2N4PBBS	−207.47990	+44.6	−208.10443	+21.5
3N4PT	−207.48483	+41.5	−208.08515	+33.6
3N6PT	−207.48114	+43.8	−208.08065	+36.5

[a] Relative energies in kilocalories per mole.

The geometries calculated for the various configurations of **5** are shown in Figure 4. As in the case of **4**, the calculated geometries of the various configurations are quite sensitive to the electronic configuration, and reflect the bonding and antibonding characteristics of the occupied π and σ nonbonding MO's.

The total and relative energies of the different electronic configurations at the 6-31G* and MP2/6-31G* levels are given in Table III. The **3N5PBBAT** and **3N6PS** configurations of **5** are calculated to be the lowest in energy and are very similar in total energy at the MP2- and UMP2/6-31G* levels. The UHF wave function of the **3N5PBBAT** configuration, however, is substantially contaminated with higher spin-state wave functions ($\langle S^2 \rangle = 2.0362$) which lowers the total calculated total energy at the UMP2 level. This suggests that the **3N6PS** configuration might actually be slightly lower in energy. Nonetheless, the two configurations must be very similar in total energy. The LUMO of **3N6PS** is the vacant σ orbital on the carbene carbon atom and is very low in energy (+1.165 eV). The results of the calculations are totally consistent with the observed chemistry of **6**, which is reported to undergo electrophilic substitution and addition reactions with substituted benzenes, and hydrogen abstraction and C–H bond insertion reactions with toluene, cumene, and cyclohexane.[8]

Of the two closed-shell singlet configurations, the **3N6PS** configuration having an aromatic π system is lower in energy than the **3N4PBBS** nonaromatic configuration, indicating that the energy gained by having an aromatic π system and lack of four-electron repulsion in the σ nonbonding MO's is greater that that gained by occupying a potentially lower energy σ MO. The energy difference at the MP2/6-31G* level is 21.3 kcal per mole, which is less than that observed in the singlet configurations fo **4** (26.4 kcal per mole). This decrease would appear be due to a decrease in the four-electron repulsion in the occupied bonding and antibonding σ MO's in **5** relative to that

Table IV. Differences in Energies (kcal/mol) between Electronic Configurations of 4 and 5

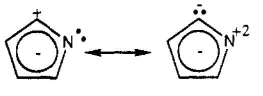
configuration	6-31G* ΔE (3N - 2N)	MP2/6-31G* ΔE (3N - 2N)
BBAT	-3.5	-10.5
6PS	-15.1	-7.2
4PBBS	-2.9	-2.1
6PT	+1.2	+2.9
4PT	+9.6	+13.5

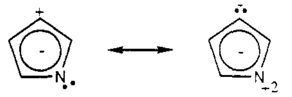
present in 4 because of the smaller overlap integral between the AO's of the σ MO's in 5.

Comparison of Energies of Configurations of 4 and 5. A comparison of the energies of the various electronic configurations of 4 and 5 provides a direct means of evaluating the effect of the position of the nitrogen atom on the relative stability of the carbene states. There is a very interesting trend in the relative stabilities. In the lowest energy **5BBAT** and **6PS** configurations the **2N** systems are more stable than the **3N** systems by 10.5 and 7.2 kcal per mole at the MP2/6-31G* level (see Table IV). As the energies of the states decrease, the **2N** systems become less stable relative to the **3N** systems, with a cross over at with the **6PT** configurations where the **3N** systems are now more stable than the **2N** systems.

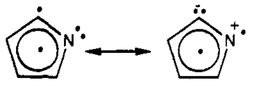
There appears to be two dominant factors which result in the observed trend: (1) a stabilization gained by delocalization of the nonbonded nitrogen AO with the carbene carbon AO to form the MO's and (2) a destabilization due to increased electron repulsion when the antisymmetric σ MO is occupied.

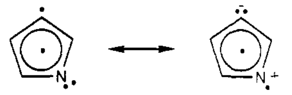
One might have expected that the greatest difference in energy would be seen with the **6PS** configuration, with the **2N** system being lower in energy because of the greater overlap integral between the nonbonded pair AO on the nitrogen atom and the σ AO on the carbene carbon atom compared to that in the **3N** system. However, such delocalization would result in greater charge density and separation in the **2N** system because of this greater overlap. This can be viewed in terms of the resonance contributing structures for the **6PS** configurations of 4 and 5 in which the multiply charged form contributes relatively more in 4 than in 5 because of the greater overlap. This must result in a substantial loss of the stabilization gained by the delocalization of the nonbonded pair of nitrogen in 4.





In the **5PBBAT** configurations delocalization of the nobonded nitrogen AO with the AO on the carbene carbon atom is possible and again is greater in the **2N** system than in the **3N** system because of the larger overlap integral between the AO's on the nitrogen and the carbene carbon atoms. In these cases, however, this delocalization does not result in the formation of additional charge density as is illustrated in the resonance contributing structures shown below. The addition of an electron to the antisymmetric σ MO should increase the electron repulsion in the σ MO's to a greater extent that the reduction in π-electron repulsion by loss of one electron.





In the **4PBBS** configurations of 4 and 5 the balance of the various contributing factors appears to be very similar.

It is not obvious what all of the contributing factors are in determining the relative energies of the **6PT** and **4PT** configurations or 4 and 5, although subtle differences in α and β electron distributions in these triplet states might play a role.

Supplementary Material Available: Tables of orbital energies and coefficients of 4 and 5 (5 pages). Ordering information is given on any current masthead page.

Polyethylene-Bound Soluble Recoverable Palladium(0) Catalysts

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Received December 21, 1988

The use of diphenylphosphine-terminated ethylene oligomers as ligands for palladium(0) and palladium(II) is described. With use of these polymeric ligands, it is possible to carry out homogeneous reactions characteristic of $(Ph_3P)_4Pd$ and $(Ph_3P)_2Pd(OAc)_2$ with essentially complete recovery of the Pd catalyst. The only limitation to repeated reuse of the catalyst is its immolative catalytic oxidation of the phosphine ligand by adventitious oxygen.

Hybrid catalysts combining the attributes of conventional homogeneous catalysts with the experimental simplicity of heterogeneous catalysts have proven to be fruitful subjects for research by both academic and industrial chemists.[1] However, while the concept of attaching a homogeneous catalyst to an insoluble polymer is both elegant and simple, there are some subtle problems associated with using insoluble polymers as supports for homogeneous catalysts. In particular, the microenvironment within a polymer and the heterogeneous nature of an insoluble polymer have led to altered or decreased activities, more difficult ligand synthesis and characterization, and undesirable diffusional limitations on reaction rates. As we and others have shown, soluble polymers are useful if largely unexplored alternatives to insoluble polymers.[2,3]

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