The Electronic Structure of Singlet Cyclopentadienylidene

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Abstract

We have carried out *ab initio* multiconfigurational self-consistent field calculations on the lowest singlet state of the carbene C_5H_4. We find that there are, along a restricted geometry deformation coordinate, two local energy minima corresponding to localized and delocalized π bonds having 4π and 6π electrons, respectively. The role of $4n + 2$ resonance in determining the nature of the electronic structure and reactivity of this carbene is analyzed and compared with that of other carbenes.

1. Introduction

In previous studies of the electronic structure of linear and cyclic carbenes [1–3], the importance of orbital hybridization of the electron-deficient carbene carbon, electron delocalization, and electron correlation have been investigated in order to gain a basic understanding of the nature of these important reaction intermediates. The most important correlation configuration of the $^1A_1$ states (within C_{2v} geometries) of methylene (CH_2), cyclopropenylidene (C_3H_2), and linear unsaturated carbenes can be described as a double excitation from an occupied a_1 orbital into a vacant b_1 orbital of the dominant configuration. A comparison [1] of the importance of this $a_1^2 \rightarrow b_1^2$ configuration in the cyclic C_3H_2 and the other systems [2, 3] shows that this correlation is less important in C_3H_2. In the C_3H_2 system, the b_1^2 configuration has 4π electrons and thus acquires antiaromatic character while the dominant a_1^2 configuration has 2π electrons and hence possesses aromatic stability because it satisfies the "$4n + 2$ rule." This indicates that for this cyclic carbene the aromatic nature of the correlation configuration must be considered along with the effects of delocation and hybridization.

In this brief report, the importance of aromatic factors is investigated for another cyclic carbene—cyclopentadienylidene. In contrast to the C_3H_2 carbene, both the delocalization effects and the aromatic nature of the $a_1^2 \rightarrow b_1^2$ configuration work in accord to increase the importance of this configuration. The result is that the b_1^2 configuration becomes not only more important than in CH_2 and C_3H_2 but it actually becomes the dominant configuration at some molecular geometries examined in this study.

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2. Methods Used

Multiconfiguration self-consistent field (MCSCF) calculations including the two configurations that are analogous to the two most important configurations of other carbenes have been performed on the lowest singlet state of the cyclic carbene cyclopentadienylidene C_5H_4. The atomic orbital basis used in these calculations is the ($4s2p$–C/$2s$–H) contracted Gaussian basis set used in the previous carbene studies by the authors [1, 2]. The integrals over the symmetry-adapted basis orbitals were calculated using the MOLECULE integral program [4]. SCF orbital expansion coefficients were calculated using the GRNFNC SCF program.* The super CI MCSCF method [5] was used for the first few iterations; then the exponential-i-lambda method [6], which is quadratically convergent, was used to accelerate convergence. The configuration analogous to the dominant a_1^2 configuration of the other carbene systems has 4π electrons while the b_1^2 configuration has 6π electrons. Approximate equilibrium geometries corresponding to electronic (diabatic) wavefunctions of a_1^2 or b_1^2 occupancy were obtained using the MNDO semiempirical SCF method [7]. Molecular geometries lying between these two extremes are characterized (purely for reasons of computational tractability) by the single parameter, α, defined in Figure 1 such that $\alpha = 0.0$ produces the approximate 6π configuration (b_1^2) optimal geometry and $\alpha = 1.0$ produces the approximate 4π configuration (a_1^2) optimal geometry. Because the two wavefunctions a_1^2 and b_1^2 used to define these two geometries are diabatic functions which mix to produce the two adiabatic states, these geometries are of limited significance. The "4π geometry" has alternating (short–long) C—C bond lengths thus indicating localized double bonds. The "6π geometry" displays the aromatic nature of this configuration by having C—C bond lengths which are more equal. *Ab initio* SCF calculations performed at the above two approximate equilibrium geometries corresponding to these two electronic configurations. The results of these SCF calculations show

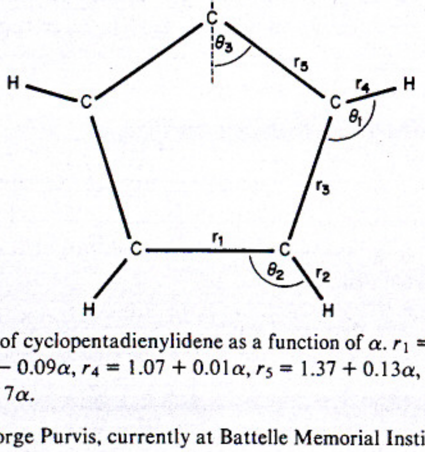

Figure 1. Geometry of cyclopentadienylidene as a function of α. $r_1 = 1.42 + 0.09\alpha$ bohr, $r_2 = 1.08$, $r_3 = 1.45 - 0.09\alpha$, $r_4 = 1.07 + 0.01\alpha$, $r_5 = 1.37 + 0.13\alpha$, $\theta_1 = 131 - 3\alpha$, $\theta_2 = 126 - 4\alpha$, $\theta_3 = 66 - 7\alpha$.

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that the 6π electron configuration is indeed the lowest in energy at the approximate 6π geometry ($\alpha = 0.0$) and that the 4π electron configuration is lowest in energy at the approximate 4π geometry ($\alpha = 1.0$). Thus there must be a "configuration curve crossing" somewhere between these two geometries. To explore this crossing, two-configuration MCSCF calculations have been performed at intermediate geometries given by values of α between 0.0 and 1.0. The purpose of these calculations was to determine the amount of configuration mixing and the shape of the potential energy surface between these two geometries. Again we stress that the surface defined for $0 \leq \alpha \leq 1.0$ is, by no means, meant to represent any kind of reaction or rearrangement surface. We have simply made one (arbitrary) choice of a deformation which preserves C_{2v} symmetry and connects the 4π and 6π geometries.

3. Discussion of Results

The lowest overall SCF-level energy was obtained with the 4π configuration at the 4π geometry. Initial SCF calculations on both the a_1^2 and b_1^2 configurations at intermediate geometries indicated that the two configurations should have equal diabatic energies at approximately $\alpha = 0.75$. Depending on the amount of configuration mixing and orbital relaxation present in the MCSCF wavefunction, the adiabatic energy minimum could be expected to lie anywhere between $\alpha = 0.5$ and $\alpha = 1.0$.

The results of our two-configuration MCSCF calculations are given in Table I. The $\alpha = 1.0$ (4π) geometry remains the lowest-energy geometry along this deformation coordinate. Although 10 kcal/mole of correlation energy was obtained at the $\alpha = 0.75$ geometry, the MCSCF energy was still higher at this geometry than the MCSCF energy at the 4π geometry. The amount of configuration mixing and the amount of correlation energy obtained decreases fairly rapidly between the $\alpha = 0.75$ geometry and the $\alpha = 1.0$ geometry until there is less mixing at $\alpha = 1.0$. The configuration mixing also decreases rapidly enough toward the $\alpha = 0.0$ geometry so that the 6π geometry represents a local energy minimum. The energy difference between the 6π geometry and the 4π geometry is 33 kcal/mole, whereas the electronic energy at the $\alpha = 0.5$ geometry is 15 kcal/mole above the local energy minimum of the 6π geometry.

If these two-configuration MCSCF calculations adequately, although ad-

TABLE I. Results of two-configuration MCSCF study.

Geometry	E(hartrees) ground/excited	$C_{4\pi}^{a}$	$C_{6\pi}^{a}$
$\alpha = 0.0$	-191.383176/-191.099907	0.0636	-0.9980
$\alpha = 0.5$	-191.359130/-191.176860	0.1027	-0.9947
$\alpha = 0.75$	-191.389714/-191.332835	0.4563	-0.8896
$\alpha = 1.0$	-191.435521/-191.224499	0.9726	-0.2326

[a] Expansion coefficients of the lowest $^1A_1$ adiabatic wavefunction.

mittedly in a geometrically constrained manner, describe the singlet-state electronic wavefunction of C_5H_4 and if the chosen reaction coordinate is representative of the transition between the above two geometries, then these two geometries should be considered independently in predicting the chemical reactivity of cyclopentadieneylidene. A potential barrier of 15 kcal/mole is sufficiently large to inhibit effectively the deformation of the 6π geometry to the more stable 4π geometry at room temperature. Because of the limited basis set and configuration list, the height of this barrier is not likely to be accurately represented. It is even possible that within more extensive calculations the barrier may be substantially reduced or may even disappear. The selective production of C_5H_4 with the 6π geometry might be achieved using photochemical elimination of electropositive substituents such as organomercurials. The 4π geometry carbene, since it is the most stable singlet, could be produced using more standard chemical procedures such as α elimination of halides induced by strong base. The reactivity of the 4π geometry carbene would be expected to be analogous to that of other electrophilic carbenes. Typical reactions include stereospecific insertion into olefins which is facilitated by the strong interaction of the carbene empty π orbital with the π system of the olefin. The reactivity of the 6π geometry carbene would be expected to be less dependent on π-system interactions and to rely more on the empty a_1 orbital of the carbene carbon. Examples of these reactions for other carbenes include insertion into Si—H and O—H bonds. Other carbenes which contain significant mixing of the two electronic states typically undergo both of these electrophilic reactions [8]. C_5H_4 might be expected to be slightly more selective because of the lack of mixing of the two electronic configurations at the 6π geometry which correspond to a local energy minimum.

The present calculations only examined a very limited part of the reaction surface and with only a limited amount of electron correlation in the wavefunction. These calculations do show that the aromatic nature of the electronic configuration plays an essential role in determining the relative importance of these configurations. We are extending these calculations by examining more of the potential energy surface and by including more electron correlation in the MCSCF wavefunction. The goal of these extensions is to more precisely determine the height of the potential barrier between the two local minima and locate the equilibrium geometry and the saddle point in the potential energy surface.

4. Summary and Conclusions

We have performed SCF and two-configuration MCSCF calculations on the cyclic carbene—cyclopentadienylidene. These calculations indicate that the lowest-energy conformation belongs to the configuration with 4π electrons and C—C bond lengths corresponding to localized double bonds. A local energy minimum involving the 6π electron configuration was found to have a geometry which corresponds to delocalized double bonds. Although a fairly large amount of configuration mixing arises at intermediate geometries, the 4π and 6π conformations are significantly different so that a potential energy barrier of height sufficient to prevent deformations between the two conformations is predicted.

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