Potential Surfaces for the Planar Cyclopentadienyl Radical and Cation

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Abstract: The potential surfaces for the planar cyclopentadienyl radical and cation have been obtained by ab initio π-space CI calculations, using a basis set of STO-3G orbitals. First-order Jahn–Teller effects in the lowest doublet state of the radical and second-order effects in the lowest singlet state of the cation result in equilibrium geometries for both these states that are substantially distorted in an e_2' mode away from D_{5h} symmetry. The energy lowering on distortion is calculated to be 7.1 kcal/mol in the radical and 13.4 kcal/mol in the cation. Pseudorotation is predicted to be extremely facile in both species. The large distortion energy calculated for the lowest singlet state of the cation results in a predicted singlet–triplet energy gap of only 7.3 kcal/mol. Problems in obtaining pure $^1E_2'$ wave functions for the cation are discussed.

The cyclopentadienyl cation and radical are open-shell molecules that have both been studied by EPR spectroscopy. The cation has been shown to be a ground-state triplet,[1] although the triplet represents a low-lying excited state in some substituted derivatives.[2] From the observed hyperfine splittings in the EPR spectrum of the radical, it has been inferred that at temperatures above 120 K the spin distribution around the ring is uniform on the EPR time scale, suggesting a very low barrier to pseudorotation in the radical.[3]

Semiempirical molecular orbital theory has been used to explore the potential surfaces for the cation[4] and the radical.[5] Ab initio SCF calculations also have been carried out on the cation.[6] The ab initio calculations on the cation predict a rather large energy difference (20.6 kcal/mol at the STO-3G level) between the triplet ground state at its D_{5h} minimum energy geometry and the lowest singlet state at its C_{2v} minimum. However, since CI was not included, the authors noted that this calculated energy difference was probably unreliable.

Our own interest in the potential surfaces for molecules containing open-shell π systems[7] prompted the ab initio CI study, the results of which are reported here. We have confirmed the very flat nature of the potential surface for pseudorotation in the planar radical and predict an equally flat surface for a similar process in the lowest singlet state of the planar cation. The singlet–triplet energy gap in the cation is found to be much smaller at the CI than at the SCF level. We have also discovered that even full π-space CI is incapable of providing a wholly satisfactory description of the potential surfaces for the two lowest singlet states of the cation around geometries of D_{5h} symmetry. The reasons for this finding are discussed, and a possible solution to the problem is proposed.

Theoretical Considerations

In the cyclopentadienyl radical, three electrons occupy a pair of π molecular orbitals that are degenerate at D_{5h} symmetry. This orbital occupancy gives rise to a $^2E_1''$ state, which, according to the Jahn–Teller theorem,[8] should undergo distortion away from D_{5h} symmetry along an e_2' distortion mode. The energy change on such a distortion is expected to be initially linear in the distortion coordinate. Thus, one component of $^2E_1''$ is stabilized by a positive e_{2y}' distortion, and the other is destabilized. A distortion in the opposite ($-e_{2y}'$) direction has the opposite effect on the energies of the two wave functions. On $\pm e_{2x}'$ distortions, the symmetry elements that distinguish $^2E_{1x}''$ from $^2E_{1y}''$ are destroyed, and so the two wave functions mix. The energy raising and lowering of the resulting wave functions are the same, to first order, as those produced by the identical amount of distortion along $\pm e_{2y}'$. Since, in the absence of higher order effects, e_{2x}' and e_{2y}' distortions have the same effect on the energy of $^2E_1''$ states, the cyclopentadienyl radical can pseudorotate from one e_2' distorted geometry to another, without ever passing through a D_{5h} geometry.[9] Moreover, small or nonexistent barriers are anticipated between the five equivalent minima, whose existence is dictated by the molecular symmetry.

In the cyclopentadienyl cation, only two electrons occupy the pair of e_1'' π MOs. Three low-lying electronic states arise: $^3A_2'$, $^1A_1'$, and a doubly degenerate $^1E_2'$.[10] Since the e_1'' MOs cannot be confined to different sets of atoms, it can be predicted that the triplet will be the ground state, and that electron repulsion will cause the optimal MOs for the lowest singlet states to differ from those for the triplet.[11] For instance, the lowest $^1E_{2x}'$ π configuration

$$^1E_{2x}' = |a_2''^2\, e_{1x}''e_{1y}''(\alpha\beta - \beta\alpha)\rangle \qquad (1)$$

mixes with a combination of excited configurations of the same symmetry that differ from it by one-electron excitations of the type $e_1'' \rightarrow e_2''$. Consequently, the lowest $^1E_2'$ configuration does not satisfy Brillouin's theorem for open-shell systems.[12] Thus, symmetry constrained MOs, which are optimal for the $^3A_2'$ state, are not the SCF MOs for the lowest singlet state. In order to obtain MOs that satisfy Brillouin's theorem, mixing of e_1'' with e_2'' must be permitted. Consequently, only C_{2v} symmetry can be imposed on the SCF wave function, even at D_{5h} geometries. Thus, $^1E_{2x}'$ must be described as $^1B_2$ and $^1E_{2y}'$ as $^1A_1$. Unfortunately, $^1B_2$ in C_{2v} corresponds to several representations of D_{5h}, including $^1A_2'$, and $^1A_1'$ is included in the D_{5h} representations to which $^1A_1$ corresponds. Therefore, the $^1B_2$ and $^1A_1$ wavefunctions are not expected to form a basis for a pure $^1E_2'$ representation of D_{5h}. Moreover, since they are contaminated by nondegenerate ($^1A_1'$ and $^1A_2'$) states, their calculated energies are expected to differ. Pure $^1E_{2x}'$ and $^1E_{2y}'$ wave functions would, of course, be degenerate at D_{5h} geometries. As we have pointed out previously, degeneracy can, nevertheless, be restored by carrying out CI, which effectively eliminates the foreign symmetry contaminants from the SCF wave function.[7b,13]

The expected mixing of e_1'' with e_2'' orbitals in $^1E_2'$ states of the cyclopentadienyl cation is also responsible for producing the first-order e_1' distortion that is anticipated on the basis of the Jahn–Teller theorem. It is easy to show that a symmetry-restricted wave function like that in eq 1, despite the prediction of the Jahn–Teller theorem, will not undergo a first-order distortion along e_1'.[14] It is the mixing of the e_2'' antibonding π orbitals into the singly occupied e_1'' orbitals that causes the π bond orders and charge densities to deviate from D_{5h} symmetry, thus giving rise to a first-order Jahn–Teller effect.

In addition to the first-order Jahn–Teller effect, a second-order effect is also expected in the cation. $^1E_2'$ can be mixed

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Table I. CI Results at D_{5h} Geometries

state	bond length, Å	energy, hartrees
$^2A_2$	1.429	−189.9053
$^2B_1$	1.429	−189.9056
$^3B_2$	1.438	−189.6901
$^1A_1$[a]	1.442	−189.6570
$^1B_2$[b]	1.442	−189.6603
$^1A_1$[c]	1.442	−189.6590
$^1B_2$[c]	1.442	−189.6589

[a] Computed with $^1A_1$ MCSCF MOs. [b] Computed with $^1B_2$ RHF MOs. [c] Computed with $^3B_2$ RHF MOs.

with the low-lying $^1A_1$ state by a distortion along e_2. Writing the symmetry-restricted π wave function for the y component of $^1E_2'$ as

$$^1E'_{2y} = (|a_2''^2 e_{1y}''^2\rangle - |a_2''^2 e_{1x}''^2\rangle)/\sqrt{2} \tag{2}$$

and noting that

$$^1A'_1 = (|a_2''^2 e_{1y}''^2\rangle + |a_2''^2 e_{1x}''^2\rangle)/\sqrt{2} \tag{3}$$

it is evident that mixing of the two wave functions stabilizes the lower of the two by increasing the occupation number of the degenerate orbital whose energy is decreased by a distortion along e'_{2y}. Unlike the case in the radical, where there is a first-order effect along e'_{2y}, the $^1E'_2$–$^1A'_1$ mixing in the cation affects the energy in second order.[15] Thus, the energy of $^1E'_{2y}$ is quadratic in the distortion coordinate, so this state should be stabilized equally by distortions along $\pm e'_{2y}$. Distortions along e'_{2y} do not mix $^1E'_{2x}$ with $^1A'_1$, but e'_{2x} distortions do. In the absence of higher order effects, the energetic consequences of the mixing of either component of $^1E'_2$ with $^1A'_1$ are identical. Therefore, since any e'_2 distortion has the same effect on the energy of $^1E'_2$, the cyclopentadienyl cation, like the radical, can pseudorotate from one distorted e'_2 geometry to another, without ever passing through a D_{5h} geometry and with little or no change in energy on pseudorotation.

The predicted existence of both first- and second-order Jahn–Teller effects in the cyclopentadienyl cation makes it similar to another four π electron annulene, the cyclopropenyl anion.[7b] There is, however, an important difference between these two molecules. As noted above, the five-membered ring system has distortion modes of both e'_1 and e'_2 symmetry, while the three-membered ring has only an e' mode. Consequently, in the lowest singlet state of the cyclopropenyl anion the first- and second-order Jahn–Teller effects occur along the same distortion coordinate, and the two effects consequently produce minima and maxima on the potential surface for pseudorotation around D_{3h} geometries.[7b] By contrast, in the isoelectronic cyclopentadienyl cation, pseudorotation about D_{5h} geometries should take place with little change in energy, since the first- and second-order effects occur for different distortion modes.

Computational Methodology

Calculations were carried out on the planar radical and cation using an STO-3G minimal basis set.[16] The C–H bond lengths were fixed at 1.10 Å, and these bonds were assumed to bisect the C–C–C angles. A program was written to generate bond angles that minimized the angle strain in the five-membered ring for a given set of C–C bond lengths,[17] thus circumventing the need for carrying out quantum mechanical calculations to optimize the bond angles at non-D_{5h} geometries. Geometries of symmetry lower than C_{2v} were not examined, so only three unique C–C bond lengths had to be varied. In optimizing the C–C bond lengths, the last significant figure was obtained by interpolation. C_{2v} symmetry constraints were imposed on the wave functions at all geometries. Molecular orbitals were defined by RHF calculations for $^2B_1$ and $^2A_2$ states of the radical and $^1B_2$ and $^3B_2$ of the cation, using the open-shell method of Davidson.[18] For the $^1A_1$ state of the cation, a two-configuration MCSCF program, written by Dr. K. Tanaka of our group, was employed. Full π-space CI was carried out for each state using the orbitals from the appropriate SCF calculation. In addition, the MOs for the $^3B_2$ state were also used to carry out CI calculations for the two singlet states.

Results

D_{5h} Calculations. Table I shows the results of the CI calculations carried out at the optimized D_{5h} geometries of the radical and cation. As expected, the CI energies for the $^2B_1$ and $^2A_2$ states were more nearly the same than the SCF energies (−189.8074 and −189.8064 hartrees, respectively). The π MOs for the two doublet states of the radical were only slightly different from the nearly pure D_{5h} symmetry MOs obtained from the SCF calculation on the $^3B_2$ state of the cation.

In contrast, the MOs for the $^1B_2$ and $^1A_1$ states of the cation were, as anticipated, quite different from D_{5h} symmetry MOs. For instance, in the $^1B_2$ state the singly occupied $2b_1$ π MO was much more localized at the unique carbon atom, where the $1a_2$ MO, which is occupied by an electron of opposite spin, has a node. This localization diminishes the ionic terms in the wave function, corresponding to the simultaneous occupancy of the same AO by these two electrons. There was an accompanying shift of electron density in $1b_1$, the lowest π MO, away from the unique carbon atom.

The MOs for the $^1A_1$ state were even more distorted. As shown by eq 2, a two-configuration wave function is required to correctly describe the $^1E'_{2y}$ state of the cation. Therefore, a C_{2v} π wave function of the form

$$^1A_1 = c_1|1b_1^2 2b_1^2\rangle - c_2|1b_1^2 1a_2^2\rangle \tag{4}$$

was sought. The $1b_1$ MO was found to be localized to essentially three of the five carbon atoms and to strongly resemble the bonding π MO in allyl. The $2b_1$ MO was largely confined to the remaining two carbon atoms, where the $1a_2$ MO was also mostly localized. The coefficients were also found to be quite different than those required of a wave function of pure $^1E'_{2y}$ symmetry; they were computed to be $c_1 = 0.93$ and $c_2 = 0.38$. Thus, the $^1A_1$ MCSCF π wave function can be characterized as essentially that for an allyl cation plus an isolated ethylene, even at D_{5h} molecular geometries. The second configuration in eq 4 provides intraorbital correlation for the two π electrons in the ethylene-like $2b_1$ MO.

At the SCF level, the energy of the $^1A_1$ MCSCF wave function (−189.6181 hartrees) is well below that (−189.5911 hartrees) of $^1B_2$. However, on inclusion of CI, as shown in Table I, the energies move much closer together and reverse in order. Nevertheless, the states remain distinctly nondegenerate at D_{5h} geometries.

Nearly degenerate singlet CI wave functions could be obtained by using the MOs from the $^3B_2$ SCF calculation to carry out CI for the $^1B_2$ and $^1A_1$ states. The small difference in energy is due to the fact that the orbitals from the $^3B_2$ SCF calculation did not emerge as absolutely pure D_{5h} symmetry MOs at the level of convergence at which the calculation was terminated. Further iteration would undoubtedly have produced the pure symmetry orbitals expected for a $^3A'_2$ state, from which degenerate $^1E'_2$ CI wave functions would have been obtained.[19] Interestingly, the CI energy calculated for the two singlets from the triplet MOs falls between the CI energies calculated from the two singlet SCFs. Thus, it is clear that the σ MOs that emerge from the $^1A_1$ MCSCF calculation are not optimal for a full π-space CI wave function for this state, since the $^3B_2$ SCF orbitals give a lower π-space CI energy.

Table II. CI Results at C_{2v} Geometries

property	$^2A_2$	$^2B_1$	$^1A_1$ (1)	$^1A_1$ (2)
C_1–C_2, Å	1.407	1.457	1.402	1.471
C_2–C_3, Å	1.496	1.371	1.535	1.369
C_3–C_4, Å	1.360	1.509	1.361	1.556
C_5–C_1–C_2, deg	108.1	108.0	108.4	108.7
C_1–C_2–C_3, deg	108.0	108.0	108.1	108.2
C_2–C_3–C_4, deg	107.9	108.0	107.7	107.4
q_1[a]	1.07	0.94	1.01	0.37
q_2	0.95	1.05	0.52	1.02
q_3	1.01	0.98	0.97	0.80
ρ_{12}[b]	0.431	0.257	0.490	0.267
ρ_{23}	0.137	0.578	0.037	0.602
ρ_{34}	0.627	0.096	0.631	−0.052
E, hartrees	−189.9167	−189.9169	−189.6784	−189.6783
ΔE, kcal/mol[c]	7.1	7.1	13.4[d]	13.4[d]

[a] q_i is the π electron density at the ith carbon atom. [b] ρ_{ij} is the π bond order between carbons i and j. [c] ΔE is the stabilization energy on distortion from D_{5h} symmetry. [d] Computed using the D_{5h} CI energy obtained from the $^1A_1$ MCSCF MOs.

Although the singlet CI wave functions calculated from $^3B_2$ SCF MOs were not exactly degenerate in energy, Mulliken population analyses showed that they gave π bond orders and charges of the type expected from $^1E_2'$ degenerate wave functions.[20] The deviation of each bond order in the $^1B_2$ wave function from the average was exactly the opposite of the corresponding bond order in the $^1A_1$ wave function, and the deviations each transformed as E_{1y}'. The π charges behaved similarly. The $^2B_1$ and $^2A_2$ CI wave functions were shown also to have nearly pure $^2E_1''$ symmetry by a similar set of criteria. A population analysis was not carried out for the CI wave function based on the $^1B_2$ SCF calculation, but the deviations from the averages of the π bond orders and charges, computed from the CI wave function that was obtained from the $^1A_1$ MCSCF calculation, showed clearly that the resulting $^1A_1$ CI wave function was not close to having $^1E_2'$ symmetry.

The average π bond order was essentially the same (0.333) in all three singlet CI wave functions for which this quantity was computed and was less than that (0.350) in the $^3B_2$ CI wave function. This accounts for the fact that the singlets have longer optimal D_{5h} bond lengths than does the triplet. The smaller average π bond order in the singlets is due to the fact, discussed above, that the SCF orbitals for the singlet state have antibonding e_2'' π orbitals mixed into the bonding e_1'' MOs. The average π bond order in the doublet states (0.354) was only marginally greater than that in the triplet. Perhaps shorter bond lengths are preferred in the radical because the increase in nuclear–electron attraction is greater than that in electron–electron repulsion on addition of a fifth electron to the cation.

Distorted Geometries. Bond length distortions of e_{1y}' and e_{2y}' symmetry can be expressed as

$$e_{1y}' = \Delta[-0.809(r_{12} + r_{15}) + 0.309(r_{23} + r_{45}) + r_{34}] \quad (5)$$

$$e_{2y}' = \Delta[0.309(r_{12} + r_{15}) - 0.809(r_{23} + r_{45}) + r_{34}] \quad (6)$$

where r_{ij} is a 1-Å *change* in the bond length between carbons i and j, and Δ specifies the actual magnitude of the overall distortion. We examined the effect of both types of distortions in the radical and the cation.

As expected, the energy of both states of the radical and the triplet state of the cation increased, approximately quadratically, on e_{1y}' distortions from D_{5h} symmetry. Also as anticipated, the energies of the singlet states of the cation changed in opposite directions on e_{1y}' distortions, since a first-order Jahn–Teller effect is predicted for $^1E_2'$ states in this mode. For positive e_{1y}' distortions, $^1A_1$ was stabilized and $^1B_2$ was destabilized, as expected from inspection of the π bond orders at D_{5h} geometries for these states. The opposite energy changes were calculated for negative e_{1y}' distortions. Using the $^1A_1$ CI wave function derived from the MCSCF calculation, an energy lowering of 0.9 kcal/mol was found for an optimal $\Delta = 0.026$. For the $^1B_2$ CI wave function computed from $^1B_2$ SCF MOs $\Delta = -0.014$ provided the maximum energy lowering, which amounted to 0.3 kcal/mol. Although the energy changes and magnitudes of optimal distortion should be the same for pure $^1E_2'$ wave functions, as noted above, $^1A_1$ and $^1B_2$ are not of pure $^1E_2'$ symmetry. Therefore, the asymmetry found in investigating e_{1y}' distortions is not surprising. The nearly pure $^1E_2'$ wave functions obtained by carrying out CI calculations with $^3B_2$ SCF MOs did behave properly on e_{1y}' distortions, but the optimal magnitude of Δ was 0.004, which produced an energy lowering of only 0.02 kcal/mol.

For e_{2y}' distortions, the results were also as expected. As could be inferred either from the D_{5h} population analyses or just the orbital occupancies in the radical, the $^2B_1$ wave function was stabilized by a positive e_{2y}' distortion, while the $^2A_2$ was stabilized by a negative distortion. The optimal magnitude of Δ was 0.076 for both states, resulting in an energy lowering of 7.1 kcal/mol for each state on distortion from D_{5h} symmetry. Complete optimization of the bond lengths for each state led to the results in Table II. The $^1B_2$ and $^3B_2$ states increased in energy on e_{2y}' distortions, but the $^1A_1$ state was stabilized on distortions of both $\pm e_{2y}'$, just as anticipated. The optimal amount of distortion and the resulting stabilization energy calculated depended upon which set of SCF orbitals was used to carry out the π-space CI calculations. For the $^1A_1$ MCSCF MOs, the optimal e_{2y}' distortions were found to be $\Delta = 0.100$ and -0.103. The corresponding stabilization energies for these distortions from D_{5h} symmetry were respectively 13.4 and 13.0 kcal/mol. For the $^3B_2$ MOs, the distortions were $\Delta = 0.080$ and -0.110, with corresponding stabilization energies of 3.3 and 4.5 kcal/mol. The much larger stabilization energies on molecular distortion calculated for the CI wave functions based on the MCSCF MOs make these CI wave functions considerably lower in energy at e_{2y}' distorted geometries than those based on $^3B_2$ SCF MOs. Therefore, the MCSCF MOs were used for carrying out the π-space CI calculations necessary to completely optimize the bond lengths at the minimum energy singlet geometries. The results are shown in Table II.

Discussion

Our calculations on the cyclopentadienyl radical indicate that $^2B_1$ and $^2A_2$ wave functions have almost exactly the same energy at their respective minimum energy geometries. The small difference in energy between the two wave functions at these geometries is probably just a consequence of the spurious splitting of 0.0003 hartrees between them at the optimal D_{5h} geometry. It is possible that calculations along an e_{2x}' distortion

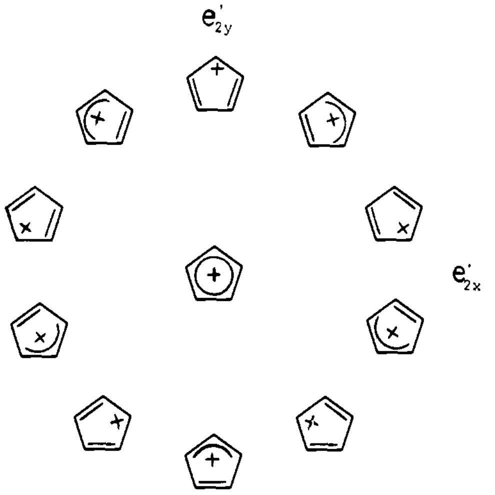


Figure 1. Pseudorotation in the lowest singlet state of cyclopentadienyl cation, distorted in an e'_2 mode.

coordinate would reveal a barrier on the lowest potential surface at the midpoint between $^2B_1$ and $^2A_2$ wave functions, but there is no theoretical reason for anticipating this to be the case. Thus, our results suggest that the potential surface for pseudorotation in the planar cyclopentadienyl radical is flat so that this process should require little input of energy. This finding is consistent with the experimental EPR spectrum of the radical down to 120 K. Our calculations do not indicate why pseudorotation is apparently frozen out on the EPR time scale at 70 K.[3] Selective stabilization of one of the two doublet wave functions by deviations from planarity in the radical is one possibility.[21]

Since the optical spectrum of the radical has also been obtained,[23] we calculated the excitation energy for an allowed $^2E'_1 \rightarrow {}^2A'_2$ transition. The latter state has its minimum at a D_{5h} geometry, while, of course, the former does not. Thus, the energy required for a vertical transition (4.37 eV) is substantially greater than the energy difference between the minima (3.95 eV). The experimental spectrum shows absorption in the range 3.7-4.0 eV.

The adiabatic ionization potential of the cyclopentadienyl radical has been measured too.[24] From the data in Tables I and II, the energy required to form the triplet cation adiabatically from the radical can be computed as 6.2 eV. The rather poor agreement with the experimental value of 8.4 eV[24] is not very surprising in view of the quality of the basis set and our neglect of σ–π correlation effects.

For the cation, the CI results based on $^1A_1$ MCSCF orbitals show that the second-order Jahn–Teller effect is very much larger than the first-order effect. The first-order effect is, in fact, considerably smaller than that found in trimethylenemethane[7a] and in cyclopropenyl anion.[7b] The smaller size of the first-order effect in the cyclopentadienyl cation is due to the fact that its degenerate π orbitals are spread over more atoms than those of the other two four-electron π systems. Consequently, localization of the open-shell electrons to disjoint sets of atoms in the degenerate singlet states is less crucial in the five-membered ring. Since, as discussed above, it is distortion of the symmetry-restricted MOs, caused by minimization of the Coulomb repulsion between the open-shell electrons, that produces the first-order Jahn–Teller effects in these systems, the smaller magnitude of this effect in the cyclopentadienyl cation can be readily understood.

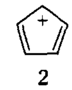
We have previously pointed out that a large second-order Jahn–Teller effect is to be generally expected in antiaromatic annulenes.[7b] In the cyclopentadienyl cation $^1E'_2$–$^1A'_1$ mixing results in the selective occupancy by a pair of electrons of the degenerate orbital that is stabilized by distortion. This effect might be anticipated to be twice as important as the first-order effect in the radical, since distortion in the radical results from the choice of degenerate MO occupancy for only one electron. The stabilization energy on e'_{2y} distortion in the cation is, in fact, calculated to be about twice as large as in the radical.

The size of the second-order effect in the cation is sufficient to reduce by about two-thirds the singlet–triplet gap computed at a D_{5h} geometry. The calculated splitting of 7.3 kcal/mol between the states at their equilibrium geometries is considerably smaller than that predicted at the SCF level[6] and much more in keeping with the ability of substituents to cause the ground state to become a singlet.[25] It should be noted that the singlet at its equilibrium distorted geometries lies below the triplet at the same geometries, so the singlet is predicted to be metastable.

It is of some interest to observe that at the level of π-space CI the second-order Jahn–Teller effect is predicted to result in a larger stabilization of cyclopentadienyl cation than of cyclobutadiene.[7c] This is probably due to the fact that in the cyclopentadienyl cation the $^1A'_1$ state that mixes with $^1E'_2$ is only 23 kcal/mol above this state at the optimal D_{5h} geometry of the latter. The corresponding energy separation in cyclobutadiene is 70 kcal/mol.[7c]

An even more important difference between the two systems resides in the pathway by which each travels from one distorted geometry to another. In cyclobutadiene, the lowest energy pathway from one rectangular geometry to another is via a square as transition state.[7c] In the cyclopentadienyl cation, however, the fact that the distortion mode (e'_2) is degenerate allows the molecule to pseudorotate from one distorted geometry to another, without ever passing through a D_{5h} geometry. The results in Table II indicate that this process can proceed with little or no expenditure of energy.[26] The difference between the two molecules may be viewed as a consequence of the fact that bond flipping in cyclobutadiene is a $[_{\pi}2_s + {}_{\pi}2_s]$ process, which is "forbidden" by orbital symmetry.[27] The bond flipping required to interconvert the two distorted $^1A_1$ wave functions, whose π bonding is represented approximately by **1** and **2**, is also a "forbidden" process. In fact, our calculations show that it requires even more energy than bond flipping in cyclobutadiene, if it is carried out in a concerted fashion via a D_{5h} transition state. However, a pseudorotation pathway of lower energy exists and is shown in Figure 1. Since it involves stepwise changes in the π bonding, rather than a concerted $[_{\pi}2_s + {}_{\pi}2_s]$ process, it is not constrained by orbital symmetry effects to pass over a barrier.


1


2

The Mulliken population analyses contained in Table II show that, while **1** is an adequate portrayal of the bonding in the lowest $^1A_1$ wave function on negative e'_{2y} distortions, the bonding in this wave function for positive e'_{2y} wave functions is really more like that in a pentadienyl cation to which **2** is the dominant resonance contributor. Thus, in Figure 1, each of the five equivalent structures that lie between structures of type **1** is actually closer to being the average of these two structures than is suggested by the depiction **2**.

The population analyses also reveal the extent to which the plus charge in **1** and in **2** can be replaced by dots, so that the thus modified structures represent the bonding in respectively the $^2A_2$ and $^2B_1$ states of the radicals. Although the singly occupied a_2 and b_1 MOs are not as localized as the plus charges, nevertheless, replacing the plus charges with dots in structures **1** and **2** does provide a crude picture of the bonding in these states of the radical. The same substitution in Figure 1 provides an approximate depiction of the pseudorotation process in this species.

Although we believe that our π-space CI calculations on the cyclopentadienyl radical and cation provide at least semiquantitatively correct descriptions of the salient features of the potential surfaces for the planar molecules, one aspect of the results for the cation is disquieting. It is a cause for concern, though not really surprise, that even full π-space CI is incapable of rendering the $^1A_1$ and $^1B_2$ wave functions for the cation degenerate at D_{5h} geometries. The reason for this finding is that the distortions of the π-orbitals from symmetry constrained MOs produce distributions of π charges that do not have D_{5h} symmetry. Consequently, at the SCF level there are accompanying distortions of the σ cores, which serve to stabilize the π charge distributions. Since the σ cores, therefore, do not belong to pure A_1' representations of the D_{5h} point group, there is no reason why π-space CI, which leaves the σ wave functions unchanged, should lead to total wave functions of pure $^1E'$ symmetry. Indeed, as discussed above, it is apparent that the σ MOs from the MCSCF calculations are not even the optimal set for the $^1A_1$ π-space CI wave functions.[28]

In the cyclopentadienyl cation, the lack of D_{5h} degeneracy of $^1A_1$ and $^1B_2$ is not a very serious problem, since the first- and second-order Jahn–Teller effects occur along different distortion coordinates. However, in the cyclopropenyl anion, there is only one distortion coordinate, so the relative energies of $^1A_1$ and $^1B_2$ wave functions are of considerable importance in describing the potential surface for the lowest singlet state. We dealt with this problem in our previous calculations on cyclopropenyl[7b] by using the $^3B_2$ MOs to carry out π-space CI for the singlet states. This guaranteed that we would obtain degenerate singlet states at D_{3h} geometries, but we expressed concern that, particularly for the $^1A_1$ state at distorted geometries, the use of the σ MOs for the triplet could give erroneous results. The present calculations on the cyclopentadienyl cation, in which we compared the results obtained with $^3B_2$ RHF and $^1A_1$ MCSCF MOs for $^1A_1$ CI wave functions at distorted geometries, indicate that this concern was well founded.

These results, which show the importance of the σ MOs on the distortion energies that are calculated, also caution against constructing potential surfaces by just comparing distortion energies for $^1A_1$ and $^1B_1$ π CI wave functions. Since the σ MOs are not reoptimized for the π-space CI wave functions, there is no reason to trust that accurate distortion energies would be obtained for either state. Moreover, recent experience in calculations on cyclobutadiene has shown that σ–π correlation can have a large effect on distortion energies.[7c] There are ample grounds for believing that the effects of this type of correlation could be quite different for open-shell $^1B_2$ and essentially closed-shell $^1A_1$ π wave functions at distorted geometries. In fact, differences in σ–π correlation must be responsible, at least in part, for the lack of degeneracy of $^1A_1$ and $^1B_2$ π-space CI wave functions at the geometries of highest symmetry in cyclopropenyl anion and cyclopentadienyl cation.

The conclusion to which one is forced by these considerations is that, in charged systems like the cyclopentadienyl cation and the cyclopropenyl anion, CI in the σ space is necessary to obtain $^1A_1$ and $^1B_2$ wave functions that have the proper relative energies at all molecular geometries. Studies on the cyclopropenyl anion, in which CI in the σ space is included, are underway.

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References and Notes

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(20) An E_{2x}' or E_{2y}' wave function on squaring gives a function that transforms as $A_1' + E_{2y}'$. In addition, $(E_{2x}')^2 + (E_{2y}')^2$ transforms as pure A_1' in D_{5h}.

(21) There is both theoretical[7b,22a] and experimental[22b] evidence for the occurrence of carbon atom pyramidalization in the cyclopropenyl radical. In addition, ring puckering has been found to be favorable in the cyclopentadienyl cation[4b,c] and so should at least be considered as a possibility in the radical.

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(28) Not only is this true at D_{5h} geometries, as evidenced by the fact that the $^3B_2$ σ MOs give lower energy $^1A_1$ π-space CI wave functions, but it is also true at distorted geometries. When the ethylenic bond in wave functions of type **1** was quite short, the MCSCF calculation converged to a false minimum where the $1a_2$ MO in the second configuration was used to correlate the allylic π electrons in $1b_1$, instead of the ethylenic pair in $2b_1$. This resulted in MCSCF energies that were much higher than those at surrounding points. Nevertheless, the MOs from these spurious MCSCF calculations gave lower CI energies than the optimal MCSCF MOs at adjacent points on the potential surface.