Orbital Interactions and Solvent Effects Determining the Stability of Condensed Cyclopentadienides in Solution

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Received November 18, 1998

The structure and the stability of various cyclopentadienides, which involve 6π, 10π, 14π, and 22π electrons, are investigated from computations at various levels of theory as well as from orbital interaction analyses. The reason that some of the cyclopentadienides are stabilized and others are destabilized by the introduction of aromatic rings is discussed in terms of absolute hardness and orbital interaction. Cyclopentadienide, a special 6π-electron system, has the largest value of absolute hardness among the condensed cyclopentadienides investigated; thus this carbanion resists both oxidation and reduction most strongly. The absolute hardness decreases when aromatic rings are introduced to cyclopentadienide to form condensed cyclopentadienides, depending on the way they are connected. Computed values of the ionization potential and oxidation potentials measured in solution have a linear correlation within isomers of the same size, but are not in agreement for different sets of isomers. Solvent effects on the ionization potential are assessed by performing self-consistent reaction field calculations, the results being in excellent agreement with experiments. It is demonstrated that the solvent effects are significant in small cyclopentadienides of 6π- and 10π-electron systems, compared to larger ones and that addition of condensed aromatic rings intrinsically stabilizes the formed condensed cyclopentadienides with respect to ionization potential.

Introduction

Cyclopentadienide ($\mathbf{1}^-$) is a special 6π-electron system with great stability, due to the magic $(4n + 2)$ Hückel number.[1] The degenerate e_1'' HOMO of cyclopentadienide $\mathbf{1}^-$ is fully occupied by four electrons, as indicated in Chart 1. Thus, the planar pentagonal structure of D_{5h} symmetry is stable from a viewpoint of electronic structure, the equivalent C–C bond distances being nearly 1.4 Å, as in benzene. The stability of $\mathbf{1}^-$ is characterized by high oxidation potential (E_{ox}) values of $+0.028$ V[2] and $+0.04$ V[3] and by small pK_a values of $15-18$[2–6] for its conjugate acid, cyclopentadiene $\mathbf{1H}$. These values significantly depend on the solvents used.

Aromatic rings are successfully introduced to $\mathbf{1}^-$ to lead to a variety of condensed cyclopentadienides shown in

Chart 1

Chart 2

Chart 2. Cyclopentadienide $\mathbf{1}^-$ is a special 6π-electron system, as mentioned above, $\mathbf{2}^-$ is a 10π system, $\mathbf{3}^-$, $\mathbf{4}^-$, and $\mathbf{5}^-$ are 14π systems, and $\mathbf{6}^-$, $\mathbf{7}^-$, and $\mathbf{8}^-$ are 22π systems, all of these belonging to the Hückel $(4n + 2)\pi$ system. It is therefore interesting to investigate the relationship between the structure and the stability of these special carbanions. Indenide $\mathbf{2}^-$ and fluorenide $\mathbf{3}^-$ are stable, but less so than $\mathbf{1}^-$, as indicated by observed E_{ox} values of these and pK_a values of their conjugate acids,[2,7–13] the stability of these condensed cyclopentadienides decreasing in the sequence $\mathbf{1}^- > \mathbf{2}^- > \mathbf{3}^-$. This

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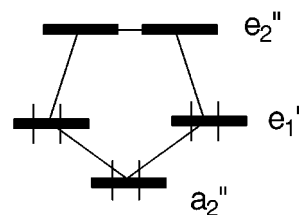(6) Cram, D. J. *Fundamentals of Carbanion Chemistry*; Academic: New York, 1965.

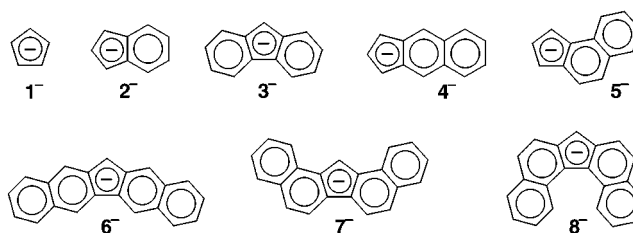(7) Steiner, E. C.; Gilbert, J. M. *J. Am. Chem. Soc.* **1965**, *87*, 382.
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fact may lead us to the view that the aromatic rings thus introduced should destabilize **1⁻** because annellation might cause the electrons to be less available to the five-membered ring.[14] However, the electron affinities of cyclopentadienyl, indenyl, and fluorenyl radicals (**1·**, **2·**, and **3·**, respectively) increase slightly in the reverse order **1·** < **2·** < **3·** in the gas phase.[15] Dibenzo[*b,h*]fluorenide **6⁻** is clearly less stable than **1⁻**, but its isomer dibenzo-[*c,g*]fluorenide **8⁻** appears to be more stable than **1⁻** in solution.[16]

In previous papers, Kinoshita et al.[17] compared computed values of the ionization potential (I_p) based on Koopmans' theorem[18] and measured values of E_{ox} in solution as stability criteria for the condensed cyclopentadienides indicated in Chart 2. The computed HOMO level was found to go down with an increase in the size of the cyclopentadienides. From a viewpoint of computed I_p values, Kinoshita et al.[17b] concluded that addition of condensed aromatic rings should intrinsically stabilize the formed condensed cyclopentadienides in solution as well as in the gas phase. Observed destabilization of the condensed cyclopentadienides in solution is most probably ascribed to a decrease in solvation energy by charge delocalization on the condensed cyclopentadienides. It was also indicated that there are important orbital interactions that determine the relationship between the structure and the stability of the condensed cyclopentadienides. In this paper we look in detail at the interesting relationship from ab initio quantum chemical computations as well as from qualitative orbital interaction analyses. Our main point is to understand why some of the cyclopentadienides are stabilized and others are destabilized, in terms of chemical hardness and orbital interaction. Another emphasis of this work is in the solvent effects that determine the stability of the condensed cyclopentadienides in solution. We show how theory and experiment are in agreement with respect to the stability of these interesting π-conjugated systems.

Computational Details

We optimized the structures of the eight cyclopentadienides at various levels of theory: the ab initio Hartree–Fock (HF), the BLYP density-functional theory (DFT),[19,20] and the B3LYP hybrid HF/DFT methods.[19–21] The 6-31G** basis set[22] is used for the HF, the BLYP, and the B3LYP methods. The BLYP

method combines the standard local exchange functional with the gradient correlation of Becke and uses the Lee–Yang–Parr (LYP) correlation functional, which includes density gradient terms. The B3LYP method consists of the Slater exchange, the Hartree–Fock exchange, the exchange functional of Becke,[19] the LYP correlation functional,[20] and the correlation functional of Vosco, Wilk, and Nusair.[23]

Among the condensed cyclopentadienides indicated in Chart 2, only **8⁻** is unlikely to be planar, due to a hydrogen contact. We thus place reasonable symmetry restrictions on the structures: D_{5h} for **1⁻**, C_{2v} for **2⁻**, **3⁻**, **4⁻**, **5⁻**, **6⁻**, and **7⁻**, and C_2 for **8⁻**. Spin-unrestricted calculations for the neutral radical species of **1·** to **8·** were also conducted at the HF and the B3LYP levels of theory to have a better understanding of the structural changes and the spin-density distributions. Since **1·** is a typical Jahn–Teller molecule, we expect elongated and compressed C_{2v} deformations to occur from the original D_{5h} structure. Ab initio HF, BLYP, and B3LYP calculations are carried out with the Gaussian 94 program package.[24]

We also performed extended Hückel calculations[25] with YAeHMOP (Yet Another extended Hückel Molecular Orbital Package)[26] in order to look in detail at the orbital interactions that determine the relationship between the structure and the stability of the condensed cyclopentadienides. This approximate method models general orbital energy trends, orbital interactions, and major charge shifts well. Parameters used for carbon and hydrogen atoms are as follows: C 2s (H_{ii} = −21.4 eV, ζ = 1.625), C 2p (H_{ii} = −11.4 eV, ζ = 1.625), and H 1s (H_{ii} = −13.6 eV, ζ = 1.3), in which H_{ii} and ζ are the orbital energies and Slater exponents, respectively.

Solvent effects that determine the stability of the condensed cyclopentadienides in solution were taken into consideration by performing self-consistent reaction field (SCRF) computations.[27] In this method, we used the electrostatic solvation model based on Onsager's reaction field theory,[27] in which the solute is placed in a uniform electric field of solvent with a relative dielectric constant ϵ_r. The solute is assumed in this model to occupy a spherical cavity of radius a_0 in the medium. A dipole in the molecule will induce a dipole on the medium, and the electric field applied to the solute by the solvent dipole will in turn interact with the molecular dipole to lead to net stabilization. Despite the simplicity, this model affords results that are in good agreement with experiment.

Structures of Cyclopentadienides

In Figure 1 we demonstrate the geometries of **1⁻** to **8⁻** computed at the B3LYP/6-31G** level of theory. This hybrid HF/DFT method has been successfully applied to many kinds of molecular structures and chemical reactions, giving structures and energetics reasonably well.[28] Computed values of Mulliken charge are also indicated

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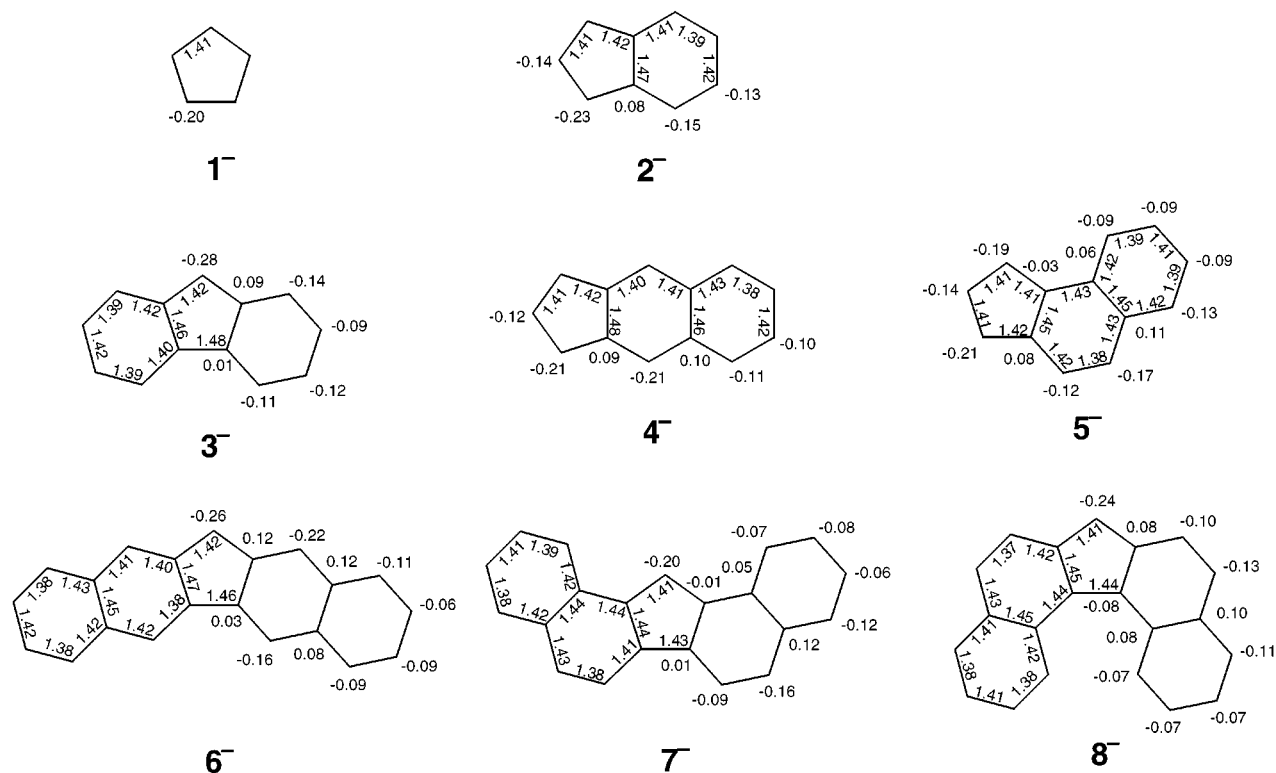
Figure 1. Optimized C—C bond distances and atomic charges of cyclopentadienides **1⁻** to **8⁻** at the B3LYP/6-31G** level of theory.
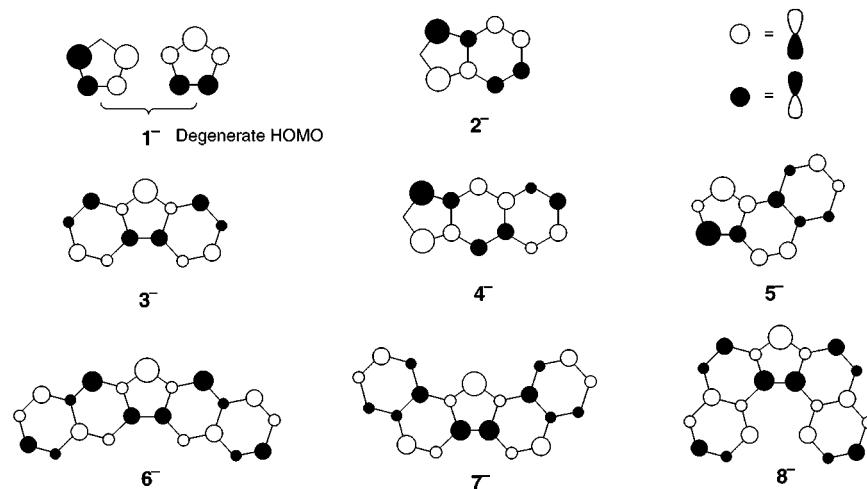

Figure 2. HOMOs of cyclopentadienides **1⁻** to **8⁻**.

in this illustration. The distance of a C—C bond sharing a pentagon and a hexagon, which we call a [5,6] bond, is greater than other C—C bonds. Thus, the qualitative pictures in Chart 2 would not be reasonable with respect to bond-length alternation. Although we do not show detailed computational results from other methodologies used in this paper, there is a general trend in these geometrical features. This can be derived in view of the frontier orbital patterns.

From an inspection of the HOMOs (highest occupied molecular orbitals), we can qualitatively understand why [5,6] bonds are longer than other C—C bonds. As shown in Figure 2, the HOMOs are out-of-phase with respect to a [5,6] bond, and accordingly there is a node at the center of a [5,6] bond. Such a nodal property results in

removal of electron density from this region of space,[29] and the two carbon atoms connecting a [5,6] bond will experience repulsive force if this orbital is occupied. As a consequence, the distance of a [5,6] bond becomes large. There is also a node at the center of a [6,6] bond in some of these cyclopentadienides so that the distance of a [6,6] bond is also large compared to other C—C bonds. Later in this paper we will describe the structure and the stability of these cyclopentadienides in terms of approximation-invariable orbital interactions. The HOMOs are highly delocalized over the condensed aromatic rings, and consequently computed values of minus charge

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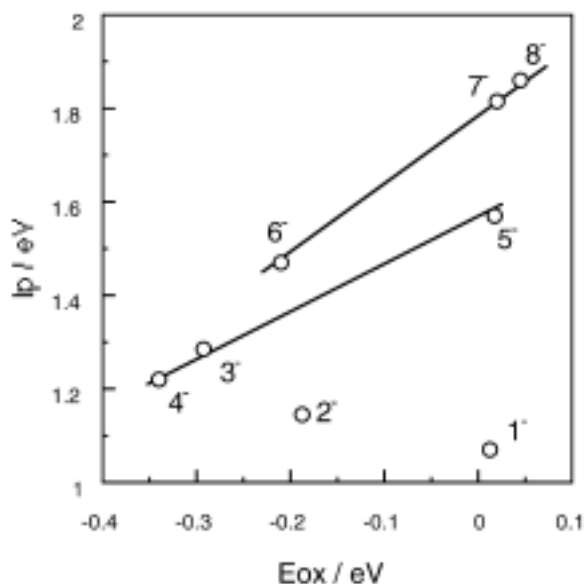
Figure 3. I_p values computed from eq 1 at the B3LYP/6-31G** level of theory as a function of E_{ox}.

indicated in Figure 1 are not localized only on the pentagon rings. Thus, the qualitative pictures in Chart 2, concerning the charge distributions, would not be correct, although they seem to be reasonable from the Hückel rule. The charge delocalization and the size of molecule are, in general, expected to affect the degree of stabilization in solution through solvent effects.

Chemical Hardness of Cyclopentadienides

The oxidation potential (E_{ox}) of the condensed cyclopentadienides is reasonably assumed to have relevance to the computed ionization potential (I_p). Kinoshita et al.[17b] reported in a previous paper that computed values of I_p (based on Koopmans' theorem[18]) and measured values of E_{ox} have a linear correlation within isomeric cyclopentadienides of the same size, the 14π (**3**⁻, **4**⁻, and **5**⁻) and the 22π (**6**⁻, **7**⁻, and **8**⁻) systems. However, the two quantities displayed no simple linear relationship for different sets of isomers. This discrepancy may be ascribed to the limit of applicability of Koopmans' theorem, in which orbital energies give approximate values to atomic or molecular ionization potentials. We thus consider I_p values of the condensed cyclopentadienides from a different, more reasonable definition:

$$I_p(N) = E(N) - E(N-1) \tag{1}$$

in which N is the number of electrons, $E(N)$ is the total energy of an anion, and $E(N-1)$ is the total energy of a corresponding neutral species. Figure 3 shows I_p values thus computed at the B3LYP/6-31G** level of theory as a function of E_{ox} measured in dimethyl sulfoxide. As mentioned above, I_p exhibits a linear correlation within isomeric cyclopentadienides of the same size, being in good agreement with the results from Koopmans' theorem.[17b] However, the positions of **1**⁻ and **2**⁻ in Figure 3 are deviated from a linear relation between the two quantities for these cyclopentadienides.

It is also interesting to look at the stability of the condensed cyclopentadienides from a viewpoint of chemical hardness.[30,31] According to molecular orbital theory,

absolute hardness and chemical potential can be defined by

$$\eta = (\epsilon_{LUMO} - \epsilon_{HOMO})/2 \tag{2}$$

and

$$\mu = (\epsilon_{LUMO} + \epsilon_{HOMO})/2 \tag{3}$$

respectively, where ϵ_{LUMO} and ϵ_{HOMO} are orbital energies of the LUMO (lowest unoccupied molecular orbital) and the HOMO (highest occupied molecular orbital), respectively. Table 1 lists computed values of HOMO energy, LUMO energy, HOMO−LUMO gap (ΔE), absolute hardness (η), and chemical potential (μ) of each cyclopentadienide at the ab initio HF, the B3LYP, and the BLYP levels of theory.

Cyclopentadienide **1**⁻ has the largest value of absolute hardness among the cyclopentadienides investigated in this study. Hardness is the resistance of the chemical potential to change in the number of electrons, so that this special carbanion is expected to resist transfer of electrons in both oxidation and reduction. Computed values of absolute hardness decrease when aromatic rings are introduced into **1**⁻, as listed in Table 1. It is interesting to compare the absolute hardness for isomeric cyclopentadienides of the same size. Let us look at computed values of absolute hardness for **3**⁻, **4**⁻, and **5**⁻, which are 14π systems consisting of **1**⁻ and two benzene rings in different ways of connection. As listed in Table 1, the hardness decreases in the sequence **5**⁻ > **3**⁻ > **4**⁻, being in line with the measured stability for single-electron oxidation, E_{ox}. We next take a look at the larger cyclopentadienides, which consist of **1**⁻ and four benzene rings in different ways of connection. Cyclopentadienides **7**⁻ and **8**⁻ have nearly equal values of absolute hardness, being clearly larger than the value for **6**⁻. This result is again in agreement with the stability for single-electron oxidation within isomers of the same size, but the computed values of absolute hardness and the measured stability for single-electron oxidation display discrepancy for different sets of isomer.

Orbital Interactions in Cyclopentadienides

In the previous sections we have described some computational results of the structure and the stability of the condensed cyclopentadienides. Now we turn our attention to why some of them are stabilized and others are destabilized by the introduction of aromatic rings. To understand the correlation between stability and structure for the condensed cyclopentadienides, we analyzed the governing orbital interactions with the fragment molecular orbital (FMO) method. Partition of a molecular orbital into two or more FMOs is a very useful way of looking at important orbital interactions in a molecule. The remarkable contrast between phenanthrene (polyphenanthrene) and anthracene (polyacene) was successfully analyzed using the FMO method in a previous paper.[32]

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Table 1. Computed Values of HOMO Energy, LUMO Energy, HOMO−LUMO Gap (ΔE), Absolute Hardness (η), and Chemical Potential (μ) for the Cyclopentadienides 1⁻ to 8⁻ (The Units Are in EV)

		1⁻	2⁻	3⁻	4⁻	5⁻	6⁻	7⁻	8⁻
HF/6-31G**	HOMO	−1.29	−1.24	−1.31	−1.25	−1.76	−1.47	−1.98	−2.04
	LUMO	12.25	8.70	7.38	6.77	7.23	5.60	6.37	6.31
	ΔE	13.54	9.94	8.69	8.02	8.99	7.07	8.35	8.35
	η	6.77	4.97	4.35	4.01	4.50	3.54	4.18	4.18
	μ	5.48	3.73	3.04	2.76	2.74	2.07	2.20	2.14
B3LYP/6-31G**	HOMO	1.10	0.66	0.29	0.36	0.02	−0.19	−0.50	−0.56
	LUMO	8.27	4.96	3.77	3.29	3.63	2.13	2.88	2.71
	ΔE	7.17	4.30	3.48	2.93	3.61	2.32	3.38	3.27
	η	3.59	2.15	1.74	1.47	1.81	1.16	1.69	1.64
	μ	4.69	2.81	2.03	1.83	1.83	0.97	1.19	1.08
BLYP/6-31G**	HOMO	2.11	1.52	1.06	1.13	0.84	0.46	0.22	0.18
	LUMO	7.64	4.52	3.34	2.91	3.22	1.77	2.25	2.32
	ΔE	5.53	3.00	2.28	1.78	2.38	1.31	2.03	2.14
	η	2.77	1.50	1.14	0.89	1.19	0.66	1.02	1.07
	μ	4.88	3.02	2.20	2.02	2.03	1.12	1.24	1.25
	E_{ox}[a]	0.035	−0.180	−0.264	−0.339	0.019	−0.210	0.020	0.044

[a] Cited from ref 17b.

Chart 3

2⁻   D   A
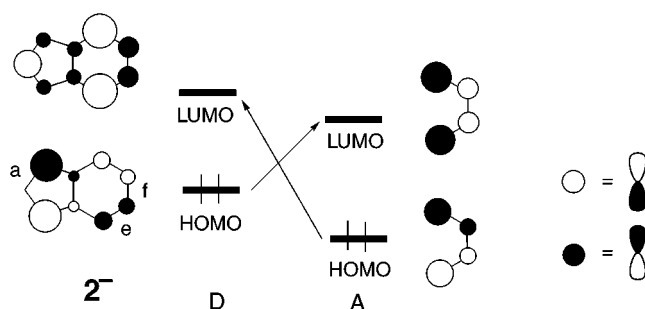
Let us first consider the role of orbital interactions determining the stability of **3⁻**, **4⁻**, and **5⁻** because these are isomeric 14π-electron systems. The three isomers can be theoretically partitioned into indenide **2⁻** and *cis*-butadiene fragments, combinations of which at the positions *a*, *f*, and *e* of **2⁻** would lead to the three isomers, **3⁻**, **4⁻**, and **5⁻**, respectively, as shown in Chart 3.[17b] The essential feature of the frontier orbitals of these fragments is that the HOMO of **2⁻** is high-lying and that the LUMO of the butadiene fragment is low-lying. In view of these frontier orbitals, we expect from qualitative second-order perturbation theory that the interaction between the HOMO of **2⁻** and the LUMO of the butadiene fragment plays a dominant role for the coupling of these assumed fragment molecules. As a consequence, **2⁻** can act as an electron donor (D) and the butadiene as an electron acceptor (A). The other interaction between the LUMO of **2⁻** and the HOMO of the butadiene fragment is less important because the energy separation between these is larger than that between the HOMO of **2⁻** and the LUMO of the butadiene fragment. However, this minor interaction also prefers the coupling at position *e*. In this way the two orbital interactions work cooperatively for stabilizing **5⁻**.

Let us next take a look at the interactions between the two frontier orbitals, the HOMO of **2⁻** and the LUMO of the butadiene fragment, in terms of stereoselection rules.[33] The HOMO−LUMO interaction clearly favors coupling of the two fragment molecules at position *e* and disfavors the coupling at position *f* because of the in-phase and out-of-phase orbital interactions, respec-

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tively, as shown in Chart 3. We therefore expect that **5⁻** should have a low-lying HOMO and a high-lying LUMO and that **4⁻** should have a high-lying HOMO and a low-lying LUMO. The coupling at position *a* is not so effective for stabilizing the resultant molecule **3⁻** because there is no orbital coefficient on site 2 of **2⁻** with respect to the HOMO. Such a qualitative inspection of the orbital interactions demonstrates that stabilization energy decreases in the sequence of position *e* > *a* > *f*, and accordingly the stability of the formed carbanions is expected to decrease in the sequence **5⁻** > **3⁻** > **4⁻**. Ionization potential as well as absolute hardness decreases in this sequence, as seen in Table 1. These qualitative predictions are in agreement with the order of stability for single-electron oxidation in the gas phase and in dimethyl sulfoxide solution (I_p and E_{ox}, respectively), as previously indicated. Of course, the Hartree−Fock and DFT computational results in Table 1 can be rationalized from these qualitative orbital interaction analyses.

We next turn our attention to the molecular orbitals of **3⁻**, **4⁻**, and **5⁻** from extended Hückel calculations. Since these molecules are composed of the same fragments in different ways of connection, we can see an important correlation between the molecular structure and the chemical stability. Computed orbital interaction diagrams for **3⁻**, **4⁻**, and **5⁻** are shown in Figures 4, 5, and 6, respectively. Only π orbitals are indicated. At the left in each interaction diagram are the molecular orbitals of **2⁻**, and at the right are the molecular orbitals of the butadiene fragment.

Let us first look at the frontier orbitals of **3⁻** in Figure 4. The b₂ HOMO of **3⁻** is derived from an out-of-phase combination of the HOMOs of **2⁻** and the butadiene fragment; as a result, it is slightly pushed up compared to the HOMO of **2⁻**. In a similar way, the a₂ HOMO of **4⁻** comes from an out-of-phase combination of the HOMOs of **2⁻** and the butadiene fragment and it is thus slightly pushed up compared to the HOMO of **2⁻**, as shown in Figure 5. Therefore the HOMOs of **3⁻** and **4⁻** are high-lying in energy, and as a consequence, the ionization potentials of these carbanions are small. On the other hand, the a″ HOMO of **5⁻** is predominantly composed of the HOMO of **2⁻**, as shown in Figure 6. There is a small in-phase contribution of the LUMO of the butadiene fragment in the a″ HOMO of **5⁻** because the HOMO of **2⁻** and the LUMO of the butadiene
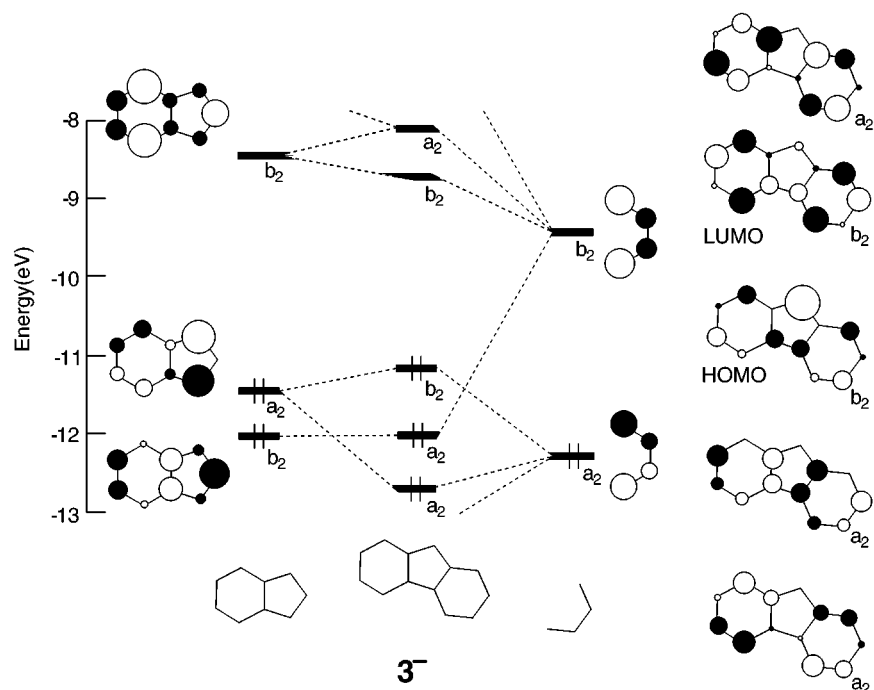
Figure 4. Orbital interaction diagram for **3⁻**, partitioned into **2⁻** and butadiene fragments.
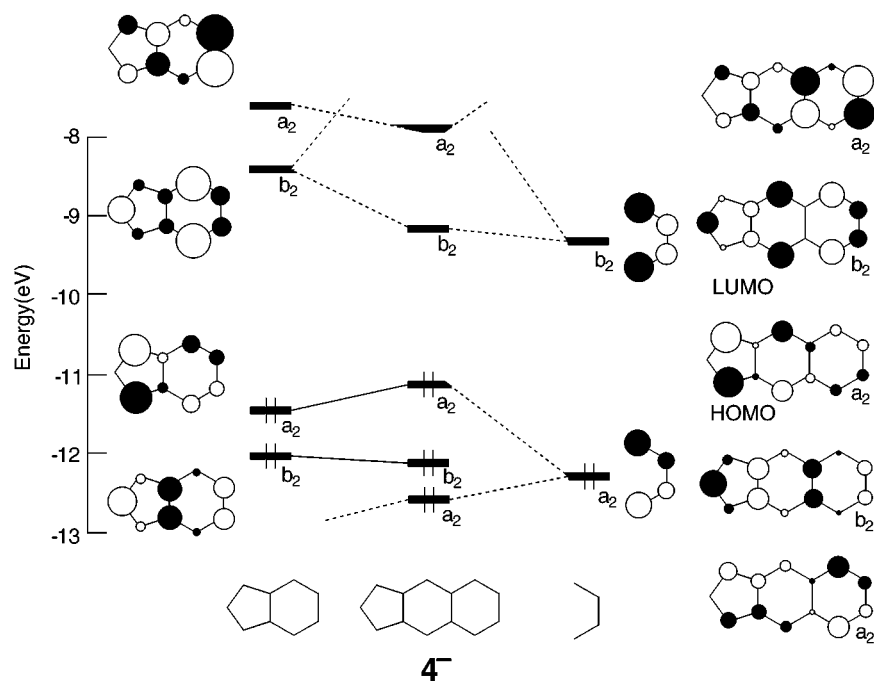

Figure 5. Orbital interaction diagram for **4⁻**, partitioned into **2⁻** and butadiene fragments.

fragment are in-phase at the position *e*; as a result, the HOMO of **5⁻** is slightly pushed down from the HOMO of **2⁻**. Thus, we qualitatively understand that the energy level of the HOMO of **5⁻** is lower than those of **3⁻** and **4⁻**, and therefore the ionization potential of **5⁻** is higher than those of **3⁻** and **4⁻**. The detailed descriptions of the orbital interactions for **3⁻**, **4⁻**, and **5⁻**, indicated in Figures 4, 5, and 6, respectively, are in agreement with the qualitative representation in Chart 3.

Solvent Effects on the Stability of Cyclopentadienides

As shown in the previous sections, neither computed ionization potential nor absolute hardness is a good measure for the stability of these cyclopentadienides determined in dimethyl sulfoxide. In particular, the observed E_{ox} values for **1⁻** and **8⁻** are close to each other, while the computed values of ionization potential (I_p) for these two anions are apart from a linear relation between the two quantities. The results presented above include no solvent effects; thus, computed values of I_p are the values in the gas phase. It is therefore not surprising that the stability of the condensed cyclopentadienides for single-electron oxidation in solution is in disagreement with the computed values of I_p. Solute molecules are, in general, stabilized by solvent molecules, and the degree of stabilization would significantly depend on the size and
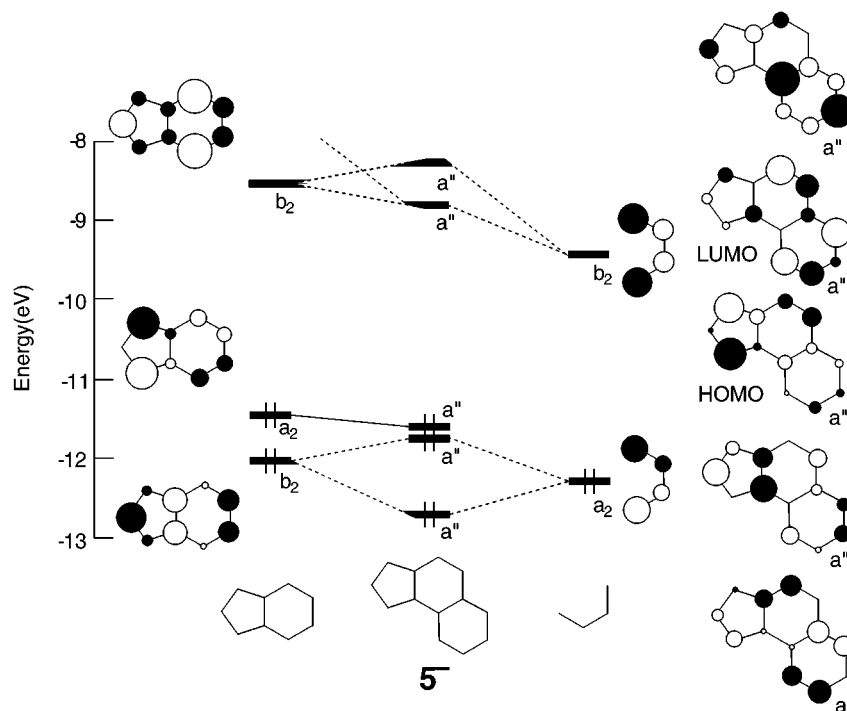
Figure 6. Orbital interaction diagram for **5**⁻, partitioned into **2**⁻ and butadiene fragments.
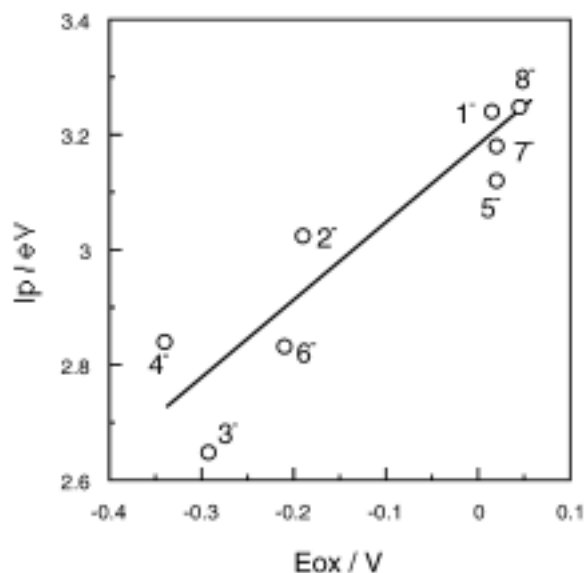

Figure 7. I_p values computed from SCRF computations at the B3LYP/6-31G** level of theory as a function of E_{ox}. The solute is placed in a uniform electric field of dimethyl sulfoxide with a relative dielectric constant of 45.

the charge distribution in solute molecules. We must therefore take solvent effects into account to increase our understanding of the stability of the condensed cyclopentadienides in solution. In this section, we present how solvent effects change the order of I_p in these carbanions.

Figure 7 illustrates I_p values obtained using eq 1 from self-consistent reaction field (SCRF) computations at the B3LYP/6-31G** level of theory as a function of E_{ox} measured in dimethyl sulfoxide. In the computations the solute is placed in a uniform electric field of solvent with a relative dielectric constant ϵ_r. We set the value for dimethyl sulfoxide to be 45. In contrast to Figure 3, in which the I_p values and the E_{ox} values displayed no linear

Chart 4
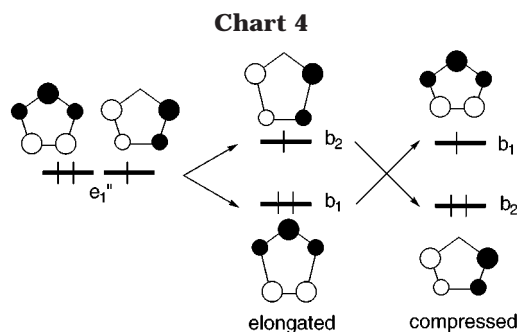
relationship for different sets of isomers, we see a correlation between the two quantities in Figure 7 as a consequence of including solvent effects. In particular, the positions of **1**⁻ and **2**⁻ are corrected according to our expectation; the computed values of I_p based on the SCRF method and the measured values of E_{ox} exhibit a linear, good correlation for all the cyclopentadienides in Figure 7. Since the dipole−dipole interaction between solute and medium is large for **1**⁻ and **2**⁻, due to charge localization, the net solvation energy is expected to be significant for these small carbanions compared to larger ones. As a consequence, the values of I_p reasonably increase when solvent effects are appropriately taken into account. We therefore conclude that the solvent effects are significant in small cyclopentadienides **1**⁻ and **2**⁻ and that addition of condensed aromatic rings intrinsically stabilizes the formed condensed cyclopentadienides as seen from computed I_p values in the gas phase. The computational results are fully consistent with our general expectation for solvent effects.

Spin Densities of Neutral Cyclopentadienyls

Since **1**⁻ has a D_{5h} structure with the 2-fold degenerate e_1'' HOMO, its neutral radical species **1**⁺ is predicted to undergo molecular distortions, due to the Jahn−Teller
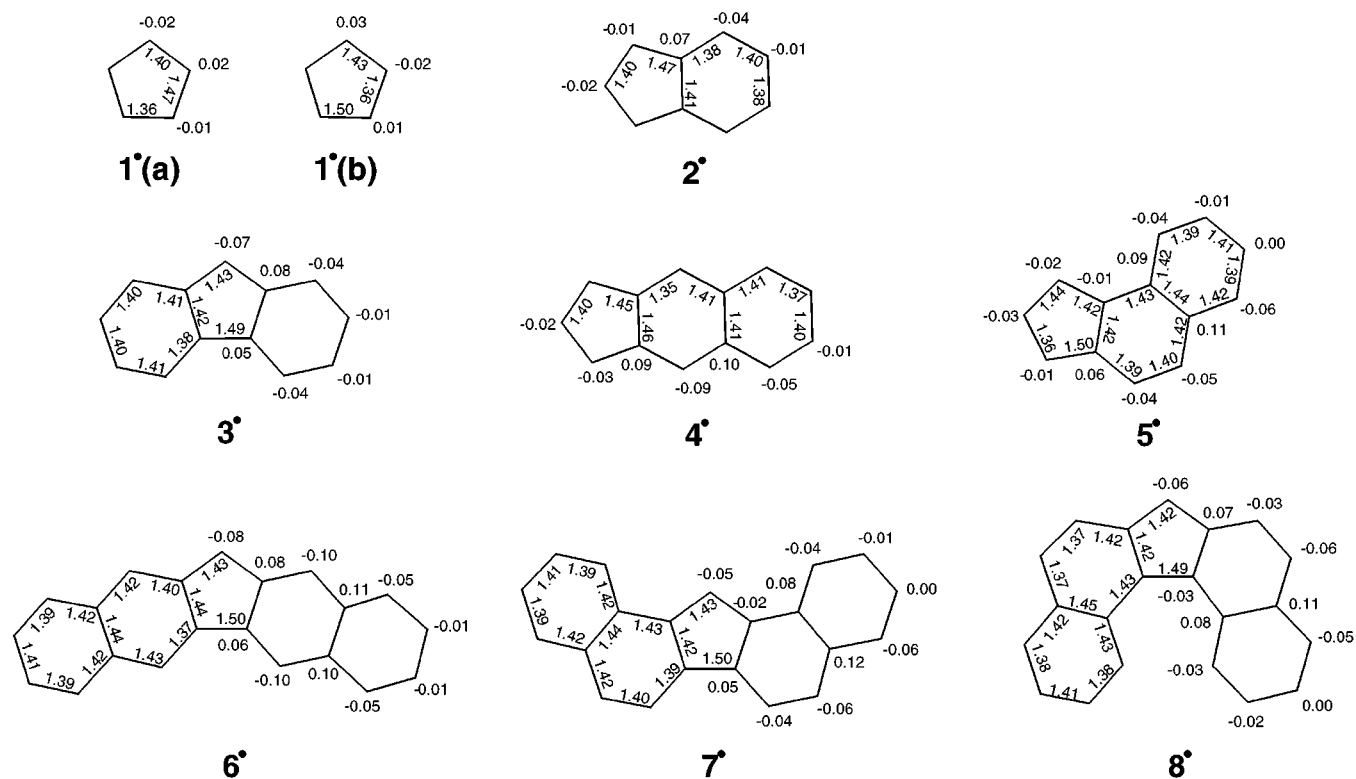
Figure 8. Optimized C−C bond distances and atomic charges of cyclopentadienyls **1·** to **8·** at the B3LYP/6-31G** level of theory. **1·(a)** and **1·(b)** are computed elongated and compressed geometries, respectively, due to the Jahn−Teller effect.
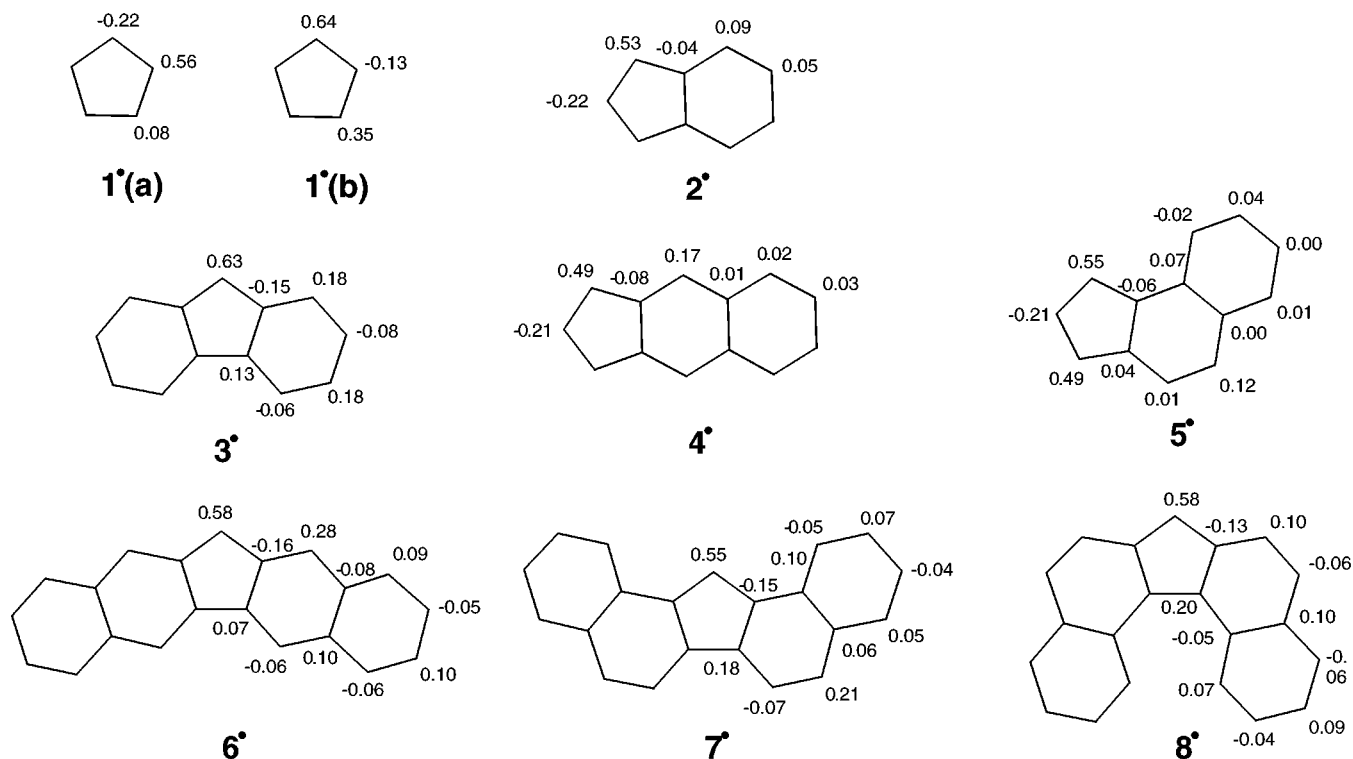

Figure 9. Spin densities of cyclopentadienyls **1·** to **8·** at the B3LYP/6-31G** level of theory. **1·(a)** and **1·(b)** are computed elongated and compressed geometries, respectively, due to the Jahn−Teller effect.

theorem.[34] According to the *epikernel principle*,[35] this molecule should be distorted into a C_{2v} structure through coupling with E_1' modes of molecular vibration. Elongated and compressed C_{2v} structures, which are nearly equal in energy, are expected, as indicated in Chart 4. In the elongated structure the b_1 and b_2 orbitals should be stabilized and destabilized, respectively, whereas in the compressed geometry the b_2 and b_1 orbitals should be

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(34) Jahn, H. A.; Teller, E. *Proc. R. Soc. A* **1937**, *161*, 220.

stabilized and destabilized, respectively. Elongated and compressed structures were actually obtained from B3LYP computations, as expected.

The other cyclopentadienyls do not have highly symmetric molecular geometries that have a degenerate set of molecular orbitals so that Jahn−Teller distortions are not expected to occur in the sense of first-order perturbation theory. Therefore we placed symmetry restrictions on these radical species as previously; C_{2v} for **2°**, **3°**, **4°**, **5°**, **6°**, and **7°**, and C_2 for **8°**. Computations were performed at the ab initio HF and the B3LYP levels of theory using the 6-31G** basis set. The spin-unrestricted version of the B3LYP method appeared to behave well for these spin-doublet species; computed $\langle S^2 \rangle$ values at the B3LYP level lie within a range from 0.75 to 0.77, whereas those at the ab initio UHF (unrestricted Hartree−Fock) level are more than 1.[36] Thus, the HF results are not reliable, due to significant contamination of higher-spin states. In fact, the amplitude of the spin-density wave computed at the UHF level was overestimated.

Figure 8 illustrates B3LYP optimized geometries of **1°** to **8°**. The elongated and the compressed forms of **1°** have nearly equal energies, as expected, because the b_1 and b_2 orbitals in the C_{2v} structures are originally degenerate in the D_{5h} structure (see Chart 4). The optimized structures of **2°** to **8°** are quite similar to those of **2⁻** to **8⁻**. However, computed [5,6] and [6,6] bond distances of **2°** to **8°** are reasonably decreased compared to those of **2⁻** to **8⁻**, due to the half occupation of the HOMOs (in **2°** to **8°**), which are out-of-phase with respect to a [5,6] and a [6,6] bond in most cases, as shown in Figure 2.

Spin density distributions in **1°** to **8°** are shown in Figure 9. These cyclopentadienides are not *alternant* hydrocarbons.[37] A conjugated system is termed alternant if the atoms in it can be divided into two groups, *starred* and *unstarred*, in such a way that no two atoms of the same group are directly linked. We can therefore find in these radical species spin frustrations, in which spin densities of the same sign are located on nearest neighboring atoms. Thus, these radical species are unstable compared to alternant hydrocarbon radicals.[38]

Concluding Remarks

Condensed aromatic rings are successfully introduced to cyclopentadienide **1⁻** in different ways of connection, leading to various types of condensed cyclopentadienides with different shapes and different stabilities. We theoretically investigated the relationship between the structure and the stability of various condensed cyclopentadienides, which involve 6π, 10π, 14π, and 22π electrons. An increase in the size of the cyclopentadienides results in an increase in the ionization potential. Cyclopentadienide **1⁻** has the largest value of absolute hardness among the condensed cyclopentadienides investigated. Computed values of absolute hardness decrease when aromatic rings are introduced into **1⁻**, depending on the way of connection. The reason that some of the cyclopentadienides are stabilized and others are destabilized is rationalized from detailed orbital interaction analyses. The stability of the condensed cyclopentadienides for single-electron oxidation in solution is not in agreement with computed values of ionization potential and absolute hardness. Solvent effects on the order of stability of the condensed cyclopentadienides in solution were taken into account by performing self-consistent reaction field (SCRF) calculations, the results being in excellent agreement with experiments. We demonstrated that the solvent effects are significant in small cyclopentadienides **1⁻** and **2⁻** rather than in larger ones, as expected, and that addition of condensed aromatic rings intrinsically stabilizes the formed condensed cyclopentadienides in solution as well as in the gas phase. The order of stability of the condensed cyclopentadienides for single-electron oxidation in solution is significantly affected by solvent effects.

(35) Ceulemans, A.; Vanquickenborne, L. G. *Structure and Bonding*; Springer: Berlin, Heidelberg, 1989; Vol. 71. The *epikernel principle* tells us that Jahn−Teller distortions preserve larger symmetry groups than could be expected from an unrestricted action of the Jahn−Teller distorting forces.

(36) The $\langle S^2 \rangle$ value for spin-doublet species is 0.75.

(37) Dewar, M. J. S. *The Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1969.

(38) (a) Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, *26*, 179. (b) Dougherty, D. A. *Acc. Chem. Res.* **1991**, *24*, 88. (c) Rajca, A. *Chem. Rev.* **1994**, *94*, 871. (d) Borden, W. T.; Iwamura, H.; Berson, J. A. *Acc. Chem. Res.* **1994**, *27*, 109. (e) Yoshizawa, K.; Hoffmann, R. *Chem. Eur. J.* **1995**, *1*, 403.