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Theoretical Study of Oxocyclohexadienylidene Isomers: Electronic Structures and Molecular Properties

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The molecular properties and electronic structures for three isomers of oxocyclohexadienylidene were investigated using multiconfiguration SCF (MCSCF) wave functions. The ground electronic states of the ortho and para isomers are the open shell triplet, whereas the meta isomer has a singlet ground state with significant open shell character. The structural features of the ground states of all three isomers are close to the quinoid type structure. Several molecular properties such as the electron spin density, electron affinity (EA), acidity and bond dissociation energy for the three isomers and/or their corresponding radicals are also considered and are compared with experimental values. In particular, the MCSCF(8,8)/6-31+G* electron spin densities for both ortho and para isomers are very close to the experimental values of the phenoxyl radical.

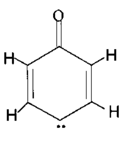
Introduction

The study of carbene chemistry has long been a subject of great interest. Insights regarding the molecular and electronic structures of carbene species are crucial for the understanding of their chemical behavior. Consequently, many theoretical and experimental studies have been performed to investigate their electronic nature as well as molecular structure.[1−10] It is well-known that some reaction mechanisms involving carbenes can be interpreted in terms of the relative energies of their ground and excited electronic states. In addition, the interaction between electronic states with different spin multiplicities, such as intersystem crossing (ISC), sometimes plays an important role in the interpretation of carbene reaction mechanisms.[1,2,11]

Carbenes containing conjugated rings are of interest[3−10] because their molecular and electronic structures are very sensitive to the interaction between nonbonding electrons and the π system. Indeed, this interaction plays a role in characterizing the nature of low-lying electronic states. Previous theoretical studies[5,6] reported that the ground state of cyclopropenylidene is a closed shell singlet, due to the very small CCC angle, while cyclopentadienylidene has an open shell triplet ground state.

In the current work, the primary interest is in the structures and properties of *p*-, *o*-, and *m*-oxocyclohexadienlylidene (**1, 2** and **3**). Although, as illustrated in this paper, the ground states of the para (**1**) and ortho (**2**) isomers are triplets, standard closed shell Lewis structures may be drawn, as shown in the schematics below. It is not possible to draw such a structure for the meta isomer. This suggests that the lowest singlet state for the meta isomer (**3**) is not closed shell and therefore requires a multiconfigurational wave function for even a qualitatively correct description.

In these molecules, one can relate both the σ and π frameworks to those of simpler molecules. A previous study[9] assumed that the π system of these molecules approximates that of the phenoxyl radical (**4**), while the σ system should be similar to that of the phenyl radical. Indeed, the ESR spin density of the para isomer (**1**, 4-oxo-2,5-cyclohexadienylidene) is estimated to be about 0.4 for the π system at the para position, in good agreement with a value of 0.42−0.45 for the phenoxyl radical.[9] It was also shown[10] that the ground electronic state of the para isomer is $^3B_1$ and its molecular structure is closer to that of the quinoid type structure (**1a**) than the benzene-like structure (**1d** or **1e**).



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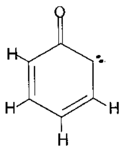

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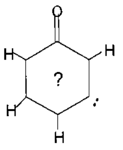

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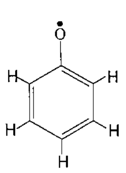

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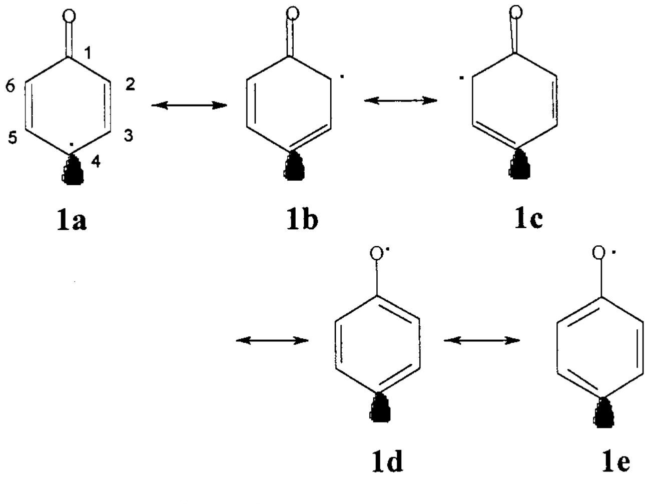

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The dot in these structures represents a single electron, while the orbital shown contains a single electron in the molecular plane**.** An open shell singlet state ($^1B_1$) is much lower in energy than the conventional closed shell singlet ($^1A_1$). The latter is a transition state and is higher than $^1B_1$ by about 12 kcal/mol at the single and double excited configuration interaction (CISD) level of theory.

It is more difficult to treat excited electronic states theoretically than the ground state, since more complex wave functions are required. A multiconfiguration SCF (MCSCF) wave function[12] is frequently essential for an adequate description of excited states and to describe the electronic behavior of cycloalkenylidene species. In addition, to achieve a more reliable energy comparison between the electronic states, it is necessary to use more sophisticated dynamic electron correlation techniques, such as multiconfiguration quasi-degenerate second-order perturbation theory (MCQDPT2)[13] or complete active space second-order perturbation theory (CASPT2).[14]

Isomers of 4-oxo-2,5-cyclohexadienylidene can formally be obtained by H atom shifts. For example, in its ortho (**2**) and meta (**3**) isomers, the divalent carbon atom is at the ortho and meta positions relative to the carbonyl group, respectively, while the divalent carbon atom is located at the para position in 4-oxo-2,5-cyclohexadienylidene. There are few experimental or theoretical investigations of the isomers of 4-oxo-2,5-cyclohexadienylidene. The experimental electron affinities of phenyl and phenoxyl radicals, which are prototypes for the molecules of interest in the present study, have been reported.[15] However, there are no reports for the electron affinities of oxocyclohexadienylidene systems. The electron affinity for aromatic radicals is interesting, because the addition of an extra electron can change the character of the aromatic ring. Indeed, the electronic and molecular structures of the anions are quite different from those of the corresponding radical. Recently, some anions with conjugated rings have been the subjects of both experimental and computational studies.[16−18]

In this paper, the molecular and electronic structures of oxocyclohexadienylidene isomers **1**, **2** and **3** are considered using multiconfiguration SCF (MCSCF) wave functions. The relative energies of the electronic states are considered, and estimates are provided for the electron affinity, electron spin density, proton affinity and bond dissociation energy for these systems. Finally, the structural features of several possible electronic states for these three isomers are discussed.

Computational Details

All calculations were performed using the GAMESS[19] electronic structure program. The geometric parameters of the electronic states of three oxocyclohexadienylidene isomers were optimized at the MCSCF level with the 6-31G* and 6-31+G* basis sets. Since there are seven π orbitals and a σ nonbonding orbital on the divalent carbon atom in **1**−**3**, the MCSCF active space used for the neutral molecules is eight electrons and eight orbitals. For anions, an extra electron is added to the active space. Thus, the active spaces for neutral and anionic species of these molecules can be denoted as (8,8) and (9,8), respectively. The geometry optimizations for the para isomer were restricted to C_{2v}, whereas ortho and meta isomers were restricted to C_s symmetry. MCSCF numerical Hessians for all of the neutral and anionic species were calculated with the 6-31G* basis set, to determine whether optimized structures are local minima or saddle points. To achieve a more reliable energy comparison among the electronic states, MCQDPT2 single point energy corrections were performed with 6-31G*, 6-31+G* and 6-311+G* basis sets. The electron spin density was calculated at the MCSCF level of theory.[20]

TABLE 1: Relative Energies (kcal/mol) for Several Electronic States of 4-Oxo-2,5-cyclohexadienlylidene (1)

state	MCSCF/ 6-311+G*	CISD+Q/ 6-31G* [a]	MCQDPT2/ 6-311+G* [b]
$^3B_1$	0	0	0
$^1B_1$	14.9	10.9	10.6
$^1A_1$	19.9	23.3	33.0
$^3A_2$	59.0	62.6	50.2
$^1A_2$	54.8	63.1	48.8
$^3B_2$	73.1	70.1	69.7
$^1B_2$	101.3	92	97.9
$^3A_1$	102.9		108.3

[a] Reference 10, includes Davidson correction for unlinked quadruple excitation. [b] MCQDPT2/6-311+G*//MCSCF(8,8)/6-31+G*.

TABLE 2: MCQDPT2/6-311+G*[a] Relative Energies (kcal/mol) for Several Electronic States of Ortho (2) and Meta (3) Isomers

state	ortho	meta
1A		0
3A″	0	0.6
1A″	8.7	2.6
1A′	46.7	46.3
3A′	66.4	62.8

[a] MCQDPT2/6-311+G*//MCSCF(8,8)/6-31+G*.

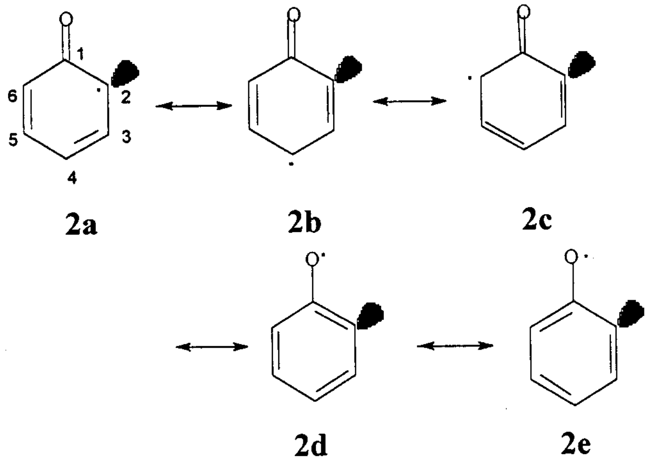
Results and Discussion

Relative Energies. The MCSCF and MCQDPT2 relative energies for electronic states of **1** are summarized in Table 1. The results of previous CISD+Q/6-31G* calculations[10] are included for comparison. The ground electronic state of this molecule is predicted to be $^3B_1$. The MCQDPT2/6-311+G*//MCSCF(8,8)/6-31+G* energy difference between the $^3B_1$ and $^1B_1$ states is 10.6 kcal/mol, in good agreement with the CISD+Q value of 10.9 kcal/mol. The closed shell $^1A_1$ state is predicted to be the second excited state. The excitation energy for this state is more sensitive to the level of theory, and it is clear that both multiconfiguration wave functions and dynamic correlation are necessary to obtain an accurate result. The MCQDPT2 and CISD+Q excitation energies differ by about 10 kcal/mol for this state. The MCSCF(8,8)/6-31G* Hessian for the $^1A_1$ state indicates that it is a transition state, whereas both $^3B_1$ and $^1B_1$ states are local minima.

The $^3A_2$ and $^1A_2$ states are 50.2 and 48.8 kcal/mol higher, respectively, than the ground state at the highest level of theory. These values differ from those of the CISD+Q calculation by more than 10 kcal/mol, although both levels of theory find these two states to be very close to each other in energy. The energies of $^3B_2$, $^1B_2$ and $^3A_1$ states relative to the ground state are computed to be about 70, 98, and 108 kcal/mol, respectively, at the MCQDPT2/6-311+G* level.

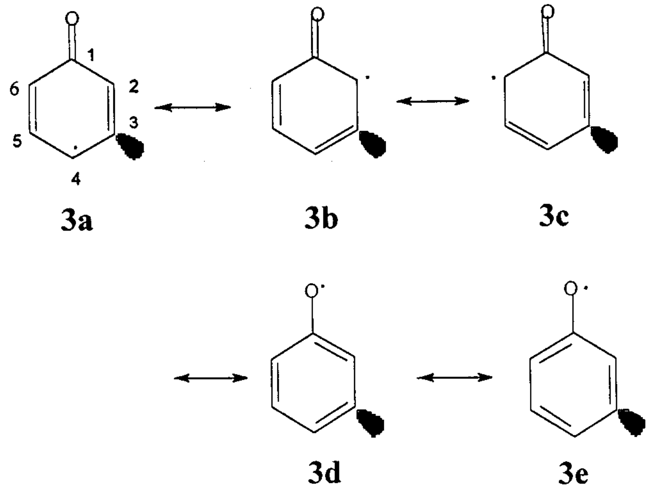
The relative energies of various electronic states of both **2** and **3** are summarized in Table 2. The electronic ground state of the ortho isomer (**2**) is predicted to be $^3A''$. This correlates with $^3B_1$ in C_{2v} symmetry, so the ground states of **1** and **2** are on the same potential energy surface. The MCQDPT2/6-311+G* calculation shows that the ground state of **1** is more stable than that of **2** by 1.8 kcal/mol. The triplet is 8.7 kcal/mol below the first excited $^1A''$ state. The MCSCF(8,8)/6-31G* Hessians confirm that these two stationary points are local minima on the potential energy surfaces. The closed shell $^1A'$ electronic state of this molecule is predicted to lie considerably higher than the first two states, 46.7 kcal/mol above the ground state. The Hessian for this $^1A'$ state has one imaginary frequency of 398.9i cm^{-1} that lowers the symmetry from C_s to C_1. The MCQDPT2 energy of the $^3A'$ state is about 66 kcal/mol higher than the ground electronic state.

The electronic structure of the meta isomer (**3**) is quite different from that of the other two isomers. The formal resonance structures for the ortho (**2a**−**2e**) and meta (**3a**−**3e**) isomers are shown below. It is clearly not possible to draw a meta resonance structure that has an unpaired electron at the divalent carbon, in contrast to the ortho (**2a**) and para (**1a**) isomers. The most stable electronic state of the meta isomer within C_s symmetry is predicted to be $^1A''$. However, the MCSCF(8,8)/6-31G* Hessian shows that $^1A''$ is a transition state with one imaginary frequency of 193.1i cm^{-1} that lowers the symmetry from C_s to C_1. The true ground state (^1A) lies about 0.6 kcal/mol below the $^3A''$ structure. The $^1A''$ state of the meta isomer lies less than 3 kcal/mol above the ground state. The MCSCF(8,8)/6-31G* numerical Hessian calculations confirm that the $^3A''$ state is a local minimum. The para ($^3B_1$) and ortho ($^3A''$) ground states are predicted to lie 1.0 and 2.9 kcal/mol, respectively, above the ground state of the meta isomer. The ground state of **3** may be characterized by the occupation numbers (NOON) of the natural orbitals in the active space. For the first four natural orbitals, which correspond to the doubly occupied RHF orbitals, the NOON are 1.94, 1.90, 1.88, 1.70. So, while this electronic state is not a singlet diradical, there are 0.58 electrons outside of the closed shell electronic configuration. Clearly, MCSCF wave functions are required for a proper description of this state.



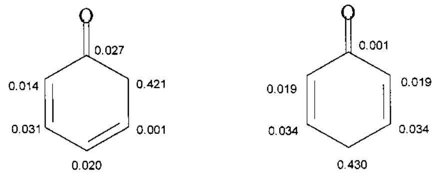
2a **2b** **2c**

2d **2e**



3a **3b** **3c**

3d **3e**



(a) (b)

Figure 1. Computed electron spin density at the nucleus for (a) ortho and (b) para Isomer. Hydrogen atoms are omitted for clarity.

The MCQDPT2 energy of the meta closed shell $^1A'$ state is about 46 kcal/mol higher than the ground state. This energy difference is very close to that of the ortho isomer. The MCSCF Hessian also shows that the $^1A'$ state is a second-order saddle point with two imaginary frequencies. The energy of the $^3A'$ state, in which two unpaired electrons are located in the π system, is predicted to lie about 63 kcal/mol above the ground state.

Electron Spin Density. The computed electron spin densities at the nuclei for the para and ortho oxocyclohexadienylidenes ground electronic states are illustrated in Figure 1. The spin density calculation for the meta isomer shows zero spin at all nuclei for this singlet state.

The electron spin density at the para position of **1** was estimated by Wasserman and Murray [9] to be about 0.4 which is very close to that of the phenoxyl radical (0.42−0.45). The MCSCF(8,8)/6-31+G* electron spin density at the para position of this molecule is computed to be 0.43, in excellent agreement with that of the phenoxyl radical. The computed electron spin density of 0.42 at the divalent carbon atom of the ortho isomer is similar to that of the para isomer. The formal resonance structures of a carbene electron in the π system of the para isomer (**1a**−**1e**) are similar to those in the ortho system (**2a**−**2e**). Therefore, it is not surprising that the two isomers exhibit similar electronic behavior.

Electron Affinity. The computed electron affinities (EA) for the three isomers along with the experimental values are listed in Table 3.[21,22] Since the ground electronic state of the anion species corresponding to **1** is $^2A_1$, the electron affinity of this molecule is estimated from the energy difference between the $^3B_1$ neutral and $^2A_1$ anion states. The predicted EA is clearly very sensitive to both basis set and level of theory. Diffuse functions and dynamic correlation are required for an adequate assessment of this property. At the best level of theory, MCQDPT2 with the 6-311+G* basis set, the EA is computed to be 42.5 kcal/mol. For the ortho and meta isomers, the same level of theory predicts an EA of 44.8 and 45.3 kcal/mol, respectively. These predictions compare favorably with experimental values of 45.2 ± 2.3 kcal/mol for all 3 isomers.

Wasserman and Murray[9] suggested that the π system of **1** might be similar to the phenoxyl radical (**4**) while its σ system approximates the phenyl radical. For both neutral and anion species in their ground electronic states, the natural orbital occupation numbers (NOON) of the nonbonding orbital at the divalent carbon atom are exactly 1.00. This means that the extra electron in the anion species is added to the π system. Thus, one would expect the electron affinity of this molecule to be close to that of the phenoxyl radical. The experimental electron affinities are 2.253 eV for the phenoxyl radical and 1.096 eV for the phenyl radical.[15] Our estimated value of 42.5 kcal/mol (1.84 eV) is closer to that of the phenoxyl radical

Proton Affinity and Bond Dissociation Energy. The anion proton affinities for the three oxocyclohexadienylidene isomers

TABLE 3: Electron Affinities (kcal/mol) for Three Isomers of Oxocyclohexadienylidene at Various Levels of Theory

molecules	MCSCF/6-31G*	MCSCF/6-31+G*	MCSCF/6-311+G*	MCQDPT2/6-31G*	MCQDPT2/6-31+G*	MCQDPT2/6-311+G* [a]
para	−2.2	7.9	8.0	26.3	41.3	42.5 (45.2 ± 2.3)
ortho	0.7	10.9	11.1	23.5	43.5	44.8 (45.2 ± 2.3)
meta	1.3	10.9	10.5	29.8	44.4	45.3 (45.2 ± 2.3)

[a] MCQDPT2/6-311+G*//MCSCF(8,8)/6-31+G*. [b] Experimental values are given in parentheses.

TABLE 4: MCQDPT2/6-311+G* [a] Proton Affinities (kcal/mol) for Three Isomers of Oxocyclohexadienyl Anions

	para	ortho	meta
C-protonation	376.1 (≥367 ± 3)[b]	375.6 (≥366 ± 4)	372.3 (≥366 ± 4)
O-protonation	345.2	342.2	342.2

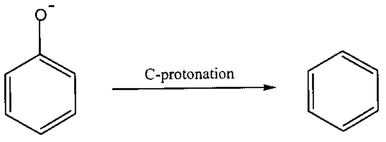
[a] MCQDPT2/6-311+G*//MCSCF(8,8)/6-31+G*. [b] Experimental values are given in parentheses.

TABLE 5: MCQDPT2/6-311+G* [a] Bond Dissociation Energies (kcal/mol) for 4, 5 and 6

	para	ortho	meta
4	105.0	106.8	104.0
5	74.1	76.7	73.9
6	104.4	103.9	100.6

[a] MCQDPT2/6-311+G*//MCSCF(8,8)/6-31+G*.

are useful for interpreting the results of gas-phase experiments, because it is difficult to measure these quantities. Protonation can occur at carbon or oxygen to afford the phenoxyl radical (**4**) or the *p*-hydroxylphenyl radical (**5**), respectively, as illustrated for the para isomer:



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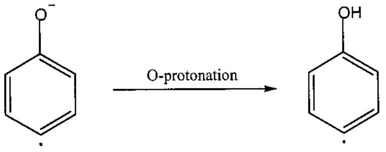

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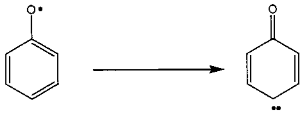
The computed proton affinities for the three oxocyclohexadienylidene anions are summarized in Table 4. As expected, C-protonation is much more favorable (~30 kcal/mol) since a more stable radical is formed. The MCQDPT2 values for C-protonation of the ortho, meta, and para isomers are 365.6, 372.3, and 376.1 kcal/mol, respectively, as compared to the experimental results of ≥366 ±4 (ortho and meta) and ≥367 ± 3 (para).[21,22] The latter quantities were assigned as lower limits because the phenoxyl radical is formed upon C-protonation, and in most cases its electron affinity is larger than the electron binding energy of the conjugate base of the reference acid. Consequently, a subsequent electron transfer takes place leading to net hydrogen atom abstraction, and exothermic proton-transfer reactions could have been missed. Moreover, one might anticipate a barrier for proton transfer in these cases, given that the bulk of the anion's charge undoubtedly is on the electronegative oxygen atom.

The energetics for C−H bond dissociation to form the three oxocyclohexadienylidene isomers and their anionic analogues have also been examined with multiconfiguration wave functions. For example, the para isomer of oxocyclohexadienylidene can be formed by bond dissociation as follows:



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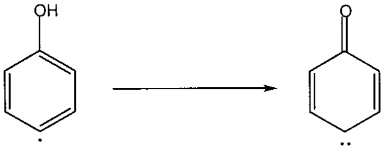

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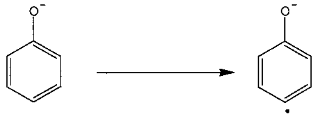
The computed bond dissociation energies are summarized in Table 5, and it can be seen that at the MCQDPT2 level the ortho, meta, and para C−H and O−H bonds in the phenoxyl radical are all worth about 105 and 75 kcal/mol, respectively. This result is consistent with the predicted relative C vs O proton affinities.

The C−H bond dissociation energies from phenoxide ion (**6**) are also summarized in Table 5. These are essentially the same as those obtained for the corresponding phenoxyl radicals.



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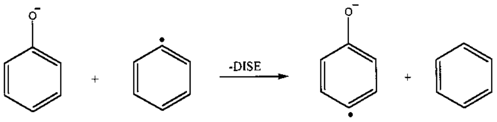
Distonic Ion Separation Energy. It is interesting to measure the interaction between the radical and charged site. This interaction energy is called the distonic ion separation energy (DISE)[21a] and is defined using the following reaction.



If the DISE is positive there is a stabilizing interaction between the anionic and radical sites, whereas a negative value indicates a destabilizing interaction.The computed MCQDPT2/6-311+G* DISEs are +2.2 (ortho), +5.5 (meta), and +1.7 (para) kcal/mol. All of these values are small but stabilizing. It is also interesting to note that the largest interaction is in the meta case, as this is the only oxocyclohexadienylidene that is a ground-state singlet.

Molecular Structure of Three Isomers. *Para Isomer*. A MCSCF(8,8)/6-31G* molecular structure for the neutral para isomer (**1**) was previously reported by Sole et al.[10] The geometric parameters for several electronic states of both neutral and anionic para isomers, calculated using the same active space and the 6-31+G* basis set, are summarized in Table 6. Adding

TABLE 6: MCSCF(8,8)/6-31+G* Geometric Parameters for Both the Radical and Anion of 4-Oxo-2,5-cyclohexadienylidene (1) (Distances in Å; Angles in deg)[a]

	Neutral								Anion			
parameters	$^3B_1$	$^1B_1$	$^1A_1$	$^1A_2$	$^3A_2$	$^3B_2$	$^1B_2$	$^3A_1$	$^2A_1$	$^2B_1$	$^2A_2$	$^2B_2$
C_1-C_2	1.464	1.433	1.480	1.467	1.466	1.446	1.387	1.406	1.442	1.452	1.435	1.442
C_2-C_3	1.375	1.400	1.354	1.447	1.448	1.438	1.445	1.394	1.394	1.379	1.457	1.451
C_3-C_4	1.410	1.385	1.481	1.390	1.387	1.428	1.417	1.472	1.391	1.445	1.413	1.386
$C-O$	1.230	1.270	1.216	1.220	1.218	1.232	1.461	1.364	1.255	1.242	1.245	1.262
$\angle C_2C_1C_6$	117.9	119.3	117.0	115.0	114.9	114.4	117.8	121.6	114.6	115.5	111.2	120.4
$\angle C_1C_2C_3$	120.7	120.3	120.4	121.9	122.0	121.1	120.1	118.9	122.7	120.8	123.1	119.7
$\angle C_2C_3C_4$	118.2	117.1	124.5	119.2	119.0	126.5	125.9	124.3	119.3	125.8	126.9	115.6
$\angle C_3C_4C_5$	124.3	126.0	113.2	122.9	123.3	110.5	110.3	112.0	121.5	111.3	109.0	128.9

[a] Atomic numbering as in **1a**.

diffuse functions on the heavy atoms has only a small effect on the geometrical parameters, and there are no dramatic differences between the neutral and anion structures. Thus, we only discuss the molecular structures of the anion here, calculated with the 6-31+G* basis set. In the para $^2A_1$ and $^2B_2$ states, the σ nonbonding orbital on the divalent carbon atom is singly occupied. This means the π active spaces have 8 electrons. However, the π active spaces in the $^2A_2$ and $^2B_1$ states have seven electrons, while the σ nonbonding orbital on the divalent carbon atom has two electrons.

In the $^2A_1$ state, the C2−C3 and C3−C4 bond lengths are essentially equal and shorter than that of the C1−C2 bond. In addition, all bond angles except for the C2−C1−C6 angle are close to 120°. This means both the quinoid (**1a**) and the benzene-like (**1d** or **1e**) resonance structures contribute to the wave function of this state. On the other hand, the $^2B_1$ structure is closer to the quinoid structure, since the C2−C3 bond is much shorter than the C3−C4 bond. The C3−C4−C5 bond angle of this state decreases to about 111°. This value is also consistent with the quinoid structure.

In the $^2A_2$ state, the computed C2−C3 bond length of 1.457 Å is somewhat larger than the other C−C bonds. This is caused by the contribution of active orbitals with C2−C3 antibonding character to the muti-configurational wave function. In the $^2B_2$ state, the C3−C4 bond length is somewhat shorter than that of the other doublet states. The C3−C4−C5 bond angle increases to 129° in this state.

Ortho Isomer. The MCSCF(8,8)/6-31+G* optimized geometrical parameters for various electronic states of both neutral singlets and triplets and anion doublet species of the ortho isomer (**2**) are summarized in Table 7. The MCSCF/6-31G* optimized geometries are essentially the same. There are four low-lying electronic states for the neutral molecule. Two of these four states ($^3A''$ and $^1A''$) are true local minima, while the $^1A'$ state is a transition state with an imaginary frequency of 398.9i cm^{-1}, at the MCSCF(8,8)/6-31G* level. Unfortunately, we cannot verify that the highest electronic state ($^3A'$) is a true minimum because of root flipping in the numerical Hessian calculation.

As noted earlier, the ground electronic state of the ortho isomer is predicted to be $^3A''$ at the MCSCF(8,8)/6-31+G* level. This means one of the carbene electrons is localized in the nonbonding σ orbital (a′), while a second unpaired electron is in a π orbital (a″). Indeed, the MCSCF(8,8)/6-31+G* NOON for the nonbonding σ orbital in the ground state is 1.00, while the other carbene electron is delocalized into the π system.

The geometries in Table 7 support the notion that the molecular structure for the ground electronic state of the ortho isomer is much closer to the quinoid type structure (**2b**) than the benzene-like one, since the C−C bond distances are quite different from each other. The C1−C2 and C1−C6 bond lengths are much longer than the other C−C bonds. This is because these two bonds have less double bond character. The C2−C3 and C5−C6 bond lengths are shorter than the other C−C bonds. The MCSCF(8,8)/6-31+G* bond orders computed by Mayer's method[20] for the C1−C2 and C1−C6 bonds are about 1.0, while values for the other bonds are bigger than 1.5 (e.g., the C−O bond order is about 1.7). This is consistent with the quinoid type structure.

TABLE 7: MCSCF(8,8)/6-31+G* Geometric Parameters for Both the Radical and Anion of the Ortho Isomer (2) (Distances in Å; Angles in deg)[a]

	neutral				anion	
parameters	$^3A''$	$^1A''$	$^1A'$	$^3A'$	$^2A'$	$^2A''$
C_1-C_2	1.449	1.454	1.518	1.488	1.438	1.469
C_1-C_6	1.466	1.448	1.481	1.435	1.441	1.473
C_2-C_3	1.371	1.344	1.458	1.448	1.374	1.414
C_5-C_6	1.380	1.406	1.349	1.443	1.395	1.372
C_3-C_4	1.404	1.458	1.363	1.448	1.412	1.407
C_4-C_5	1.430	1.385	1.466	1.365	1.399	1.421
C_1-O_7	1.230	1.236	1.222	1.247	1.250	1.250
$\angle C_2C_1C_6$	114.7	114.6	122.6	121.7	111.1	121.7
$\angle C_1C_2C_3$	124.6	124.9	112.1	111.8	127.0	112.6
$\angle C_1C_6C_5$	120.8	121.2	119.2	121.4	123.1	120.8
$\angle C_2C_3C_4$	118.2	118.3	123.9	126.3	119.4	126.0
$\angle C_4C_5C_6$	121.4	120.9	119.9	119.7	122.4	118.9
$\angle C_3C_4C_5$	120.3	119.9	122.3	119.1	117.2	120.0
$\angle C_2C_1O_7$	123.2	123.4	118.0	119.4	124.7	122.3

[a] Atomic numbering as in **2a**.

The overall features of the molecular structure for the $^1A''$ state are similar to those of the ground state, although the C3−C4 and C5−C6 bonds are somewhat longer than those in the $^3A''$ state. Since this is an open shell singlet state with A″ symmetry, one electron is expected to be in the π system. Indeed, the NOON of this orbital is 1.0. Since the electron density of the divalent atom is quite low, the resonance structure (**2a**) contributes less to this state than the others. Thus, both the C3−C4 and C5−C6 bonds of the $^1A''$ state are somewhat longer than those in the ground state. Since the $^1A'$ wave function is symmetric to reflection in the π nodal plane, the molecular and the electronic structures of $^1A'$ are quite different from those of the $^1A''$ and $^3A''$ states. The two carbene electrons are localized on the nonbonding σ orbital.

The overall molecular structures of the doublet species (Table 7) are closer to the quinoid shape than the benzene-like one. In the $^2A'$ state, eight electrons are delocalized onto the π system with one electron in the σ nonbonding orbital of the divalent carbon atom. The C3−C4 bond in the $^2A'$ state is somewhat longer than the C2−C3 bond, while the C4−C5 and C5−C6 bond lengths are similar. The $^2A''$ state has seven π electrons and two σ nonbonding electrons on the divalent carbon, and most C−C bonds are somewhat longer than in the $^2A'$ state.

TABLE 8: MCSCF(8,8)/6-31+G* Geometric Parameters for Both the Radical and Anion of the Meta Isomer (3) (Distances in Å; Angles in deg)[a]

	neutral					anion	
parameters	^1A	$^1A''$	$^3A''$	$^1A'$	$^3A'$	$^2A'$	$^2A''$
C_1-C_2	1.486	1.462	1.463	1.490	1.454	1.448	1.458
C_1-C_6	1.491	1.463	1.460	1.478	1.451	1.446	1.461
C_2-C_3	1.354	1.370	1.361	1.408	1.468	1.375	1.397
C_5-C_6	1.359	1.376	1.381	1.351	1.406	1.388	1.375
C_3-C_4	1.364	1.400	1.407	1.422	1.467	1.390	1.442
C_4-C_5	1.464	1.424	1.417	1.465	1.389	1.410	1.424
C_1-O	1.216	1.232	1.233	1.219	1.236	1.250	1.243
$\angle C_2C_1C_6$	115.1	117.4	117.4	118.2	116.7	114.1	117.2
$\angle C_1C_2C_3$	115.8	117.9	117.6	126.0	125.1	119.7	125.9
$\angle C_1C_6C_5$	122.0	121.2	121.4	117.6	120.2	123.0	119.1
$\angle C_2C_3C_4$	127.6	125.1	125.6	109.9	112.1	126.7	112.3
$\angle C_4C_5C_6$	118.3	120.7	120.6	120.1	121.5	122.1	120.3
$\angle C_3C_4C_5$	116.1	117.6	117.4	128.2	124.4	114.3	125.2
$\angle C_2C_1O$	123.0	121.3	121.4	120.5	121.5	123.0	123.1
$\angle C_1C_2C_3C_4$	−6.0						

[a] Atomic numbering as in **3a**.

Meta Isomer. The MCSCF(8,8)/6-31+G* optimized geometrical parameters for the meta isomer (**3**) are listed in Table 8. As noted before, the ground electronic state of this conformer is ^1A, and the first and second excited states are $^1A''$ and $^3A''$, respectively. These three low-lying states are almost degenerate. As can be seen in Table 6, the C1−C2 and C1−C6 bonds in the ground state are longer than those in the $^1A''$ and $^3A''$ states, whereas, the C2−C3, C5−C6 and C−O bonds are shorter than those of $^1A''$ and $^3A''$ states. So, the structure of the ground state is closer to the quinoid structure than are the $^1A''$ and $^3A''$ states, even though its symmetry is somewhat distorted from C_s to C_1. The geometries of the first and second excited states ($^1A''$ and $^3A''$) are very similar, because the two states have the same two singly occupied orbitals, with different net spin multiplicity. The overall structural features of the $^1A''$ and $^3A''$ states of the meta isomer are much closer to a quinoid type structure than those of the ortho isomer. The $^1A'$ and $^3A'$ states of the meta isomer show a rather distorted quinoid structure. The ground state for the anion species of the meta isomer is $^2A'$. The molecular structures of the doublet species also show a quinoid shape.

Conclusions

The molecular and electronic structures of three isomers of oxocyclohexadienylidene have been investigated using multiconfigurational SCF wave functions. The ground electronic states of the para (**1**) and ortho (**2**) isomers are open shell triplets. The closed shell singlet configuration for these isomers is the second excited state and is a transition state with an imaginary frequency. At the best level of theory, MCQDPT2 with the 6-311+G* basis set, the energy difference between the ground and closed shell singlet states of the para and ortho isomers is 33.0 and 46.7 kcal/mol, respectively. On the other hand, the ground state of the meta isomer (**3**) is computed to be ^1A, about 0.6 kcal below the $^1A''$ transition state. In this meta ground state, there is considerable electron density outside the Hartree−Fock closed shell orbitals, so there is significant open shell character in this state. The second excited state ($^3A''$) is about 3.0 kcal/mol above the ground state.

The ground state of the para isomer ($^3B_1$) is 1.8 kcal/mol lower than that of ortho isomer ($^3A''$) at the MCQDPT2/6-311+G* level. The ground state of the meta isomer (^1A) is calculated to be 1.0 kcal/mol lower than that of the para isomer. While this means the calculations predict the global minimum to be the (ground-state singlet) meta isomer, an energy spread of less than 3 kcal/mol is too small for this to be definitive at this level of theory.

The use of multireference based wave functions is essential for a proper description of the properties of these states. The MCSCF(8,8)/6-31+G* spin densities at the nuclei for the ortho and para isomers are similar to the experimental value of the phenoxyl radical system, while the (ground-state singlet) meta isomer has zero spin density at the nuclei. The best estimated electron affinities (EA) for the ortho, meta, and para isomers are 1.92, 1.96, and 1.84 eV. These compare favorably with the experimental values of 1.96 ± 0.1 eV for all 3 isomers and are somewhat smaller than that of the phenoxyl radical (2.25 eV). The MCQDPT2 proton affinities at carbon for all three isomers are about 375 kcal/mol, while the values are around 30 kcal/mol less at oxygen. The C−H and O−H bond dissociation energies forming the three oxocyclohexadienylidene isomers and their anions also were examined. The results show that the C−H BDEs are about 100 kcal/mol and are about 30 kcal/mol higher than the O−H BDEs. Moreover, the C−H bond dissociation energies of the anionic isomers are almost the same as those of the neutrals. The distonic ion separation energy (DISE) is defined and computed for three radical ions. It is about 3 kcal higher for the meta isomer but is small in all three cases. Structures of the ground electronic states for all three isomers are discussed and found to resemble a quinoid-type structure.

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Supporting Information Available: Table of vibrational frequency data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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(22) Electron and proton affinities were measured in a Fourier transform mass spectrometer. All three radical anions react with *p*-dinitrobenzene and NO_2 via electron transfer, but no reaction is observed with *p*-quinone. This enables us to assign the electron affinities as 1.96 ± 0.1 eV. Proton transfer is observed when all three anions are reacted with trifluoroethanol and stronger acids, but not with phenylacetylene, hydrogen fluoride, diethylhydroxylamine or acetone. With *p*-fluoroaniline proton transfer is observed upon reaction with the para isomer but not the ortho or meta anions. Consequently, we assign PA = $\geq 367 \pm 3$ (para) and $\geq 366 \pm 4$ (ortho and meta).