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Very-Low-Lying Electronic States Result from n → π Excitations in Open-Shell Annulenes, Annelated with α-Dicarbonyl Groups

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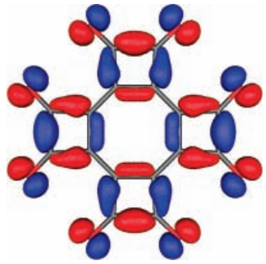
ABSTRACT



UB3LYP/6-31G* calculations find that α-dicarbonyl-annelated cyclopentadienyl radical 1 has a σ ground state, which is formed by excitation of an electron from the in-phase combination of carbonyl lone-pair orbitals into the singly occupied π orbital. Similarly, tetrakis-annelated cyclooctatetraene 3 is calculated to have very-low-lying singlet and triplet excited states, which result from excitations of electrons from the b_{1g} combination of lone pair orbitals into the empty π nonbonding MO of the COT ring.

In the course of our studies of π bond localization in cyclopentadienyl radicals,[1] our UB3LYP/6-31G* calculations found that the $^2A_1$ state of α-dicarbonyl-annelated cyclopentadienyl radical **1** is lower in energy than either the $^2A_2$ or $^2B_1$ state. As indicated in Figure 1, the $^2A_1$ state differs from $^2A_2$ and $^2B_1$ by the transfer of an electron from the high-lying, in-phase combination of carbonyl lone pair orbitals[2] into the singly-occupied low-lying, π-bonding orbital of the cyclopentadiene ring, to afford an aromatic cyclopentadienyl anion.

As a consequence of the mixing of the in-phase combination of lone pairs of the carbonyl groups with the σ bond that joins these groups, this C−C bond is much longer in the $^2A_1$ state than in $^2A_2$ or $^2B_1$ (Figure 1). The weakness of this bond in the $^2A_1$ state of **1** results in an imaginary

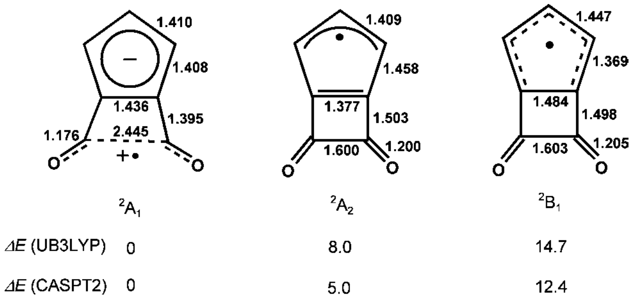


Figure 1. Bond lengths in the UB3LYP/6-31G*-optimized C_{2v} geometries of the $^2A_1$, $^2A_2$, and $^2B_1$ states of **1**. Relative UB3LYP/6-31G* and CASPT2/6-31G* energies are given in kcal/mol.

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[1] Zhou, X.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **2007**, *129*, 10785.

[2] The in-phase combination of carbonyl lone pair orbitals is destabilized by mixing with the σ bond between the carbonyl groups. In contrast, the out-of-phase combination is stabilized by mixing with the unfilled, σ^*, orbital of the bond that joins the carbonyl groups.

10.1021/ol703014a CCC: $40.75

frequency for a vibration that breaks C_{2v} symmetry by localizing the radical on one carbonyl group and the positive charge on the other. Geometry optimization in C_s symmetry leads to fulvene−ketene radical **2** in Figure 2, which is computed to be 7.4 kcal/mol lower in energy than the $^2A_1$ state of **1**.

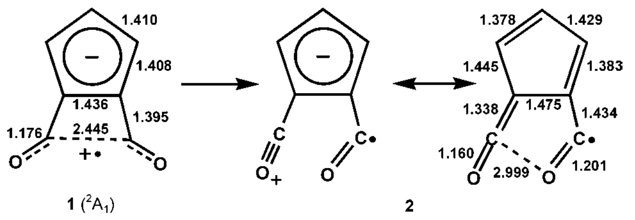

Figure 2. Comparison of the bond lengths (Å) in the UB3LYP/6-31G*-optimized C_s geometry of fulvene−ketene radical **2** with those in the $^2A_1$ state of **1**, which is calculated to be 7.4 kcal/mol higher in energy than **2**. The syn conformation of the acyl radical, shown above, is 2.7 kcal/mol lower in energy than the anti conformation in which the acyl oxygen points away from the ketene group, thus suggesting a weak bonding interaction between the acyl oxygen and the ketene carbon.

In order to confirm that the $\sigma \rightarrow \pi$, $^2A_1$ ground state, predicted for **1**, is not an artifact of the UB3LYP[3] calculations that we performed, we also carried out ab initio (15/13)-CASSCF and CASPT2[4] calculations. The active space consisted of the five π orbitals of cyclopentadienyl radical, the π and π^* orbitals of both carbonyl groups, the σ and σ^* orbitals of the C−C bond connecting the two carbonyl groups, and the two oxygen lone pair orbitals that mix strongly with these C−C σ and σ^* orbitals.[2] The UB3LYP/6-31G* geometries were used for these single-point CASPT2 calculations which were also performed with the 6-31G* basis set.[5]

The UB3LYP and CASPT2/6-31G* relative energies of the three lowest-energy states of **1** are compared at the bottom of Figure 1. The reasonably good agreement between these two methods suggests that the UB3LYP methodology, which we used for the much larger molecules on which we subsequently performed calculations, gives electronic state orderings that are at least qualitatively correct.

The results of our calculations on **1** and **2** led us to investigate whether in cyclooctatetraene (COT) **3** (Figure 3) two σ electrons might be transferred from the highest energy combination of carbonyl group lone-pair orbitals into the π system, thus giving an electronic state with 10 π electrons. Baldridge and Siegel have reported that their B3PW91 calculations on **3** found endo localization of the eight π electrons, depicted in **3a**, to be favored over exo localization, shown in **3b**.[6] However, no mention was made in this paper of a low-lying state of **3** with 10 π electrons (**3c**).

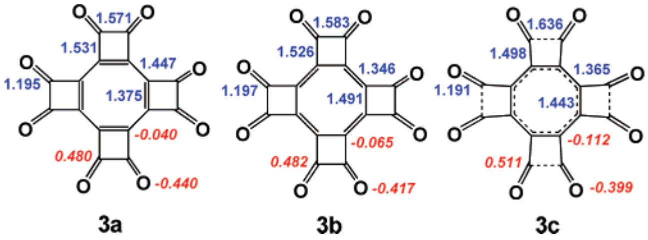

Figure 3. Bond lengths (Å, in blue) and NBO charges (italics in red) in the B3LYP/6-31+G*-optimized D_{4h} geometries of **3a**−**c**. **3a** and **3b** each have 8 π electrons, but **3c** has 10 π electrons. The additional two π electrons in **3c** come from the b_{1g} σ MO, shown in Figure 4, which is doubly occupied in **3a** and **3b**.

Our B3LYP calculations with both the 6-31+G*[7] and 6-311+G(2df,2p)[8] basis sets confirmed the finding of Baldridge and Siegel that the endocyclic localization of the eight π electrons, as shown in **3a**, does, indeed, provide the lowest energy, planar geometry for COT **3**. However, we found that the optimized geometry of **3b**, which also has eight π electrons, but exocyclic double-bond localization, is 22.5 kcal/mol (23.9 kcal/mol with the larger basis set) higher than that of planar **3a**, rather than the 4−5 kcal/mol reported by Baldridge and Siegel.

The reason for the apparent disagreement between our results and those of Baldridge and Siegel became evident when we examined the Supporting Information for their paper.[6] The C−C bonds between the carbonyl groups in the geometry that Baldridge and Siegel assigned to **3b**, are 1.624 Å long, which is nearly 0.06 Å longer than the C−C bonds between the carbonyl groups in the geometry that they optimized for **3a**. We were, in fact, able to optimize a similar geometry for their “**3b**”, with bond lengths of 1.636 Å between the carbonyl groups and a B3LYP/6-31+G* energy that was only 8.5 kcal/mol (6.1 kcal/mol with the larger basis set) higher than that of **3a**. However, checking the orbital occupancies at this geometry confirmed our suspicion that, unlike **3a** or our **3b**, the geometry with the long bonds between the carbonyl groups has 10 π electrons and, hence, belongs to **3c**.[9]

The two additional π electrons in **3c** come from what is the highest occupied σ MO in **3a** and **3b**. As shown in Figure 4, this b_{1g} MO involves oxygen lone-pair orbitals, interacting in an antibonding fashion with σ orbitals that are bonding between pairs of carbonyl groups.[2] Consequently, removal

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(3) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1998**, *37*, 785.

(4) (a) Anderson, K.; Malmqvist, R. A.; Roos, B. O. *J. Chem. Phys.* **1992**, *96*, 1218. (b) Anderson, K.; Malmqvist, R. A.; Roos, B. O.; Sadlej, A. J.; Wolinski, K. *J. Chem. Phys.* **1990**, *94*, 5483.

(5) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(6) Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **2002**, *124*, 5514.

(7) (a) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (b) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.

(8) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(9) The type of alternation of COT ring-bond lengths in **3c** is similar to that expected in and calculated for **3b**. This similarity is, presumably, what led Baldridge and Siegel to ascribe the optimized geometry of **3c** to **3b**. Since **3c** and **3b** both have $^1A_{1g}$ wave functions, it would be hard to tell **3c** and **3b** apart, unless the long bonds between the carbonyl groups in **3c** led one to check which σ and π MOs were actually occupied in **3c**.

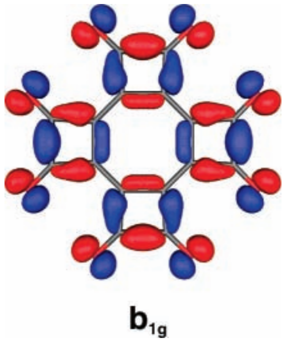

Figure 4. b_{1g} MO, which is the occupied σ orbital of highest energy in **3a** and **3b**, but which is empty in **3c**.

of the pair of electrons from the b_{1g} σ MO makes the C−O bonds shorter and the C−C bonds between the carbonyl groups longer in **3c** than in **3a** or **3b**.

One might naïvely expect that excitation of two electrons from the b_{1g} MO in Figure 4 into the lowest unoccupied (LU)MO of the COT ring would make the carbonyl groups in **3c** much more positively charged and the COT ring carbons much more negatively charged than those in **3a** and **3b**. However, the NBO[10] charges in Figure 3 show that in going from **3a** to **3c**, the net charge transferred from each carbonyl group to each ring carbon amounts to only 0.072 e. Clearly, the π^* orbitals of the carbonyl groups must accept a great deal of negative charge from the filled π MOs of the COT ring, thus transferring electron density from the COT ring back into the carbonyl groups in **3c**.

This back-donation from the filled π orbitals of the COT ring into the π^* orbitals of the carbonyl groups of **3c** results in enhanced π bonding between the ring and carbonyl carbons. Presumably, this is the reason why these C−C bonds are ca. 0.03 Å shorter in **3c** than in **3a** or **3b**.[11]

An analysis of the interactions between the π orbitals, involved in back-donation to the carbonyl groups, explains why the bond lengths in the eight-membered ring of **3c** resemble those in **3b** more closely than those in **3a**. In D_{4h} symmetry, the degenerate pair of π HOMOs of planar COT have b_{1u} and b_{2u} symmetry and interact with combinations of π^* carbonyl orbitals of the same symmetry. In the b_{1u} combination of unfilled, π^*, C═O orbitals, the 2p AOs on the carbonyl carbons within each four-membered ring are in phase; whereas, in the b_{2u} combination these 2p-π AOs are out-of-phase. Consequently, the b_{1u} combination of π^* C═O orbitals is lower in energy and thus accepts more electron density from the π orbitals of the COT ring than the b_{2u} combination of π^* C═O orbitals.[12]

The b_{1u} and b_{2u} π MOs of **3c** are shown in Figure 5. The effects of the larger contribution of the π^* carbonyl orbitals to the b_{1u} than to the b_{2u} MO can be seen in the larger contribution of the 2p AOs on oxygen to the b_{1u} MO. The smaller contribution of the 2p AOs of the COT ring to the b_{1u} than to the b_{2u} MO leads to less π bonding between pairs of AOs in the COT ring that are endocyclic, rather than exocyclic, to the four-membered rings in **3c**. Consequently, the COT ring bonds that are endocyclic to the four-membered rings in **3c** are 0.078 Å longer than the COT ring bonds that are exocyclic.[9]

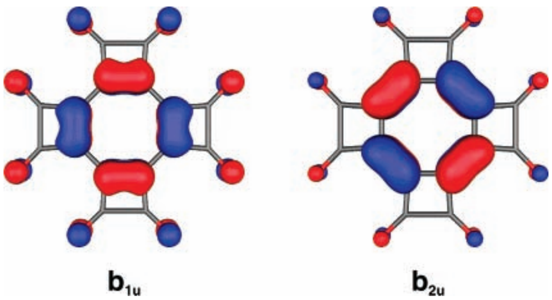

Figure 5. Occupied b_{1u} and b_{2u} π MOs of **3c**, viewed from above the ring, so only the top lobes of the 2p AOs are visible.

As shown by the NBO charges in Figure 3, the carbonyl oxygens in **3c** are less negatively charged than those in **3a**. This presumably accounts for the results of PCM calculations,[13] which predict that a solvent with the dielectric constant of water would actually increase the calculated energy difference between **3a** and **3c** from 8.5 to 21.3 kcal/mol. Of more importance than the magnitude of this predicted energy change, caused by differential solvation of **3a** and **3c**, is the sign of the change. It indicates that dissolution of **3** in a very polar solvent would *not* increase the favorability of the transfer of two electrons from the σ HOMO of **3a** to the π LUMO, but would, instead, have the opposite effect.

From the perspective of the Hückel 4n + 2 rule, **3c**, with 10 π electrons, should be aromatic, whereas **3a**, with 8 π electrons, should be antiaromatic. Probing for the existence of induced diamagnetic and paramagnetic ring currents by calculating nucleus-independent chemical shifts (NICS) values[14] has become a widely used method for assessing aromaticity/antiaromaticity. The calculated NICS(0) values of 22.7 ppm for planar **3a** and −18.3 ppm for planar **3c** strongly support the premise that **3a** is antiaromatic, whereas **3c** is aromatic.

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[10] Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

[11] The population of a C−O antibonding orbital in **3c** should also tend to make the C−O bond lengths in this state longer than those in **3a** and **3b**. The reason that the C−O bond lengths in **3c** are actually shorter than those in **3a** and **3b** is that depopulation of the b_{1g} σ orbital *removes* electron density from a σ orbital which, as shown in Figure 4, is antibonding between the oxygens and the carbonyl carbons to which they are attached.

[12] This is the reason why occupancy of the b_{1u} MO in **3a** is favored over occupancy of the b_{2u} MO in **3b**.[2,6] The NBO charges in Figure 3 confirm that more electron density is delocalized from the ring carbons into the carbonyl groups in **3a** than in **3b**.

[13] (a) Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117. (b) Miertus, S.; Tomasi, J. *Chem. Phys.* **1982**, *65*, 239.

[14] (a) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317. (b) Chen, Z.; Wannere, C. S.; Corminboeuf, C.; Puchta, R.; Schleyer, P. v. R. *Chem. Rev.* **2005**, *105*, 3842.

Nevertheless, **3a** is calculated to be lower in energy than **3c**. Moreover, with two more π and two less σ electrons than **3a**, **3c** might be expected to undergo facile cleavage of a four-membered ring, to form a bis-ketene. Indeed, this reaction of **3c** is calculated to have a C_{2v} transition structure[15] and a barrier of less than 0.1 kcal/mol. Thus, **3c** is of "purely theoretical" interest.

It might be expected, however, that excitation of just one electron from the b_{1g} σ HOMO of **3a** into the π LUMO would give an electronic state of **3** that (a) has an energy which is intermediate between those of **3a** and **3c** and (b) for which ring opening might not be as favorable as it is for **3c**. In order to test these hypotheses, we performed unrestricted (U)B3LYP calculations on the $^3A_{2u}$ state, formed by this one-electron, $\sigma \rightarrow \pi$ excitation in planar **3a**.

Indeed, our calculations found that the $^3A_{2u}$ state is computed to be only 0.1 kcal/mol higher in energy than planar **3a** ($^1A_{1g}$) with the 6-31+G* basis set and 0.5 kcal/mol lower than planar **3a** with the larger 6-311+G(2df,2p) basis set. Moreover, ring opening, analogous to that predicted to be favorable for **1**, is computed to be endothermic for the $^3A_{2u}$ state of **3** by 16.4 kcal/mol. This difference can be attributed to delocalization of the unpaired σ electron over all four of the four-membered rings in the $^3A_{2u}$ state of **3**, combined with less strain relief on opening of a four-membered ring in **3** than in **1**.[16]

The equilibrium geometry of the $^3A_{2u}$ state of **3** (shown in Figure 6) is computed to be planar. In contrast, for the lowest singlet state of **3** (i.e., **3a**), a D_{2d} geometry, with a tub-shaped COT ring, is calculated to be 3.3 kcal/mol (3.9 kcal/mol with the larger basis set) lower in energy than the planar D_{4h} geometry. Thus, with both basis sets, singlet **3a** at its D_{2d} equilibrium geometry is calculated to be *ca.* 3 kcal/mol lower in energy than the n → π triplet state of **3** at its D_{4h} equilibrium geometry.[17]

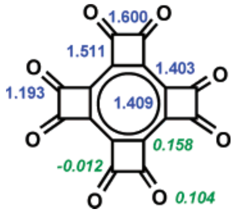

Figure 6. Bond lengths (Å, in blue) and spin densities (italics in green) in the UB3LYP/6-31+G* optimized D_{4h} geometries of the lowest triplet state ($^3A_{2u}$) of **3**. This triplet state has one unpaired electron in the b_{1g} σ MO, shown in Figure 4, and one in the b_{2u} π MO, shown in Figure 5. Because this state of **3** has 9 π electrons, its bond lengths are intermediate between those in Figure 3 for **3a**, which has 8 π electrons, and **3c**, which has 10 π electrons.

The computational predictions of a very low-lying n → π triplet state in **3**[18] and an energy difference of only 6.1 kcal/mol between **3a** and **3c** suggests that other COT derivatives, related to **3**, may actually have ground states with 10 π electrons. We are currently carrying out calculations to investigate this hypothesis, and we will report our findings in due course.

Acknowledgment. We thank the National Science and Robert A. Welch Foundations for supporting this research. Some of the calculations reported here were performed on computers purchased with funds provided by the National Science Foundation under grant CHE-0342824. This manuscript is dedicated to Professor E. J. Corey on the occasion of his 80th birthday.

Supporting Information Available: Cartesian coordinates and absolute energies for **3** and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] Cyclobutenediones usually undergo ring opening via C_2 transition structures, so that the plane which distinguishes between σ and π orbitals is lost. See, for example: McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1994**, *116*, 7233.

[16] The smaller angles, external to an octagon than to a pentagon, result in less strain relief on opening of a four-membered ring in **3** than **1**.

[17] The $^3A_{2g}$ state of **3**, which has 8π electrons, with the unpaired electrons in the b_{1u} and b_{2u} π MOs, is calculated to be 12.2 kcal/mol (14.1 kcal/mol with the larger basis set) higher in energy the $^3A_{2u}$ state, which has the b_{1u} π MO doubly occupied and the unpaired electrons in the b_{1g} σ MO and the b_{2u} π MO.

[18] Benzene lacks the low-lying, nonbonding, π MO that is present in **3**. Therefore, it is not surprising that the analog of **3** with a tris-annelated benzene ring[19] is calculated by us to have a larger n → π triplet excitation energy than **3**.

[19] (a) Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 9583; (b) Hamura, T; Ibusuki, Y.; Uekusa, H.; Matsumoto, T.; Siegel, J. S.; Baldridge, K. K.; Suzuki, K. *J. Am. Chem. Soc.* **2006**, *128*, 10032.