

Calculations of the Equilibrium Isotope Effects on the Reductions of Benzene- d_6 and Cyclooctatetraene- d_8

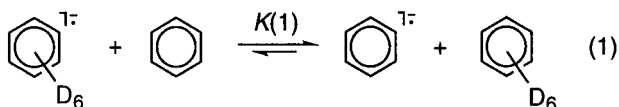
David A. Hrovat,[†] J. H. Hammons,[‡] Cheryl D. Stevenson,[§] and Weston Thatcher Borden^{*,†}

Contribution from the Departments of Chemistry, University of Washington, Box 351700, Seattle, Washington 98195-1700, Swarthmore College, Swarthmore, Pennsylvania 19081, and Illinois State University, Normal, Illinois 61790-4160

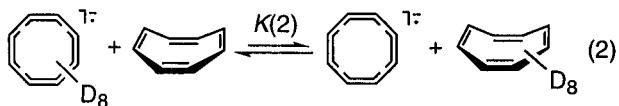
Received May 2, 1997[⊗]

Abstract: B3LYP/6-31+G* density functional calculations have been performed in order to understand why large, equilibrium isotope effects have been observed in the reduction of benzene to the corresponding radical anion but not in the reduction of cyclooctatetraene (COT) to COT^{•−}. The calculations reproduce these experimental trends. However, the calculations also find that reduction of *planar* COT, like that of benzene, has a substantial, equilibrium isotope effect. Therefore, the small isotope effect, both calculated and observed, for reduction of COT is due to an inverse isotope effect on the planarization of the tub-shaped ring in COT. The isotope effect computed for forming planar (D_{8h}) triplet COT/COT- d_8 at 173 K is 0.38. This is the predicted isotope effect on the adiabatic singlet–triplet splitting in COT. The isotope effect computed for forming planar (D_{4h}) singlet COT/COT- d_8 at the same temperature is 0.41. This is the predicted isotope effect on ring inversion. The reason why planarization of COT has an inverse isotope effect is discussed, and an experimental test of the prediction of an inverse isotope effect on ring inversion of COT is proposed.

Stevenson and co-workers have found very large, secondary isotope effects on the equilibrium constant for the reduction of aromatic hydrocarbons to their radical anions.¹ For example, at 173 K, reduction of a mixture of benzene/benzene- d_6 with potassium in THF in the presence of 18-crown-6 was found to favor formation of C₆H₆^{•−} over that of C₆D₆^{•−} by a factor of 3.85.^{1e} This is the equilibrium constant for the reaction shown in eq 1; and $K(1) = 3.85$ at 173 K corresponds to a 0.47 kcal/mol smaller electron affinity for benzene- d_6 than for benzene.



A very different result was found when a similar study was undertaken of the equilibrium isotope effect on the reduction of cyclooctatetraene (COT) vs COT- d_8 .² At 173 K the equilibrium constant for the reaction in eq 2 was found to be $K(2) = 0.86$. The small, inverse equilibrium isotope effect found for reduction of COT/COT- d_8 is in marked contrast to the large, normal, isotope effect found for reduction of C₆H₆/C₆D₆.



A possible reason, suggested by Stevenson and co-workers,² for the very different equilibrium constants found for the reactions in eqs 1 and 2 is that benzene is an aromatic molecule, whereas COT is not. A second obvious difference between benzene and COT, which is related to the first, is that benzene is planar; but COT has a tub-shaped (D_{2d}) equilibrium geometry.

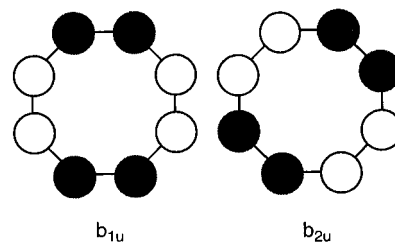


Figure 1. Schematic depiction of the NBMO's of D_{8h} COT, which are occupied by three electrons in COT^{•−}. Only one lobe of each p- π AO is shown, and the MO's are given the D_{4h} symmetry labels that are appropriate for the planar, Jahn–Teller distorted, radical anion.

However, in contrast to neutral COT, COT^{•−} is planar;^{3,4} and the large change in geometry that occurs on its formation from COT might result in an equilibrium isotope effect for reduction of COT that is quite different from that for reduction of benzene.

Were planar COT^{•−} to have D_{8h} symmetry, three electrons would occupy the two nonbonding (NB)MO's, shown schematically in Figure 1. However, COT^{•−} undergoes a first-order Jahn–Teller distortion⁵ to a pair of equivalent D_{4h} structures with alternating short and long C–C bonds,⁴ so that two

(1) (a) Stevenson, C. D.; Espe, M. P.; Reiter, R. C. *J. Am. Chem. Soc.* **1986**, *108*, 533. (b) Stevenson, C. D.; Espe, M. P.; Reiter, R. C. *J. Am. Chem. Soc.* **1986**, *108*, 5760. (c) Lauricella, T. L.; Pescatore, J. A.; Reiter, R. C.; Stevenson, R. D.; Stevenson, C. D. *J. Phys. Chem.* **1988**, *92*, 3687. (d) Stevenson, C. D.; Sturgeon, B. E.; Vines, S. K.; Peters, S. J. *J. Phys. Chem.* **1988**, *92*, 6850. (e) Stevenson, C. D.; Reidy, K. A.; Peters, S. J.; Reiter, R. C. *J. Am. Chem. Soc.* **1989**, *111*, 6578. (f) Stevenson, C. D.; Sturgeon, B. E. *J. Org. Chem.* **1990**, *55*, 4090. (g) Stevenson, C. D.; Halvorsen T. D.; Reiter, R. C. *J. Am. Chem. Soc.* **1993**, *115*, 12405.

(2) Stevenson, C. D.; Peters, S. J.; Reidy, K. A.; Reiter, R. C. *J. Org. Chem.* **1992**, *57*, 1877.

(3) (a) Katz, T. J.; Strauss, H. L. *J. Chem. Phys.* **1960**, *32*, 1873. (b) Katz, T. J. *J. Am. Chem. Soc.* **1960**, *82*, 3785. (c) Strauss, H. L.; Katz, T. J.; Fraenkel, G. K. *J. Am. Chem. Soc.* **1963**, *85*, 2360. (d) Kimmel, P. I.; Strauss, H. L. *J. Phys. Chem.* **1968**, *72*, 2813. (e) Wenthold, P. G.; Hrovat, D. A.; Borden, W. T.; Lineberger, W. C. *Science* **1996**, *272*, 1456.

(4) Hammons, J. H.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 4500.

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

[†] University of Washington.

[‡] Swarthmore College.

[§] Illinois State University.

[⊗] Abstract published in *Advance ACS Abstracts*, September 15, 1997.

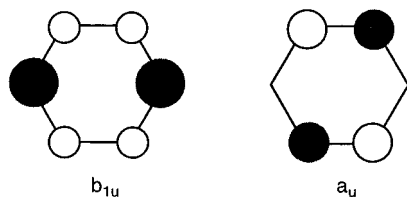


Figure 2. Schematic depiction of the antibonding π MO's of D_{6h} benzene, which are occupied by one electron in $C_6H_6^{\bullet-}$. Only one lobe of each p- π AO is shown, and the MO's are given the D_{2h} symmetry labels that are appropriate for the planar, Jahn–Teller distorted, radical anion.

electrons occupy a π MO that becomes weakly bonding after distortion. The MO occupied by the unpaired electron becomes weakly antibonding.

In contrast, were benzene to maintain D_{6h} symmetry upon reduction, the odd electron would occupy one of the strongly antibonding π MO's, shown in Figure 2. However, like $COT^{\bullet-}$, the radical anion of benzene is subject to a first-order Jahn–Teller effect;⁵ and the resulting changes in geometry⁶ reduce the antibonding interactions between the AO's in the MO that is occupied by the odd electron. Nevertheless, the MO that is occupied by the unpaired electron is less antibonding in $COT^{\bullet-}$ than in $C_6H_6^{\bullet-}$ —a difference that also has its origin in the aromaticity of benzene and the antiaromaticity of D_{8h} COT.

This difference between the nature of the singly occupied MO's in the two radical anions is reflected in the difference of 2.2 eV between the electron affinities (EA's) of planar (D_{4h}) COT (1.1 eV)^{3e} and of benzene (−1.1 eV).⁷ This difference between the singly occupied MO's in the two radical anions might also be responsible for the difference between the isotope effects for formation of these ions.

In order to investigate why such different secondary, equilibrium isotope effects have been observed for the reductions of benzene- d_6 and COT- d_8 , we have calculated these isotope effects. We find that the values of $K(1)$ and $K(2)$, computed for the gas-phase reactions in, respectively, eqs 1 and 2, are in good agreement with those that have been measured in solution by Stevenson and co-workers.^{1,2} Our calculations indicate that the difference between the equilibrium isotope effects on reduction of benzene and COT resides in the planarization of COT upon accepting an electron to form $COT^{\bullet-}$. The results of our calculations allow us to make the experimentally testable prediction of the existence of a large, inverse, kinetic isotope effect on the rate of ring inversion of neutral COT.

Computational Methodology

Schaefer and co-workers have found that B3LYP/6-31+G* density functional theory (DFT) calculations perform well in predicting electron affinities (EA's).⁸ Therefore, the electronic structure calculations that are described in this paper were all performed with the hybrid, Becke, three-parameter functional,⁹ incorporating the nonlocal correlation functional of Lee, Yang, and Parr,¹⁰ and using the 6-31+G* basis set.¹¹ The geometries of benzene, COT, and their respective radical anions were all optimized with B3LYP/6-31+G* calculations. The optimized

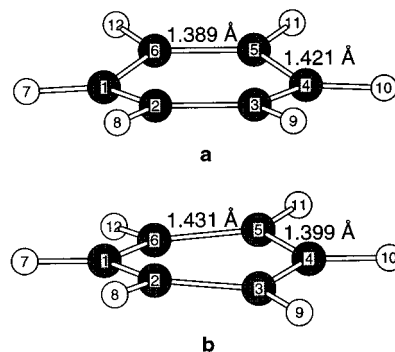


Figure 3. Selected parameters for the Becke3-LYP/6-31+G* optimized geometries of the benzene radical anion: (a) the C_{2v} minimum with a dihedral angle of 170.2° between the plane containing carbons 1, 2, and 6, and the plane of the four equivalent carbons, and (b) the D_2 transition state structure with a dihedral angle between carbons 1, 2, 3, and 4 of 12.9° and an imaginary frequency of $205.9i$ cm^{-1} .

geometries are available as Supporting Information.¹² B3LYP/6-31+G* vibrational analyses were performed at the optimized geometries, in order to obtain force constants and vibrational frequencies; and the DFT vibrational frequencies were used without scaling. These DFT calculations were carried out with Gaussian 94.¹³

The Bigeleisen equation¹⁴ was employed to calculate the equilibrium isotope effects, $K(1)$ and $K(2)$, for reduction of, respectively, benzene/benzene- d_6 (eq 1) and COT/COT- d_8 (eq 2). The isotope effect calculations were performed at the B3LYP/6-31+G* geometries, utilizing the output of the Gaussian 94 B3LYP/6-31+G* vibrational analyses. The isotope effect calculations were performed with the program, QUIVER.¹⁵

Results and Discussion

Benzene and Benzene Radical Anion. Planar, Jahn–Teller distorted, D_{2h} geometries for $C_6H_6^{\bullet-}$ with two short and four long and with two long and four short C–C bonds⁶ were both optimized. However both optimized geometries were found to have one negative force constant. The former D_{2h} geometry optimized to a nonplanar structure with C_{2v} symmetry and the latter to a nonplanar D_2 structure.¹⁶ These geometries are shown in Figure 3.

Both nonplanar geometries were computed to be 1.3 kcal/mol lower in energy than their planar counterparts. Like the first-order Jahn–Teller distortions of the C–C bond lengths, the deviations from planarity in each of these two structures reduce the antibonding interactions between adjacent p- π AO's

(12) See any current masthead page for ordering and Internet access instructions.

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, Revision B.3*; Gaussian, Inc.: Pittsburgh PA, 1995.

(14) (a) Bigeleisen, J.; Mayer, M. G. *J. Chem. Phys.* **1947**, *15*, 261. (b) Wolfsberg, M. *Acc. Chem. Res.* **1972**, *5*, 225.

(15) Saunders, M.; Laidig, K. E.; Wolfsberg, M. *J. Am. Chem. Soc.* **1989**, *111*, 8989. We thank Professor Saunders for supplying us with a copy of this program.

(16) The optimized planar (D_{2h}) geometry with two long and four short bonds is a transition-state structure that connects two equivalent twisted D_2 geometries. This D_{2h} geometry is 0.02 hartrees lower than the D_{2h} geometry with two short and four long bonds. The latter geometry has positive force constants for all out-of-plane distortions. It is a transition state structure for pseudorotation of planar $C_6H_6^{\bullet-}$,⁶ but it is not the transition state for direct interconversion of equivalent C_{2v} global minima on the potential surface for pseudorotation of C_6H_6 . Previous *ab initio* calculations have reported only planar (D_{2h}) geometries for the two Jahn–Teller distorted forms of $C_6H_6^{\bullet-}$. (See Klimkans, A.; Larsson, S. *Chem. Phys.* **1994**, *189*, 25 and references cited therein.)

(6) Liehr, A. D. *J. Phys. Chem.* **1963**, *67*, 389.

(7) (a) Boness, M. J. W.; Larkin, I. W.; Hasted, J. B.; Moore, L. *Chem. Phys. Lett.* **1967**, *1*, 292. (b) Jordan, K. D.; Michejda, J. A.; Burrow, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 1295.

(8) (a) Schaefer, H. F., III. *Theochem*, in press. (b) Galbraith, J. M.; Schaefer, H. F., III. *J. Chem. Phys.* **1996**, *105*, 862. (c) Tschumper, G. S.; Fermann, J. T.; H. F., III. *J. Chem. Phys.* **1996**, *104*, 3676. (d) King, R. A.; Galbraith, J. M.; Schaefer, H. F., III. *J. Phys. Chem.* **1996**, *100*, 6061.

(9) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(10) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(11) (a) Hariharan, P. C. and Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (b) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

in the benzene MO in Figure 2 that is singly occupied. However, of the possible types of distortions from planarity that effect this reduction, the one favored is the one which increases the interactions that are most bonding between the p - π AO's on *para* carbons in each singly occupied MO. These interactions are those between C-1 and C-4 in the b_{1u} MO, which is occupied in the structure shown in Figure 3a, and between the pairs C-2 and C-5 and C-3 and C-6 in the a_u MO, which is occupied in the structure shown in Figure 3b. Bonding interactions between these pairs of *para* carbons favor a boatlike C_{2v} geometry, over a chairlike C_{2h} geometry, for the Jahn–Teller distorted structure shown in Figure 3a and a twisted D_2 geometry, over a boatlike C_{2v} geometry, for the Jahn–Teller distorted structure shown in Figure 3b.

The C_{2v} geometry shown in Figure 3a was found to be a minimum, 0.1 kcal/mol below the D_2 geometry shown in Figure 3b. The latter was found to be a transition structure, connecting two of the C_{2v} minima on the pathway for pseudorotation of $C_6H_6^{\bullet-}$.⁶ However, the zero-point energy (ZPE) of 0.3 kcal/mol that is associated with the 225 cm^{-1} vibrational mode for pseudorotation at the C_{2v} minimum is greater than the 0.1 kcal/mol barrier to pseudorotation.¹⁷ Therefore, the lowest vibrational level for pseudorotation is predicted to take $C_6H_6^{\bullet-}$ through all three equivalent structures with C_{2v} symmetry and the three equivalent structures with D_2 symmetry that connect them. This prediction is consistent with the experimental finding that the EPR spectrum of $C_6H_6^{\bullet-}$ in solution at low temperatures shows that all six protons are equivalent.¹⁸

Comparing the electronic energies calculated for $C_6H_6^{\bullet-}$ and C_6H_6 in the gas phase, the radical anion of benzene is computed to be unbound by 1.29 eV. After correcting for the larger ZPE of benzene, the radical anion is calculated to be unbound by 1.11 eV, in excellent agreement with the experimental EA of -1.1 eV from electron transmission spectroscopy (ETS).⁷

The limited size of the 6-31+G* basis set prevents the loss of the unpaired electron from $C_6H_6^{\bullet-}$ in our calculations. This basis set deficiency allows our DFT calculations to provide a reasonable description of the temporary ion state of $C_6H_6^{\bullet-}$ that is formed by electron capture in the gas-phase in the ETS experiments.⁷ However, there was no guarantee that our DFT calculations would provide a reasonable approximation to the electronic structure of $C_6H_6^{\bullet-}$ in solution, the phase in which the secondary isotope effects on the equilibrium between C_6H_6 and $C_6H_6^{\bullet-}$ were measured.

Nevertheless, there is reasonably good agreement between the equilibrium isotope effect that we calculate for reduction of benzene- d_6 and that measured by Stevenson and co-workers.¹ The 6-fold axis of symmetry that is present in benzene- d_6 results in nearly identical equilibrium constants, K , being computed for the reaction in eq 1, using either the C_{2v} or the D_2 structure in Figure 3.¹⁹ The calculated equilibrium constants at 173 K are, respectively, $K(1) = 4.63$ and 4.67 , which are both about 20% larger than the experimental value of $K(1) = 3.85$.

The 3-fold axis of symmetry that is present in benzene-1,3,5- d_3 also results in the C_{2v} and D_2 geometries of the radical anion both giving essentially the same calculated isotope effect of $K = 2.15$ at 173 K.¹⁹ As would be expected, the value of $K = 2.15$ that we calculate for benzene-1,3,5- d_3 is close to the square root of the value of $K(1) = 4.63$ that we compute for benzene- d_6 . The experimental value of $K = 2.70$ for benzene-1,3,5- d_3 is substantially larger than both our calculated value of $K =$

2.15 and of $K = 1.96$, the square root of the experimental value for benzene- d_6 .¹

COT and COT^{•-}. Unlike the case with $C_6H_6^{\bullet-}$, our calculations predict COT^{•-} to be bound. The adiabatic EA for D_{4h} COT^{•-} \rightarrow D_{2d} COT is computed to be 0.79 eV, which increases to 0.86 eV after correction for the larger ZPE of the neutral species. The more nearly vertical EA for formation of planar D_{4h} singlet COT is 1.24 and 1.34 eV after ZPE corrections. Our DFT calculations overestimate both EA's of COT by about 0.2 eV.^{3e,20}

The isotope effect of $K(2) = 1.22$ that we calculate for reduction of COT/COT- d_8 is normal, whereas, the experimentally measured isotope effect of $K(2) = 0.86$ is inverse.² However, both the calculated and measured values for $K(2)$, the equilibrium constant for the reaction in eq 2, are much closer to unity than the calculated and measured values of, respectively, $K(1) = 4.63$ and $K(1) = 3.85$ ¹ for the reduction of benzene/benzene- d_6 in eq 1. Thus, in qualitative agreement with the experimental results of Stevenson and co-workers,^{1,2} our calculations find that the equilibrium isotope effect for reduction is much smaller for COT/COT- d_8 than for benzene/benzene- d_6 .

In order to try to understand the origin of this difference between COT and benzene, we recalculated $K(2)$ for the reaction in eq 2, starting with a planar geometry for neutral COT. Calculations were performed on both the lowest triplet state of COT ($^3A_{2g}$) at its D_{8h} equilibrium geometry and on the lowest singlet state (1A_g) at its optimized D_{4h} geometry, with alternating short and long C–C bonds. The latter is the geometry of lowest energy for *planar* singlet COT, but this D_{4h} geometry is the transition state for ring inversion on the global potential energy surface for the lowest singlet.²¹

The barrier to ring inversion in singlet COT is calculated to be 10.3 kcal/mol, which increases to 11.0 kcal/mol after correction for Δ ZPE. Despite the fact that the D_{4h} transition state for ring inversion has one less real vibrational frequency than the D_{2d} equilibrium geometry, the planar transition state has a higher ZPE, due largely to the higher frequency C–H bending vibrations in the transition state. The DFT barrier to ring inversion in COT is in good agreement with the barrier obtained by CASSCF/6-31G* calculations²¹ and with experi-

(19) When just one or two hydrogens in benzene are substituted by deuteria, the zero-point energies of the two structures in Figure 3 and, hence, the value of K calculated for each structure depends on the carbon(s) to which the deuteria are attached. For example, a deuterium attached to just C-1 in each of the structures in Figure 3a,b gives, respectively, calculated values of $K = 1.37$ and $K = 1.24$ at 173 K. Due to the way that K is defined for the reaction in eq 1, deuterium at C-1 of the structure in Figure 3b is predicted to be favored over deuterium at C-1 of the structure in Figure 3a by a factor of 1.10 at 173 K. This preference exists because substitution of deuterium for hydrogen at C-1 of the structure in Figure 3b occurs at the carbon in either structure that is least affected by the presence of the electron in the antibonding MO that is occupied in that structure. In contrast, deuterium substitution at C-1 of the structure in Figure 3a occurs at the carbon in either structure that is most affected by the odd electron. Substitution of deuterium for hydrogen results in the greatest lowering of the ZPE when substitution occurs at the carbon that is least affected by the presence of the electron in the antibonding MO. C-1 and C-4 of the structure in Figure 3b lie on a node of the MO (a_u in Figure 2) that is occupied in this structure, and the preference for deuterium being attached to these carbons is responsible for the experimental finding that the *para* hydrogen has a smaller hyperfine coupling constant than the *ortho* and *meta* hydrogens in the radical anion of benzene- d_1 . (Lawler, R. G.; Fraenkel, G. K. *J. Chem. Phys.* **1968**, *49*, 1126.) In contrast, since both NBMO's of COT have equal coefficients at all eight carbons, the deuterium in the radical anion of COT- d_1 does not perturb the spin densities; so all seven of the remaining protons are found to have the same hyperfine coupling constant. (Carrington, A.; Longuet-Higgins, H. C.; Moss, R. E.; Todd, P. F. *Mol. Phys.* **1965**, *9*, 187.)

(20) Wentworth, W. E.; Ristau, W. *J. Phys. Chem.* **1969**, *73*, 2126.

(21) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 5879.

(17) Because the D_2 transition state has an imaginary frequency for pseudorotation, its ZPE is calculated to be 0.3 kcal/mol less than that of the C_{2v} minimum.

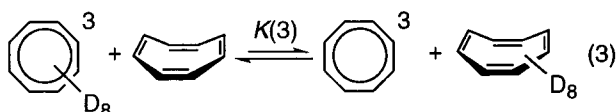
(18) (a) Tuttle, T. R.; Weissman, S. I. *J. Am. Chem. Soc.* **1958**, *80*, 5342. (b) Townsend, M. G.; Weissman, S. I. *J. Chem. Phys.* **1960**, *32*, 309.

mental estimates.²² Our DFT calculations place the D_{4h} singlet transition state for ring inversion 4.0 kcal/mol below the D_{8h} triplet equilibrium geometry.²³ This energy difference decreases to 3.6 kcal/mol after correction for the slightly greater ZPE of the planar singlet. The experimental value is $\Delta E_{ST} = -12.1$ kcal/mol;^{3c} so the DFT calculations greatly underestimate the energy of the triplet, relative to the singlet.

Starting with either the D_{8h} triplet or the D_{4h} singlet, a large equilibrium isotope effect is computed for reduction of *planar* COT. Values of $K(2)_T = 3.41$ and $K(2)_S = 3.00$ are calculated for addition of an electron to, respectively, the lowest triplet and singlet states of planar COT/COT- d_8 . Although these values are not as large as the value of $K(1) = 4.63$ that is computed for reduction of benzene/benzene- d_6 , they do show that reduction of *planar* COT, like that of benzene,¹ has a large, normal, equilibrium isotope effect.

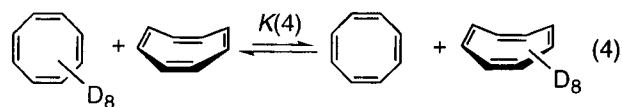
Our calculations thus indicate that the very small equilibrium isotope effects, both calculated and found,² for the reduction of COT/COT- d_8 must be due to the existence of an inverse isotope effect on planarization of the tub-shaped (D_{2d}) equilibrium geometry of COT. The size of the inverse isotope effect for planarization of COT must be comparable to the size of the normal isotope effect for reduction of *planar* COT, since the product of these isotope effects gives the small overall isotope effect for reduction of COT to COT^{•-}.

More specifically, the value of $K(2) = 1.22$, calculated for the reaction in eq 2, when combined with $K(2)_T = 3.41$, computed for the same reaction of the D_{8h} triplet states of COT and COT- d_8 , gives the isotope effect at 173 K for converting the D_{2d} equilibrium geometry of the singlet ground state of COT to the D_{8h} equilibrium geometry of the lowest triplet as $K(3) = K(2)/K(2)_T = 0.36$. $K(3)$, the equilibrium constant for the reaction in eq 3, is the isotope effect on the adiabatic singlet-triplet splitting in COT/COT- d_8 .



Similarly, $K(4)$, the equilibrium constant for the reaction in eq 4, is the isotope effect on the ring inversion of singlet COT/COT- d_8 via a D_{4h} transition state. Our DFT/6-31+G* value is $K(4) = K(2)/K(2)_S = 0.41$ at 173 K. Using unscaled (8/8)CASSCF/6-31G* vibrational frequencies, a value of $K(4) = 0.32$ is obtained.^{24,25}

Our computed values of $K(3)$ and $K(4)$ predict large inverse isotope effects on planarization of COT/COT- d_8 . This means that the frequencies of the vibrations that involve significant motions of the hydrogens must, in general, be higher at planar



geometries of COT (e.g., at the D_{8h} equilibrium geometry of the triplet and the D_{4h} transition state for ring inversion of the singlet) than at the tub-shaped (D_{2d}) equilibrium geometry of the singlet state. This is, in fact, the case for most of the C-H bending vibrations; and this is why, as noted above, the ZPE of COT increases on planarizing the eight-membered ring.

The origin of the higher C-H bending frequencies in planar than in tub-shaped COT is, presumably, the change in hybridization at the eight carbons that occurs on planarization. The increase in the size of the internal C-C-C bond angles from 127.6° to 135° upon planarization suggests that the amount of carbon 2s character in the C-C bonds increases, which results in an increase in the amount of 2p character in the C-H bonds. Since 2p orbitals are directional in character; whereas, 2s orbitals are spherically symmetric, an increase in 2p character in C-H bonds increases the C-H bending frequencies.

An increase in the ZPEs for these modes is, of course, less for deuterium than for protium. Thus, the change in the hybridization of the C-H bonds that occurs on going from tub-shaped to planar COT makes planarization of COT- d_8 less energetically costly than planarization of undeuterated COT, and this is the origin of the substantial inverse isotope effect that is computed for this process.

Verification of our prediction of an inverse isotope effect on the adiabatic singlet-triplet splitting in COT is likely to be more challenging experimentally than confirmation of our prediction of an inverse isotope effect of nearly the same size on the rate of ring inversion in COT. The rates of ring inversion in monosubstituted derivatives of COT can easily be measured by using ¹H NMR to monitor the coalescence of the resonances for the diastereotopic methyl protons in isopropyl or isopropoxyl substituents.²² Our calculations predict that coalescence will occur at lower temperatures when deuterium, rather than protium, is attached to the remaining seven carbons of the COT ring. We are undertaking experiments to test this prediction, and the results will be reported in due course.

Acknowledgment. We thank the National Science Foundation for support of this research, both at the University of Washington and Illinois State University.

Supporting Information Available: B3LYP/6-31+G*-optimized geometries, energies, frequencies, and thermodynamic quantities for benzene, benzene radical anion, cyclooctatetraene, and cyclooctatetraene radical anion (5 pages). See any current masthead page for ordering and Internet access instructions.

JA9714144

(22) (a) Anet, F. A. L.; Bourn, A. J. R.; Lin, Y. S. *J. Am. Chem. Soc.* **1965**, *86*, 3576. (b) Oth, J. F. M. *Pure Appl. Chem.* **1971**, *25*, 573.

(23) Unrestricted (U)DFT calculations were performed for the triplet, but the triplet showed virtually no spin contamination.

(24) Scaling all the (8/8)CASSCF/6-31G* vibrational frequencies by 0.9 gives $K(4) = 0.36$. It is generally found that *ab initio* vibrational frequencies require greater scaling than vibrational frequencies obtained from DFT calculations.

(25) Since the transition state for bond shifting in COT²² has D_{8h} symmetry,^{3c,21} bond shifting in singlet COT, like ring inversion, requires planarization of the eight-membered ring. Consequently, the (8/8)CASSCF/6-31G* isotope effect on bond shifting in COT- d_8 of $K = 0.37$ (0.42 after scaling the vibrational frequencies by 0.9)²⁴ is similar to that computed for ring inversion.