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ARTICLES

Tunneling and Sterically Induced Ring Puckering in a Substituted [8]Annulene Anion Radical

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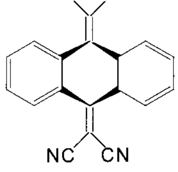
Received July 13, 2001. Revised Manuscript Received December 3, 2001

Abstract: Electron paramagnetic resonance (EPR) studies have revealed that the steric interaction between the methyl hydrogens on a *tert*-butoxy substituent and the cyclooctatetraene (COT) ring system sterically induces a puckering of the eight-membered ring in the anion radical of *tert*-butoxy-COT. The induced nonplanarity of the COT ring system causes a large attenuation of the EPR coupling constants. Since the C−D bond length is slightly shorter than is the C−H bond length, replacement of the *tert*-butyl group with a *tert*-butyl-d_9 group results in less steric interaction and measurably larger electron proton coupling constants. The oscillation between the two close to planar alternating bond length (ABL) D_{2d} conformers of the COT moiety was found to be extremely rapid ($k > 10^{12}$ s^{-1}) and quantum mechanical tunneling is proposed to be involved.

Introduction

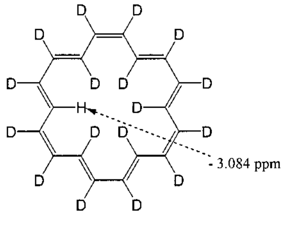
Due to the slight anharmonicity of the potential energy curves, the lower zero-point energy of the C−D bond relative to that of the C−H bond results in shorter mean and maximum bond lengths of the C−D bond. X-ray crystallography studies of naphthalene reveal a reduction of the bond length from 1.085 (C−H) to 1.073 (C−D) Å.[1] As a result of the shorter C−D bond length, in 1993 it was observed that deuterium substitution of the ring hydrogens in the solid copper salt of 2,5-dimethyl-*N*,*N*′-dicyanoquinonediimine significantly alters the appearance of the resulting EPR signal.[2] Analogously, the X-ray structure determinations of tetracyanoanthraquinodimethane reported in the same year by Heimer and Matten[3] revealed that that this compound (structure I), which is distorted from planarity into a bent “butterfly” shape due to steric repulsion between the cyano groups and the encroaching peri hydrogens, is distorted to a smaller degree (the system is flatter) when the ring protons are replaced with deuteriums.



I

No series of compounds have contributed more to the study of aromaticity than have the annulenes. Considering only the number of π-electrons, the Hückel $4n + 2$ rule successfully predicts the aromaticity or antiaromaticity of many of these fully conjugated monocyclic systems,[4] despite the fact that this theory was developed without consideration of the effects of attached protons. Recently however, the importance of this electron count rule has been challenged.[5] It has been theorized that the σ-framework imposes the relative π-delocalization and thus aromaticity of a particular system.

The first (smallest) thermodynamically stable annulenes (at ambient temperatures) with internal protons are [16]annulene and [18]annulene, and unlike [6]annulene and [8]annulene, these two larger systems are affected by the steric interactions of internal protons. Indeed, recent NMR results suggest that these steric interactions, which have a profound effect on the planarity of the [18]annulene system, can be attenuated by replacing the internal protons with deuteriums.[6] Specifically, deuteriation of [18]annulene results in a diatropic shift of the low-temperature ^{1}H NMR resonances of [18]annulene-d_{17} relative to those of [18]annulene (structures II and III at 215 K).[6]



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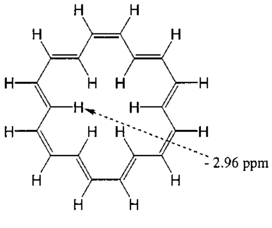

III

The case of [16]annulene also fits the paradigm. The addition of π-electrons to the $4n$ π-electron [16]- and [8]annulene systems

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(1) Burger, S.; Kunzer, H. *Tetrahedron* **1983**, *39*, 1327.

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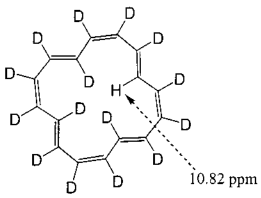
has profound effects upon their structures. The neutral molecule of [16]annulene exhibits a clear paratropic ring current, while the dianion of [16]annulene shows a dramatic diatropic ring current. The paramagnetic ring current in the neutral molecule and the diamagnetic ring current in the dianion are significantly augmented upon deuteriation. Specifically, deuteriation of [16]annulene results in a paratropic shift of the low-temperature ^{1}H NMR resonances of [16]annulene-d_{15} relative to those of [16]annulene (structures IV and V at 215 K).[7] On the other hand, deuteriation of the [16]annulene dianion results in a diatropic shift of the low-temperature ^{1}H NMR resonances of [16]annulene-d_{15} relative to those of [16]annulene (structures VI and VII at 215 K).[7]



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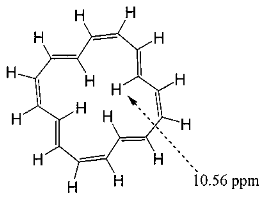

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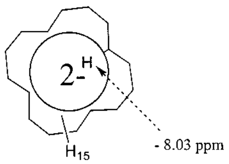

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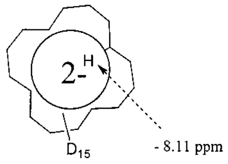
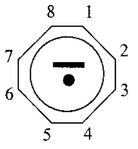


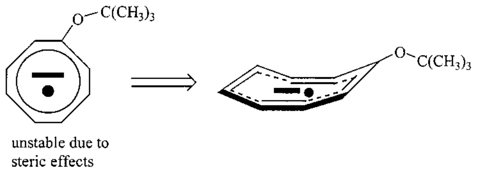
VII

Shaik and Jug with their collaborators[5] have presented evidence indicating that delocalization of π-electrons, and bond equalization, is enforced by the σ framework (C−C═C bond angles). Consequently, it is possible that σ-framework changes, which occur upon deuteriation, may contribute to the increased level of delocalization upon deuteriation of these neutral and dianionic systems. In contrast, no analogous effect was observed in the anion radical of [16]annulene.[7] This is probably due to NMR chemical shifts being more sensitive to changes in planarity of neutral systems than are EPR spectral parameters to changes of planarity in anion radicals.

The anion radical of [8]annulene is planar with a D_{4h} structure (structure VIII) and, of course, does not have internal protons.[8a] The [8]annulene anion radical moiety containing a bulky *tert*-butoxy substituent, however, cannot obtain perfect planarity due to the steric interactions between the methyl and ring protons,[8b] as shown in reaction 1.



VIII



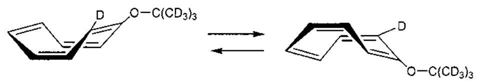
(1)

Reduction of a primary or secondary alkoxycyclooctatetraene (alkoxy-COT) in HMPA, where ion association is absent,[9] with K metal results in a solution exhibiting a quartet of pentets upon EPR analysis. A variety of systems including *iso*-propoxy-COT$^{\cdot -}$, *n*-propoxy-COT$^{\cdot -}$, menthoxy-COT$^{\cdot -}$, and cyclohexoxy-COT$^{\cdot -}$ yield very similar spectra with a_Hs of about 5.6 G for protons on positions 3, 5, and 7 and around 1.0 G due to the protons on positions 2, 4, 6, and 8.[8] The appearance of the EPR spectrum of *tert*-butoxy-COT$^{\cdot -}$ is significantly different due to the differences in magnitudes of the two hyperfine splittings (3 Hs at 4.967 G and 4 Hs at 1.297 G). By analogy to the [16]- and [18]annulene systems, the steric interaction preventing planarity should be attenuated via the replacement of protons with deuteriums. Since EPR coupling constants are so sensitive to the planarity of the [8]annulene ring system, the proposed study could represent the first observation of an isotopic perturbation in the planarity of an anion radical.

Experimental Section

Synthetic Procedures. The synthesis of the *tert*-butoxy-d_9-COT was based on Krebs' preparation.[10] COT was brominated to yield [4,2,0]-bicyclo-5,6-dibromo-1,3-octadiene, which was then dehydrohalogenated with potassium *tert*-butoxide to yield monobromocyclooctatetraene.

Potassium metal (0.12 mol) was reacted with a slight excess of perdeuterated *tert*-butyl alcohol in dry tetrahydrofuran (THF) to give a solution of the alkoxide (KOC_4D_9). The mixture was subsequently refluxed for 6 h in a nitrogen atmosphere. The resulting alkoxide solution was then added dropwise to a stirred solution consisting of 0.9 equiv of bromocyclooctatetraene in THF at −79 °C under a nitrogen atmosphere. After the addition was complete, the solution was allowed to warm to room temperature, and the THF was removed under reduced pressure. Water (5 equiv) was then added to quench the reaction. The products were extracted with diethyl ether. The ether solution was dried and the ether was removed under reduced pressure. The intermediate in the reaction between the monobromo-COT and the alkoxide is cyclooctatrieneyne.[10] Consequently, the excess C_4D_9OD results in the formation of 1-*tert*-butoxy-d_9-2-deuteriocyclooctatetraene [(C_8H_6D-O-$C(CD_3)_3$], which exists in two dynamic conformations (reaction 2).



(2)

The resulting *tert*-butoxy-COTs were purified via vacuum distillation (10^{-3} Torr, 95−100 °C). NMR and mass spectral analysis are consistent with a mixture of C_8H_6D-O-$C(CD_3)_3$ and *tert*-butoxy-d_9-cyclooctatetraene [C_8H_7-O-$C(CD_3)_3$]. In the former case the parent mass spectral peak represents the molecular ion of C_8H_6D-O-$C(CD_3)_3$ ($m/e = 186$).

Instrumentation. The reductions were carried out by allowing HMPA solutions of the alkoxycyclooctatetraene to come into contact with potassium metal in vacuo as previously described.[11] The X-band EPR spectra were recorded with a Bruker EMX-080 spectrometer with a modulation amplitude of 0.05 G and a low microwave power of 0.2

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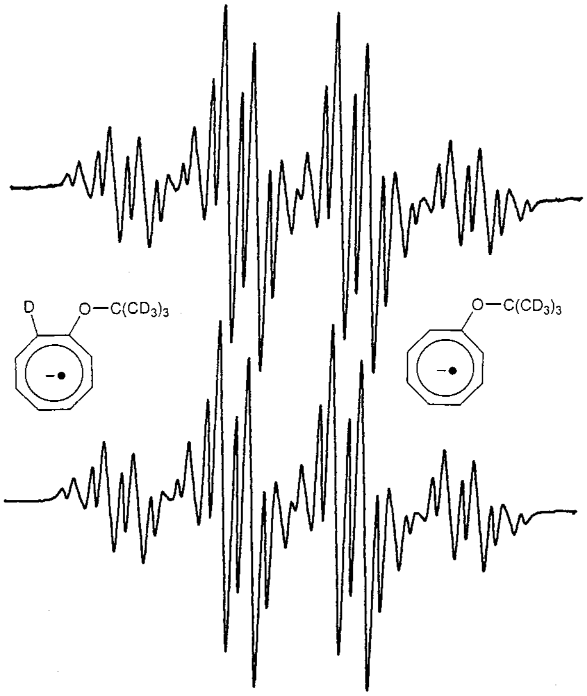


Figure 1. (A) X-band EPR spectrum (scan range = 25 G) of the anion radicals of C_8H_6D-O-$C(CD_3)_3$ and C_8H_7-O-$C(CD_3)_3$ in HMPA at 298 K. (B) Computer simulation generated with $a_H = 1.285$ G for 3 Hs, 4.985 G for 3 Hs and 0.1895 G for 1 D, representing C_8H_6D-O-$C(CD_3)_3^{\cdot -}$, and with $a_H = 1.285$ G for 4 Hs and 4.985 G for 3 Hs, representing C_8H_7O-$C(CD_3)_3^{\cdot -}$. The ratio of [C_8H_6D-O-$C(CD_3)_3^{\cdot -}$]/[C_8H_7-O-$C(CD_3)_3^{\cdot -}$] is 71/29.

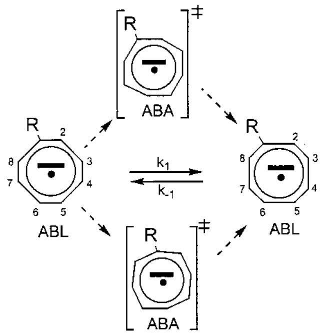
mW attenuated by 30 db (to avoid any hint of signal saturation). The temperature was controlled with a Bruker variable temperature unit.

Calculations. The TITAN version 1 program from Wavefunction, Inc., and Schrödinger, Inc., was used for all molecular orbital calculations. The B3LYP/6-31+G* protocol has previously proven to be very effective in predicting the bond angle variations and their effects upon observed EPR spectra in 1,2-disubstituted COT anion systems.[12] Further, this level of theory predicts carbon p_z spin densities (ρ), which can be used with the McConnell relationship ($a_H = Q\rho$) to accurately predict a_H values for substituted COT anion radicals that are not undergoing dynamic processes.[13] Consequently, it was felt that this protocol would be the most appropriate for this study.

Results and Discussion

The potassium metal reduction of our mixture of C_8H_6D-O-$C(CD_3)_3$ and C_8H_7-O-$C(CD_3)_3$ in hexamethylphosphoramide (HMPA)[9] leads to the corresponding anion radicals that are free of ion association and persist for hours at room temperature (Figure 1). A nearly perfect computer simulation of the spectrum can be generated (Figure 1, lower trace). The EPR spectrum of this solution is sufficiently well resolved to allow measurement of the coupling constants to within 2 mG, and the spectrum exhibits both anion radicals simultaneously in a ratio of [C_8H_6D-O-$C(CD_3)_3^{\cdot -}$]/[C_8H_7-O-$C(CD_3)_3^{\cdot -}$] = 71/29. The ring protons on positions 3, 5, and 7 are identical in both radicals ($a_H = 4.985$ G), and the ring protons on position 4, 6, and 8 are also identical ($a_H = 1.285$ G). In position 2 the value for a_D is 0.1895 G in C_8H_6D-O-$C(CD_3)_3^{\cdot -}$, and $a_H = 1.285$ G in C_8H_7-O-$C(CD_3)_3^{\cdot -}$ (Figure 1, lower trace).

Scheme 1



The anion radical of *tert*-butoxycyclooctatetraene [C_8H_7-O-$C(CH_3)_3^{\cdot -}$] recorded under identical conditions yields a_H values of 1.297 and 4.967 G for the pentet and quartet,[8c] respectively. The difference between these two coupling constants (Δa_H) is equal to 3.670 G. Remarkably, deuteriation of the *tert*-butyl group increases this difference [$\Delta a_H = 3.700$ G for C_8H_7-O-$C(CD_3)_3^{\cdot -}$] by 30 mG. This deuterium effect is due to a reduced steric interaction between the ring and the *tert*-butyl group, which in turn allows the ring to assume a more planar geometry. Replacing the *tert*-butyl group with something much smaller, e.g., an isopropoxy group, results in a much larger Δa_H of 4.59 G for C_8H_7-O-$CH(CH_3)_2^{\cdot -}$.[8]

The best theory[8a] shows that the ground state of unsubstituted cyclooctatetraene (COT) anion radical is represented by a degenerate pair of Jahn–Teller (J–T) distorted D_{4h} alternating bond length (ABL) structures, and the transition state for the reaction in Scheme 1 is represented by a pair of D_{4h} structures with alternating bond angle (ABA) geometries.

The ABL states with degenerate SOMOs (Ψs in eqs 3 and 4) represent minima, while the ABA states having degenerate SOMOs (Φs in eqs 5 and 6) are maxima along the pseudo-rotation path:[8a]

$$\Psi_4 = (0.5/\sqrt{2})(\psi_1 + \psi_2 - \psi_3 - \psi_4 + \psi_5 + \psi_6 - \psi_7 - \psi_8) \quad (3)$$

$$\Psi_5 = (0.5/\sqrt{2})(\psi_1 - \psi_2 - \psi_3 + \psi_4 + \psi_5 - \psi_6 - \psi_7 + \psi_8) \quad (4)$$

$$\Phi_4 = (1/2)(\psi_1 - \psi_3 + \psi_5 - \psi_7) \quad (5)$$

$$\Phi_5 = (1/2)(\psi_2 - \psi_4 + \psi_6 - \psi_8) \quad (6)$$

Ψ_4 and Ψ_5 are given by [$(1/\sqrt{2})\Phi_4 + (1/\sqrt{2})\Phi_5$ and $(1/\sqrt{2})\Phi_4 - (1/\sqrt{2})\Phi_5$], respectively when R = H. For a system with an electron-releasing substituent (e.g., an alkoxy group), the energy of Φ_4 is raised, while that of Φ_5 is unperturbed. Consequently the molecular orbitals (Ψ_4' and Ψ_5'), heavy in Φ_4 (eqs 7 and 8, $m > n$), describe the system:

$$\Psi_4' = (m\Phi_4 + n\Phi_5) \quad (7)$$

$$\Psi_5' = (m\Phi_4 - n\Phi_5) \quad (8)$$

When $m \gg n$, it is anticipated that the EPR spectrum should appear as a simple 1:3:3:1 quartet, but small negative spin densities, as described by Borden and co-workers,[8a] for the nodal positions must be included. Single-point, B3LYP/6-31+G* calculations carried out on the hypothetical (D_{2d} for the COT

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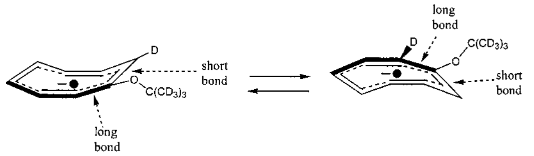
(13) Wenthold, P. G.; Hrovat, D. A.; Borden, W. T.; Lineberger, W. C. *Science* **1996**, *272*, 1456.

moiety) tub-shaped alkoxy-$\mathrm{COT}^{\cdot -}$ predict that $a_{\mathrm{H}} \approx 2.5$ G for all seven ring protons. Hence, the predicted total spectral width is only 17.5 G as opposed to the 23−24 G observed for $\mathrm{COT}^{\cdot -}$ and most alkoxy-substituted COT anion radicals. The important point is that any loss of planarity of the eight-membered ring system causes a decrease in the *Q* value in the McConnell relationship, which results in a lowering of the coupling constants and a consequent decrease in the total EPR spectral width. This is why the total EPR spectral width of $\mathrm{C_8H_7\text{-}O\text{-}C(CH_3)_3}^{\cdot -}$ is so much smaller than those observed for the other alkoxy-$\mathrm{COT}^{\cdot -}$ systems. This effect has also been empirically observed in other substituted COT anion radical systems.[14]

Substituting the nine methyl hydrogens with deuteriums increases Δa_{H} by 30 mG. However, the replacement of single pseudo-*ortho* hydrogen with a deuterium does not measurably alter Δa_{H}. The remaining pseudo-*ortho* hydrogen on $\mathrm{C_8H_6D\text{-}O\text{-}C(CD_3)_3}^{\cdot -}$ can exist in two different positions relative to the *tert*-butoxy moiety, as the C−C bond separating the hydrogen and the substituent can be either short or long.[8a] Despite this fact, only a single a_{H} is observed for this hydrogen. From the COT anion radical bond lengths predicted by Borden and co-workers,[8a] a single-point B3LYP/6-31+G* treatment predicts that a_{H} for the proton on the 2 position is larger than that on the 8 position by 14%, and the proton on the 3 position is larger than that on the 7 position by about 6%.



(9)

In neutral COTs the effects of bond shift can clearly be observed via NMR experiments as first described by Anet.[15] Even though the EPR time scale is roughly 9 orders of magnitude faster than is the NMR time scale, analogous effects cannot be observed in the EPR spectrum of $\mathrm{C_8H_6D\text{-}O\text{-}C(CD_3)_3}^{\cdot -}$. Quantum mechanical tunneling is most likely involved. If reaction 9 were slow on the EPR time scale, we would observe two different EPR spectra for $\mathrm{C_8H_6D\text{-}O\text{-}C(CD_3)_3}^{\cdot -}$. Clearly, two spectra for $\mathrm{C_8H_6D\text{-}O\text{-}C(CD_3)_3}^{\cdot -}$ are not observed. Further, with this degree of asymmetry, computer simulations reveal that line width modulation effects due to reaction 9 would be noticeable if the process were slow enough to be observed on the EPR time scale (see Figure 2). The theoretically and empirically[13] observed unequal bond lengths along with the absence of the predicted line width modulation effects pose a substantial paradox that can have only one explanation. Specifically, the oscillation between the two ABL conformers (reaction 9) would have to appear to be so rapid as to be in the extreme line narrowing condition.[16]

The absence of line width effects due to reaction 9 can be conveniently explained if quantum mechanical tunneling is involved. We propose that tunneling is important in the interchange between the two degenerate ABL conformations of the anion radical of *tert*-butoxy-substituted [8]annulene. The possibility of heavy-atom tunneling effects in monosubstituted COTs has already been suggested.[17] This is probably the situation in most substituted [8]annulene anion radical systems. Tunneling involving eight carbons may seem unlikely. However, given the bond lengths predicted by Borden and co-workers[8a] of 1.359 and 1.435 Å, the displacements that the carbons must undergo are only $\{2[(1.434 - 1.359)/2]^2\}^{1/2} = 0.054$ Å. This represents a narrower barrier than that found in the cyclobutadiene system,[18] and the cyclobutadiene system does tunnel.

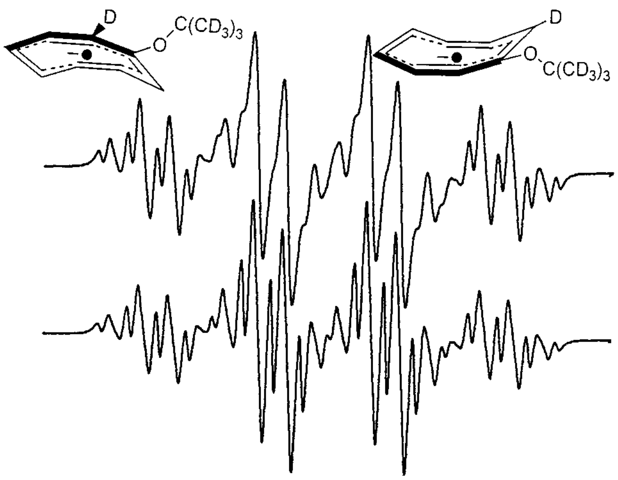


Figure 2. (Upper trace) Simulated spectrum of a hypothetical static ABL conformation of the 79/21 mixture of $[\mathrm{C_8H_6D\text{-}O\text{-}C(CD_3)_3}^{\cdot -}]/[\mathrm{C_8H_7\text{-}O\text{-}C(CD_3)_3}^{\cdot -}]$. The alternating long and short bonds render the 2 and 8 protons nonequivalent, and they have a_{H}s of 1.375 and 1.195 G and a_{D}s of 0.203 and 0.176 G. The 3 and 7 protons have a_{H}s of 5.135 and 4.835 G, the a_{H}s for the 4 and 6 protons are 1.375 and 1.195 G, and the a_{H} for proton 5 is 4.985 G. (Lower trace) The frequency of oscillation between the two ABL forms (reaction 9) is 1×10^7 s^{-1}. At this exchange rate, the ratio of peak heights for the first and second quartets is only 2.7 as opposed to 3.00 in the experimental spectrum (Figure 1). At higher exchange rates the theoretical value is approached. However, even at an exchange rate of 10^{12} s^{-1}, the ratio of heights of the quartets remains only 1:2.9 as opposed to the 1:3 ratio observed in the experimental spectrum and expected from the Pascal relationship. Thus the actual rate of oscillation appears as if it were even faster than 10^{12} s^{-1}.

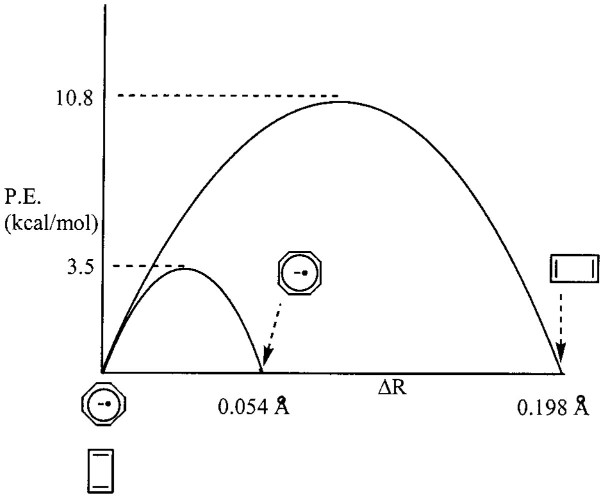
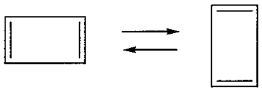


Figure 3. Model potential energy functions for the carbon atom displacements of [4]annulene and of the [8]annulene anion radical.



(10)

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Carpenter[18] was the first to propose that quantum mechanical tunneling involving four carbons may be significant in the cyclobutadiene system (reaction 10). He pointed out that the narrowness of the barrier (bond length change of 0.198 Å) makes the bond-shifting reactions susceptible to tunneling. In the case of C_8H_7-O-$C(CH_3)_3^{\cdot -}$ the carbon displacements are less than a third as great as they are in the cyclobutadiene system. The barrier to reaction 9 is only 3−4 kcal/mol compared to the barrier for reaction 10, which is predicted to be about 10.8 kcal/mol. Empirically, the rate of reaction 9 appears to be very rapid, $k_1 > 10^{12}$ s^{-1}, since no EPR line width effects are observed. We suggest that the alkoxy-COT anion radical system, having a narrower and lower barrier, is more susceptible to tunneling than is [4]annulene, Figure 3.

Acknowledgment. We thank the National Science Foundation (Grant CHE-9617066) for support of this work.

JA0117128

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