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The Anion Radical of [18]Annulene

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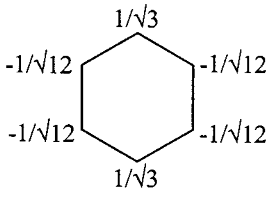
The anion radicals of [18]annulene and of [6]annulene undergo Jahn−Teller distortions from the D_{6h} conformations of their respective neutral molecules. The conformation of lowest energy for the anion radical of benzene has a C_{2v} symmetry, and that for the anion radical of [18]annulene is D_{2h}. The very rapid pseudo-rotation of the benzene C_{2v} system causes the six protons of the benzene anion radical to appear as if they were equivalent in the EPR experiment. Fast pseudo-rotation rendering the uniform distribution of spin density in the [18]annulene anion radical system is prevented by the nonplanarity of the radical. Hence, the EPR spectrum of the [18]annulene anion radical must be interpreted in terms of a static (on the EPR time scale) D_{2h} conformation, which pseudo-rotates over a C_{2h} transition state. B3LYP calculations support these conclusions.

Introduction

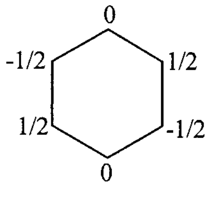
Benzene is the smallest $4n + 2$ π-electron annulene. Although the benzene anion radical is one of the most intensely studied open shell systems,[1] it has remained the only anion radical of an aromatic annulene previously reported. The presence of internal protons renders the next two $4n + 2$ π-electron annulenes ([10]annulene and [14]annulene) thermodynamically and kinetically unstable. The next stable $4n + 2$ π-electron system (aromatic in the Hückel sense) is [18]annulene. This makes theoretical sense, as an expanded version of three benzene ring systems in one cyclic array is the smallest benzene multiple that is aromatic. The addition of an electron to the [6]- or [18]-annulene system leads to spontaneous symmetry breaking distortions, and understanding of the quantum mechanics of these $4n + 3$ systems is of importance in many areas of investigation, including superconductivity.[2a] These facts render the addition and subtraction of π-electrons from [18]annulene of intense experimental and theoretical interest.

The six equivalent protons of [6]annulene have a coupling constant of −3.72 G, which is well within the range expected for a planar anion radical.[1] This is the expected EPR result based upon the D_{6h} conformation of benzene. However, the quantum mechanical considerations are more intriguing. The observed equivalence of the six protons has been explained in terms of the odd electron occupying, with equal probability, Φ_4 and Φ_5 (Structures I and II).[1] For example the spin density on the #2 carbon was taken as $[(1/\sqrt{12})^2 + (1/2)^2]/2 = 1/6$, and isotope effects were interpreted in terms of unequal occupation of Φ_4 and Φ_5.[1] Of course, this explanation is based on a D_{6h} interpretation, so Φ_4 and Φ_5 are a degenerate pair and can mix.

Qualitative MO theory[1a,e] and, more recently, density functional theory calculations at the B3LYP/6-31+G* level show that the D_{6h} (all cisoid double bonds) system is at a hyper-saddle point.[2b] The system undergoes a Jahn-Teller distortion to yield two nonplanar molecular geometries (C_{2v} and D_2) where the b_{1u} and a_u MOs are no longer degenerate. The LUMO (b_{1u} in D_{6h} symmetry) allows some advantage, presumably due to favorable 1−4 p−p AO overlap, and is the ground state in the boatlike C_{2v} geometry. The a_u LUMO is of lower energy in a twisted D_2 system, which has one "imaginary" frequency and represents the transition state (T-S) for the pseudo-rotation of the C_{2v} system, Figure 1. [2b]



I (Φ_4) {b_{1u}}



II (Φ_5) {a_u}

The very rapid pseudo-rotation of the C_{2v} system, described in Figure 1, causes the six protons of the benzene anion radical to appear as if they were equivalent in the EPR experiment. Isotope effects can now be described in terms of equilibrium isotope effects (EIEs) on the pseudorotation. The *isotropic* EPR spectrum of the benzene anion radical at temperatures near absolute zero (currently an impossible experiment) can be predicted from the spin densities in the radical with C_{2v} geometry and would appear as a triplet of pentets in the absence of quantum mechanical tunneling.

Accordingly, if the [18]annulene anion radical ($[18]^{-\cdot}$) were to exclusively assume the conformation of a regular octadecagon, one would anticipate a simple EPR spectrum resulting from the unpaired electron being distributed uniformly over the 18-membered ring system. Two slightly different coupling constants would be anticipated, because only six cisoid double bonds can be present if the near 120° C−C bond angles are to be preserved. This necessitates the presence of 6 internal and 12 external hydrogens. NMR experiments[3] with neutral [18]annulene show that, despite its aromatic nature, steric interactions between the internal hydrogens inhibit the [18]annulene neutral system from

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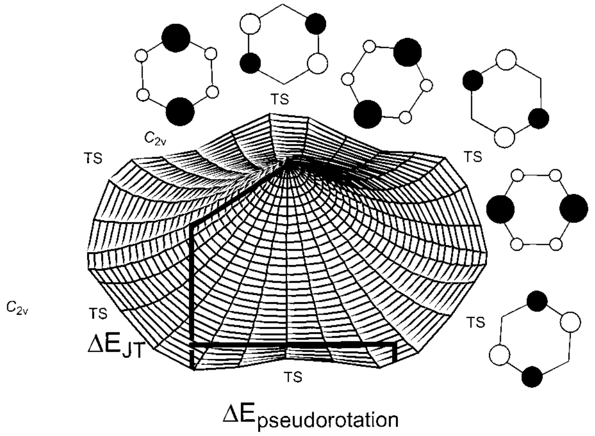


Figure 1. Schematic (Mexican hat) representation of the pseudorotation of the benzene anion radical leading to the ostensive equivalency of the 6 protons in an EPR experiment. The D_{6h} structure is at the apex of the "hat".

settling from local minima into an exclusively planar conformation.

These same steric interactions also render the molecule thermally unstable.[4a] Öth has presented a small picture of the EPR spectrum of $[18]^{-\cdot}$; however, it has not been described or analyzed.[4b] A very striking feature of the published spectrum is the unusually large spectral width of nearly 36 G. This might suggest a non-D_{6h} structure, which would include contributions to the EPR couplings from negative p_z spin densities. In the absence of internal H−H steric effects, however, the σ-framework approaches ideality (120° C−C=C bond angles). The consequence of this is increased enforcement of π-delocalization and symmetrization of the radical.[5] Hence, we were motivated to observe a more resolved spectrum and develop a quantum mechanical understanding (analogous to the case of [6]annulene) of the electron distribution. The problem is of even more interest in view of the suggestion that $[18]^{-\cdot}$, under the right circumstances, could represent a superconducting material.[2a,c]

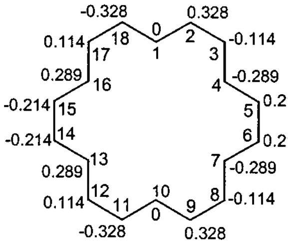
Experimental Section

[18]Annulene was prepared and purified as previously described.[3,4] The reductions were carried out under high vacuum via the exposure of a dilute (0.01 to 0.001 M) solution of [18]-annulene in hexamethylphosphoramide (HMPA) to a freshly distilled potassium metal surface. X-band EPR data were obtained using a Bruker EMX spectrometer operating at 9.8 GHz with a standard rectangular cavity. Modulation frequency: 60.00 kHz, modulation amplitude: 0.05 G. A low microwave power of 0.2 mW attenuated by 30 db was used to avoid any hint of signal saturation. The spectra were simulated using EWSim, v. 4.0, from Scientific Software Services, Normal, IL.

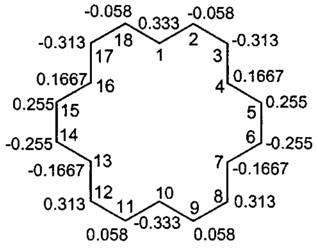
Full geometry optimization calculations on [18]annulene were carried out using the B3LYP/6-31+G* protocal and the TITAN version 1 program from Wavefunction, Inc., and Schrodinger, Inc.

Results and Discussion

In a Hückel MO sense, since [18]annulene (in the D_{6h} point group) possesses a degenerate pair of LUMOs, (Φ_{10} and Φ_{11} in Structures III and IV), the addition of an extra electron can be thought of as affording an anion radical with a LUMO, which is either a B_{2g} (Φ_{10} SOMO) or a B_{3g} (Φ_{11} SOMO).[2a] Since there is only one electron in the degenerate antibonding molecular orbitals of planar $[18]^{-\cdot}$, there is (as in the case of [6]annulene) a necessary J−T distortion from D_{6h} symmetry that leads to two different structures.[2a,6] Group theory says that one will have D_{2h} symmetry and the other will have C_{2h} symmetry, and they are both found on the same vibronic potential energy surface ("Mexican hat," e.g., Figure 1).



III (Φ_{10}) {B_{2g}}



IV (Φ_{11}) {B_{3g}}

Group theory analysis has shown that only the e_{1g} vibration will couple with the LUMOs,[2a] and the distortions may be either forward or backward along the coordinates of the e_{1g} vibration. For example, the D_{2h} anion radical can become a system with either a $^2B_{2g}$ or a $^2B_{3g}$ LUMO. These resulting radicals do not have identical energies, as the $^2B_{2g}$ state can better profit from second-order Jahn-Teller stabilization. Likewise the C_{2h} geometry is a result of Jahn-Teller distortion along the e_{1g} mode.

Calculations of the D_{2h} optimized geometries (B3LYP/6-31+G* level of theory) suggest that the $^2B_{2g}$ state is a minimum and is lower in energy than the $^2B_{3g}$ state by a very small amount, only 9 cal/mol. However, the $^2B_{3g}$ state possesses one imaginary frequency. We were able to find a C_{2h} geometry with a $^2B_{3g}$ ground-state LUMO. Its energy is 95 cal/mol higher than that of the lowest D_{2h} state. Distorting this C_{2h} ($^2B_{3g}$) radical along the "imaginary" coordinate results in the T-S with the C_{2h} geometry. Thus the system with C_{2h} geometry and a $^2B_{3g}$ LUMO is the transition state for pseudo-rotation of the system with D_{2h} geometry. Fast, on the EPR time scale, pseudo-rotation would lead to nearly identical spin densities on all 12 external hydrogens.

The potassium metal reduction of [18]annulene in HMPA leads to the corresponding anion radical ($[18]^{-\cdot}$), which is free of ion association[7] and persists for nearly an hour at room temperature. The striking complexity of the EPR signal (Figure 2) immediately rules out the rapid pseudo-rotation described above, and the large total spectral width necessitates major contributions to the coupling from carbons with negative spin densities.[8]

Using a peak to peak line width (Δw_{pp}) of 0.12 G, the experimental spectrum is nicely simulated using coupling constants of $a_H = 5.875$ G (1H), 5.625 G (1H), 2.23 G (4Hs), 1.68 G (2Hs), 1.59 G (4Hs), 1.50 G (2Hs), 0.91 G (2Hs), and 0.050 G (2Hs), Figure 2B. Further, by simply increasing Δw_{pp} Öth's published (but uncharacterized)[4b] spectrum is reproduced. The presence of the species giving rise to this EPR spectrum broadens the NMR resonances for the neutral and dianionic species, and its EPR signal disappears after the addition of a second electron leaving only the [18]annulene dianion.[4b] So, despite its relative complexity and unusually large spectral width, the EPR spectrum shown in Figure 2 is undoubtedly due to the anion radical of [18]annulene. See the expansions of Figures 2A and 2B, Figure 3.

Subtracting the two large couplings 5.875 and 5.625 G from the total spectral width leaves a number (23.6 G) that represents a normal Q value in the McConnell Relationship, $a_H = Q\rho$, where $Q = 22.5$ to 27 G and ρ represents the spin density.[1e] This would suggest that these two splittings arise from large

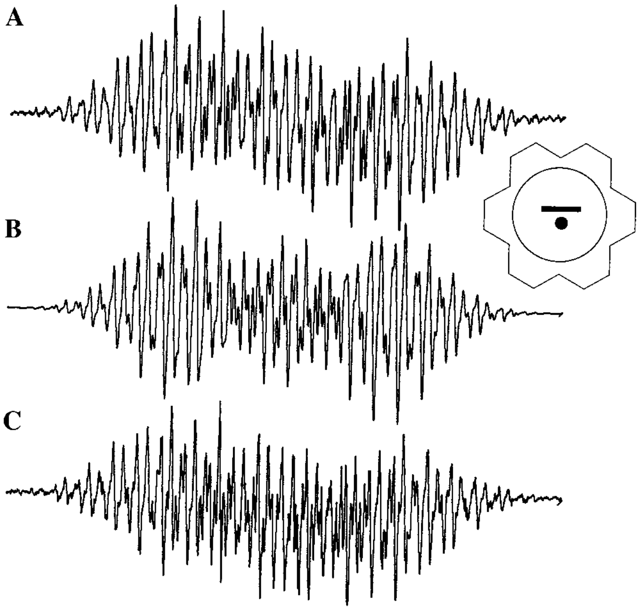


Figure 2. (A) EPR spectrum (36.5 G scan) of the [18]annulene of the anion radical obtained by reducing a 10^{-3} M solution of $C_{18}H_{18}$ in HMPA with K, and recording the spectrum at 0 °C. (B) Computer simulation generated using the coupling constants described in Table 1 and a ΔW_{pp} of 0.12 G. Simply increasing ΔW_{pp} to 0.3 G in this simulation reproduces Oth's[4b] published spectrum. (C) EPR spectrum (36.5 G scan) of the [18]annulene of the anion radical recorded in HMPA at 25 °C. Residual minor differences in the real and simulated spectra are, in part, due to assumed equivalency of protons 2, 9, 11, and 18. However, the multiplicity of interacting parameters makes further refinement of the simulation impractical.

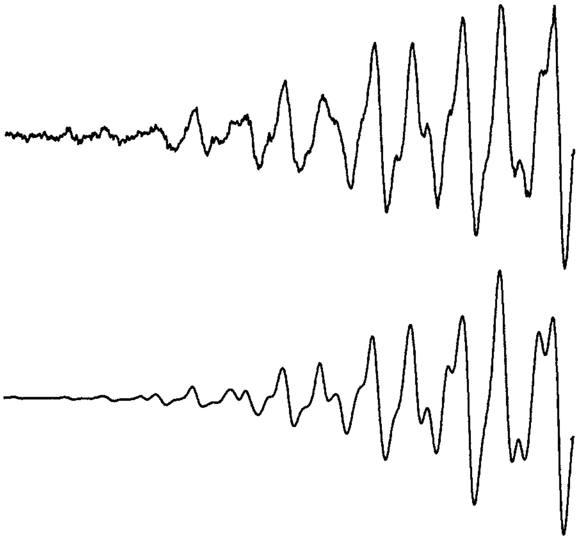


Figure 3. (Upper) The first 10 G of the EPR spectrum of the [18]-annulene of the anion radical recorded in HMPA at 0 °C. (Lower) Computer simulation generated using the coupling constants described in Table 1 and a ΔW_{pp} of 0.12 G.

negative spin densities at the nodal positions of the B_{2g} state. These are analogous to the large negative spin densities found at the nodal positions of monosubstituted [8]annulene anion radicals.[9] The negative spin in the #1 and #10 positions renders the total spectral width much larger than is the Q value.

Steric interactions involving the internal protons prevent the hydrogens in the #1 and #10 positions from being simultaneously in the plane of the ring. Indeed, due to steric interactions hydrogens are forced out of the plane of the ring in the aromatic neutral molecule.[3] A B3LYP/6-31+G* calculation on $[18]^{-\cdot}$ gives reasonable agreement with the experimental spin densities, Table 1. The calculation, however, predicts a planar D_{6h} system with only very small spin densities on the #1 and #10 carbons. We must keep in mind that the calculations are representative of the gas-phase anion radical, and the morphologies of the solvated ion may be different. PM3 calculations on the B3LYP optimized geometry do predict a very high spin density (−0.5) on the #1 and #10 carbons, which is only slightly perturbed by constraining the #1 hydrogen 5° above the plane of the ring system. We must also be cognizant of the fact that solvation enthalpies for anion radical−alkali metal cation systems in HMPA are greater than 175 kcal/mol;[10] consequently, some perturbation in the electron distribution due to solvation is to be expected.

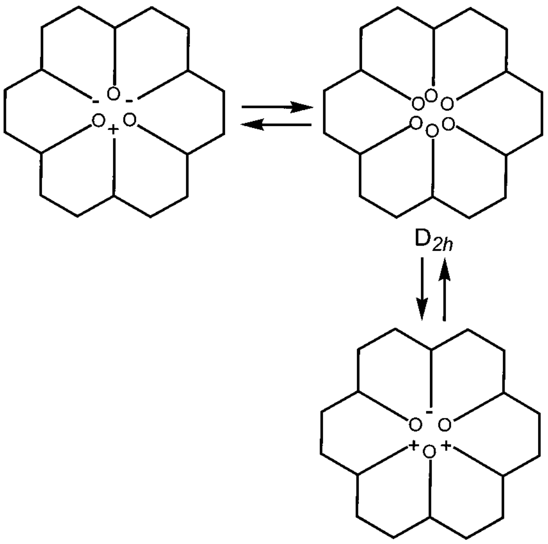
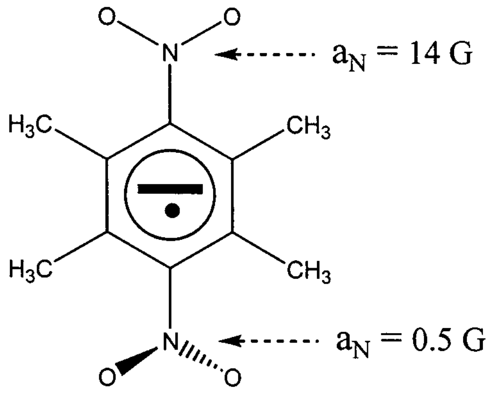


Figure 4. Proposed conformers for the [18]annulene anion radical. A plus sign indicates that the proton extends forward from the plane of the molecule, while a minus sign signifies that it protrudes back into the page. Zeros indicate the internal protons in the plane of the ring.

TABLE 1: Coupling Constants (absolute values) for $[18]^{-\cdot}$, Spin Densities Using $Q = 22.5$ G, B3LYP Predicted Spin Densities for the D_{6h} System, Hückel Predicted Spin Densities for the $^2B_{2g}$ State, and Hückel Predicted Spin Densities Considering Fast Pseudo-rotation

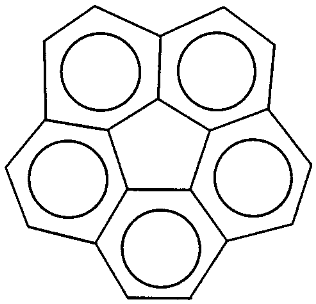
position	a_H	ρ	$\rho_{(B3LYP)}$	$\rho_{(Huckel,B2 g)}$	$\rho_{(Hückel, ave.)}$
1	5.88	−0.26	0.000	0.000	0.056
10	5.63	−0.25	0.000	0.000	0.056
2,9,11,18	2.23	0.099	0.113	0.108	0.056
8,12	0.91	0.040	0.009	0.013	0.056
3,17	0.05	0.002	0.009	0.013	0.056
4,7	1.68	0.075	0.084	0.084	0.056
16,13	1.59	0.071	0.084	0.084	0.056
5,15	1.59	0.071	0.043	0.046	0.056
6,14	1.50	0.067	0.043	0.046	0.056

The steric crowding of the internal protons forces some of them out of the plane of the ring system and reduces the symmetry of the anion radical. This is not at all surprising, as the same thing happens in the neutral system, which is aromatic and supports a diatropic ring current.[4] With internal proton(s) now protruding outside of the plane of the ring system, a nonplanar conformation with the electron localized in a B_{2g} like MO best represents the system. This analysis is supported by the difference in the two large splittings, which is essential for reproducing the observed line intensity pattern. The general appearance of the simulated spectrum is critically sensitive to the magnitude of this difference. If $[18]^{-\cdot}$ in HMPA were planar and locked in a C_{2h} conformation, a large 1:2:1 triplet (from two equivalent protons on positions 1 and 10) would necessarily be obvious in the EPR spectrum, as simulations have confirmed. The nonplanarity accounts for the splitting of the degeneracy of positions 5, 6, 14, and 15, and positions 3, 8, 12, and 17. The inability of the protons in the #1 and #10 positions to be equivalent is analogous to the nonequivalency of the two nitrogens in the *para*-dinitrodurane anion radical. These two nitrogens are not equivalent, on the EPR time scale, because both NO$_2$ groups cannot be simultaneously coplanar with the benzene ring system, Structure V.[11]



V

Fast pseudo-rotation rendering the uniform distribution of spin density in the [18]$^{-\cdot}$ system is apparently prevented by the nonplanarity of the radical, Figure 4. Slow pseudo-rotation, on the EPR time scale, has only once been previously reported. The EPR spectrum of the potassium anion radical salt of corannulene (Structure VI) yields the expected simple 11-line EPR signal at room temperature.[12] This spectrum is interpreted in terms of the rapid pseudo-rotation about the C_{5v} J-T crossing. New splittings appear as the temperature is lowered below 233 K, leading the authors to generate computer simulations based upon the assumption of slow pseudo-rotation.[12] The simulations, however, do not resemble the real spectra. Further, a very clear anisotropy appears in the real EPR spectra.[12] It has been shown that the changes in the planarity of a hydrocarbon anion radical do not alter its observed isotropic *g*-value.[13] Consequently, it seems very unlikely that a slowing of the pseudo-rotation can drastically perturb the *g*-value of the corannulene anion radical. The extra splittings observed at the lower temperatures are most likely due to impurities including, perhaps, the trianion radical. Due to the very low barriers to pseudo-rotation and the strong possibility of tunneling, it is unlikely that one can slow this process down to observable rates in fluid solution.



VI

The ^{1}H NMR chemical shifts for the [18]annulene neutral molecule exhibit strong thermal dependence.[3] This is a result of the presence of the thermally excited isomers shown in Figure 4. B3LYP calculations suggest that the ground state of [18]annulene is planar and D_{6h}. However, one or more of the isomers shown in Figure 4 must be in equilibrium with the ground state to account for the results described.[3] Likewise, the ground state of [18]$^{-\cdot}$ is probably D_{6h} in nature, but at elevated temperatures there is a contribution from the nonplanar structures shown in Figure 4. Only near 0 K would one observe the planar D_{6h} $^2B_{2g}$ system exclusively. HMPA solutions can only be cooled to about 270 K, but the addition of tetrahydrofuran allows further cooling. Lowering the temperature, however, only results in broadening of the EPR hyperfine resonances and loss of spectral resolution giving rise to the poorly resolved spectrum previously shown.[4b] It is possible that this broadening is a result of the slowing of the kinetic relationship between the ground state and the excited state into the realm of the EPR time scale.

In terms of the "Modern Electronic Theory for Ground States of Conjugated Systems",[5] the quantum mechanical Jahn-Teller considerations for [18]$^{-\cdot}$, caused by the presence of the odd electron, and the steric interactions of the internal protons, couple with the normal intrinsic symmetry distortive forces of the π-component to overcome the symmetrizing force of the σ-framework. Thus, in the case of the anion radical of [18]annulene, which is a larger "floppier" system (as compared to benzene), the σ-resistance to desymmetrization is insufficient, and the molecular conformation relaxes to a symmetry lower than D_{6h}.

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