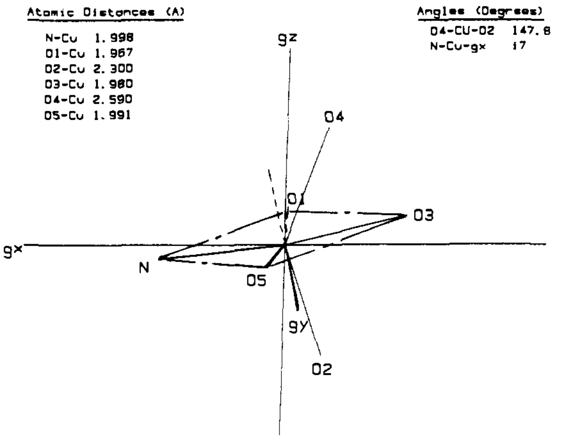

Figure 11. Coordination sphere of copper glutamate with the origin of the *g* axis system centered at copper. The solid lines are on the plane of the paper. The dashed lines point into the plane of the diagram while the thick, solid lines point out of the plane.

from the Cu–O_2 and Cu–O_4 vectors, the plane formed by the N, O_1, O_3, and O_5 atoms is 17° from the g_x–g_y plane.

Figure 11 depicts this orientation of the *g* axis system with respect to atom positions. The O_4, Cu, and O_2 atoms make an angle of 148° in the copper glutamate molecule. Each of the "axial" oxygen atoms is 16° from the g_z axis in this structure. The axial oxygens are magnetically equivalent in this picture, which is apparently favored over a structure in which one oxygen would be forced to lie along the g_z axis. The N, O_1, O_3, and O_5 atoms form nearly a square with the O_5 near the positive g_y axis and O_1 near the negative g_y axis. The nitrogen atom lies near the positive g_x axis while O_3 lies near the negative g_x. The magnetic nonequivalency of the *x* and *y* axes is probably due to this arrangement of atoms. Our experimental data are completely in accord with this structure.

Conclusions

ENDOR and EI-EPR investigations of ^{14}N and ^{15}N copper glutamate have been conducted to determine hyperfine coupling constants, quadrupolar coupling constants, powder pattern intensity effects, and the relative orientation of magnetic axes. This paper demonstrates that one can select paths of angles by setting the EPR field to a fixed value in the EPR powder pattern. Subsequent analysis of ENDOR spectra requires calculations of all the angles selected by the given field including the affects of nearest-neighbor nitrogen atoms. Low-intensity nitrogen ENDOR transitions, usually ignored in ENDOR studies, require a complete analysis and are accounted for here. This study also shows evidence that the complete equation for the quadrupolar interaction must be used to analyze experimental data correctly. The ENDOR spectra of these compounds indicated that the nitrogen did not lie on one of the principal *g* axes, which is the usual assumption. EI-EPR was utilized to determine the direction of the nitrogen hyperfine axis system with respect to the *g* axis system; however, this direction is only consistent with the analysis as there is no unique solution. Knowledge of the relative directions of the hyperfine and *g* axes allows one to determine the orientation of the *g* axis system with respect to atomic coordinates.

Acknowledgment. This work was supported by National Institutes of Health Grant GM-22793. We express our appreciation to Dr. Thomas Henderson for many helpful discussions and Dr. David Rowlands for writing the spectrometer acquisition software.

Registry No. Copper glutamate, 36015-31-3.

The Phenylcyclooctatetraene Anion Radical and Dianion: An Intramolecular Charge and Spin Distribution Isotope Effect

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Abstract: EPR studies on the anion radicals and ^{13}C NMR studies of the dianions of phenylcyclooctatetraene ([6]–[8]), phenylcyclooctatetraene-d_7, and phenyl-d_5-cyclooctatetraene show that deuteriation of the cyclooctatetraenyl moiety perturbs and phenyl group spin and charge distributions in the anion radical and dianion, respectively. However, deuteriation of the phenyl moiety does not alter these distributions in the cyclooctatetraenyl moiety. The upfield shift in the chemical shifts of the phenyl carbons in the dianion and the increased spin density in the phenyl moiety in the anion radical, resulting from deuteriation of the eight-membered ring, is explained in terms of the different degrees of twist between the COT and phenyl rings. Since there is more zero-point energy in the coplanar arrangement and the force constant for C–D or C–H stretching mode should be maximized in a coplanar arrangement, $[6]–[8]^{\bullet-}$ will tend to be more twisted than will $[6]–[8]\text{-}d_7^{\bullet-}$. The deuteriation studies have further shown that the nature of the spin distribution in the anion radical of [6]–[8] has long been fundamentally misunderstood.

A quarter of a century ago the anion radical of phenylcyclooctatetrane ($[6]–[8]^{\bullet-}$) was reported for the first time.[1] The spin distribution in this system is of particular interest since [6]–[8] is the only existing molecular system where aromatic and antiaromatic (in the Hückel sense) annulenes ([6]annulene and [8]annulene) are directly interconnected. Consequently, the spin and charge distributions in $[6]–[8]^{\bullet-}$ have been the subject of numerous reports.[2] In 1974 Rieke and Copenhafer[2a] obtained an EPR spectrum of this anion with unprecedented resolution via the Li reduction of [6]–[8] in an HMPA–DME solvent mixture.

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(1) Carrington, A.; Moss, R. E.; Todd, P. E. *Mol. Phys.* **1966**, *12*, 95.

(2) (a) Rieke, R. D.; Copenhafer, R. A. *Electroanal. Chem. Interfacial Electrochem.* **1974**, *56*, 409. (b) Stevenson, G. R.; Echegoyen, L. *J. Am. Chem. Soc.* **1974**, *96*, 5452. (c) Stevenson, G. R.; Echegoyen, L. *J. Phys. Chem.* **1975**, *79*, 929. (d) Alegria, A.; Diaz, N.; Echegoyen, L.; Maldonado, R.; Colon, J. T. *J. Org. Chem.* **1982**, *47*, 5386. (e) Stevenson, G. R.; Forch, B. E. *J. Phys. Chem.* **1981**, *85*, 378. (f) Stevenson, G. R.; Echegoyen, L. *J. Am. Chem. Soc.* **1986**, *108*, 5509. (g) Echegoyen, L.; Nieves, J.; Maldonado, R.; Alegria, A.; Stevenson, G. R.; Reiter, R. C.; Clark, G. *J. Phys. Chem.* **1986**, *90*, 1241.

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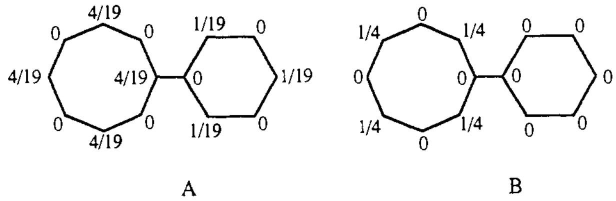
Table I. Experimental and Calculated Spin Densities and a_H Values for [6]–[8]$^{\bullet-}$

posn	ρ_{Huckel}[a]	$\rho_{PPP\text{-}SCF}$	ρ_{expl}[b]	ρ_{expl}[c]	a_H[c] (G)
2,8	0.1250	0.1463	0.150	0.147	3.77
4,6	0.1250	0.1621	0.150	0.147	3.77
3,7	0.1053	0.0708	0.088	0.089	2.29
5	0.1053	0.0656	0.088	0.089	2.29
ortho	0.0263	0.0214	0.018	0.014	0.370
meta	0.00	0.0015	0.089	0.014	0.370
para	0.0263	0.0256	0.018	0.0097	0.250

[a] Calculated by averaging the sums of the squared coefficients of the degenerate MO's A and B. Resonance integrals equal 0. [b] $Q = -25.7$ G.[2a] [c] This work.

Their computer simulation appears to be in good agreement with the actual spectrum, and the resulting hyperfine couplings correspond well to the HMO predictions (structures IA and IB; Table I). Further, the splittings from the protons on the eight-membered ring have been confirmed via deuteriation of the phenyl ring,[2b] and they consist of a quintet of quartets due to four and three equivalent protons, respectively, in the [6]-d_5–[8]$^{\bullet-}$ system.[2c]



I

The relatively small spin density in the phenyl moiety allows an alternative to treating the two-ring system as a unit, as above. That is, the quartet–quintet pattern can be interpreted as resulting from a perturbation of spin distribution in the eight-membered ring by an electron-withdrawing phenyl substituent. This splits the degeneracy of the two nonbonding molecular orbitals by lowering the energy of Ψ_{n+} and increases the spin density in Ψ_{n-} (C_{n-}^2) relative to that in Ψ_{n+} (in $\Psi = C_{n-}\Psi_{n-} + C_{n+}\Psi_{n+}$) (Figure 1A).[2c] If it is assumed that C_{n+} and C_{n-} are controlled by a simple Boltzmann distribution (eq 1), then Figure 1A leads to an accurate

$$C_{n+}^2 = e^{\Delta E/RT}/(1 + e^{\Delta E/RT}) = 1/(e^{-\Delta E/RT} + 1) = a_{H(3)}/[a_{H(4)} + a_{H(3)}] \quad (1)$$

prediction of the observed splittings.[2b,c] This type of reasoning is also consistent with the fact that anion radicals of [8]annulene substituted with electron-releasing substituents (i.e., the *tert*-butoxy group)[3] exhibit quartets of quintets, consistent with Ψ_{n+} being higher in energy than is Ψ_{n-} and most of the spin density being in Ψ_{n+} ($\Delta E > 0$).

The distinction between the two interpretations (whole-molecule HMO approach and the perturbation approach) of the spin distribution in the cyclooctatetraenyl moiety of the [6]–[8]$^{\bullet-}$ system cannot be completely resolved since both theories predict the observed hyperfine pattern from the eight-membered ring. However, the story is different if we concentrate on the phenyl moiety. The vast majority of the charge and spin density resides in the cyclooctatetraenyl moiety. Thus, the [8]annulene anion radical can be viewed as an electron-releasing substituent on the slightly charged benzene ring system. This perspective leads to a splitting of the degeneracy of the two antibonding MO's (Figure 1B), resulting in the spin density in the phenyl moiety predominantly occupying the antisymmetric wave function (Ψ_a). This should lead to four relatively large proton splittings (ortho and meta) and a small one (para). On the other hand, the two degenerate MO's shown in structures IA and IB would yield a larger splitting from three equivalent protons (ortho and para) and a smaller splitting from the two meta protons. Indeed, the spectrum has been simulated using coupling constants of 0.46 G for all four ortho and meta protons and 0.23 G (Rieke's and Copenhafer's value) for the para proton,[2a] and the agreement with the real spectrum seems to be improved. However, since the phenyl ring couplings are very small compared to those from the larger ring, the hyperfine pattern from the former is mostly unresolved. We have used deuteriation of the cyclooctatetraenyl moiety to circumvent this dilemma and have shown that the interpretation held true for the past quarter century is incorrect.

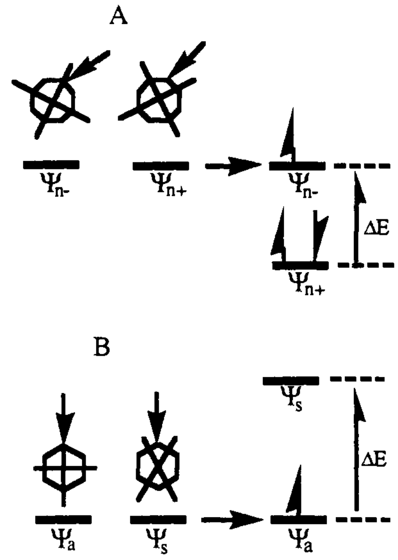


Figure 1. (A) Two nonbonding degenerate orbitals of planar [8]annulene (COT) split by the presence on an electron-withdrawing group at the site of the arrow. (B) Two antibonding degenerate orbitals of planar [6]-annulene and their splitting due to the presence of an electron-donating group.

A single electron-releasing substituent on the [6]annulene anion radical results in a relative decrease in the spin density in the symmetric wave function (Ψ_s), which is increased in energy. The antisymmetric wave function (Ψ_a) is unperturbed by the presence of an electron-releasing substituent (Figure 1B). In the simplest model, the odd electron in the [6]annulene moiety can be described as existing in a linear combination of the two formerly degenerate MO's; $\Psi = C_s\Psi_s + C_a\Psi_a$.[2b,4] Neglecting π–π spin polarization, C_s is related to the coupling constants (eq 2) and the magnitude of the splitting of the degenerate MO's by the Boltzmann distribution (eq 3). Using the coupling constants $a_{H(para)} = 0.59$

$$C_s^2 = 3a_{H(para)}/[2a_{H(para)} + 4a_{H(meta)}] \quad (2)$$

$$C_s^2 = 1/(e^{\Delta E/RT} + 1) \quad (3)$$

G and $a_{H(meta)} = 5.45$ G reported for the toluene anion radical[5] at 173 K, $C_s^2 = 3(0.59)/[2(0.59) + 4(5.45)] = 0.077$ and $\Delta E = 3.6$ kJ/mol. This is a little larger (13%) than the 3.2 kJ/mol calculated by Alper and Silbey,[6] but their calculation includes the effects of vibronic interactions.

Results and Discussion

EPR Study. The partial reduction of phenylcyclooctatetraene-d_7 ([6]–[8]-d_7) with sodium metal in hexamethylphosphoramide (HMPA), where ion association is absent,[2a] yields an anion radical that completely exposes the proton splittings from the phenyl ring upon EPR analysis at 25 °C (Figure 2). This spectrum cannot be interpreted in terms of structures A and B, as evidenced by the fact that use of phenyl a_H values in a 3/2 ratio clearly generates spectral simulations for [6]–[8]-$d_7^{\bullet-}$ which have no center "packet" of lines. While exact values of coupling constants are obscured by line overlap, extensive simulation efforts made it clear that only a 4/1 ratio of phenyl proton types leads to simulations with an odd number of bundles of overlapping peaks, in excellent agreement with the real spectrum. This model, applied to the simulation

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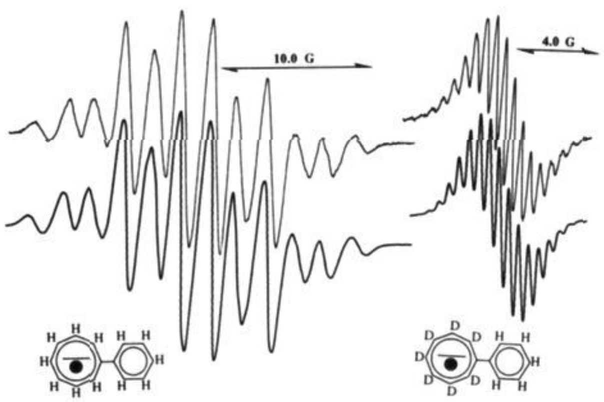
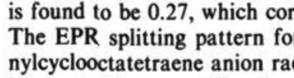


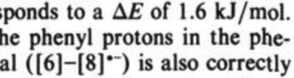
Figure 2. EPR spectrum of the anion radicals of phenylcyclooctatetraene (left) and of phenylcyclooctatetraene-d_7 (right) recorded at 25 °C in HMPA. The computer simulations generated using the coupling constants shown in structures IIA and IIB are shown below the spectra.

of the phenylcyclooctatetraene anion radical ($[6]-[8]^{\bullet-}$), leads to only cosmetic improvements in the fit of the simulation to the spectrum; it is the $[6]-[8]-d_7^{\bullet-}$ case which is definitive.

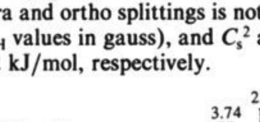
The quintet of doublets, as opposed to the expected quartet of triplets, from the benzene ring system indicates that the [8]-annulene anion radical is acting as an electron-releasing perturbation upon the weakly charged benzene system as shown in Figure 1B, and the partial spin density in this moiety resides predominantly in Ψ_a. Utilizing the expressions shown in eqs 2 and 3, C_s^2 is found to be 0.27, which corresponds to a ΔE of 1.6 kJ/mol. The EPR splitting pattern for the phenyl protons in the phenylcyclooctatetraene anion radical ($[6]-[8]^{\bullet-}$) is also correctly interpreted in terms of four larger splittings (ortho and meta) and one smaller splitting (para). However, in this case, the difference between the para and ortho splittings is not so great (structures IIA and IIC, a_H values in gauss), and C_s^2 and ΔE are found to be 0.38 and 1.2 kJ/mol, respectively.



IIA

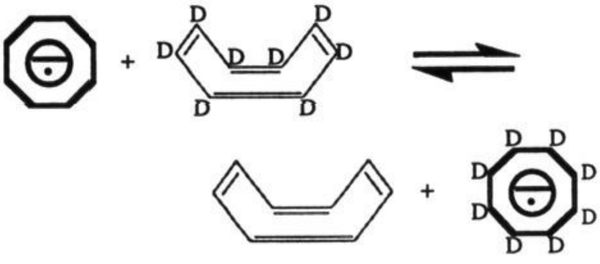


IIB



IIC

It appears the deuteriation of the cyclooctatetraenyl moiety has altered the spin distribution in the phenyl moiety in a way that makes the negatively charged eight-membered ring system act as a stronger electron-releasing agent. Indeed, perdeuteriation of [8]annulene does result in a slight increase in its solution electron affinity (reaction 4).[7a]



$\Delta G^{\circ} = -208$ J/mol (4)

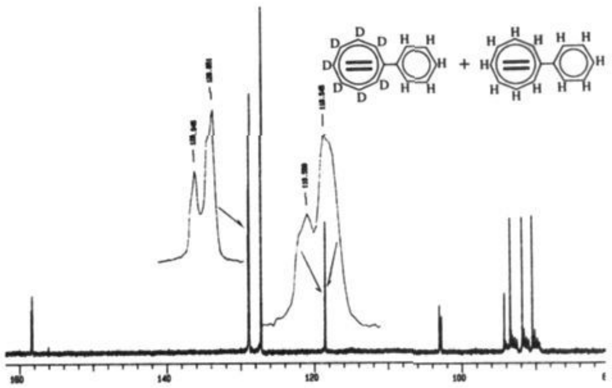


Figure 3. 300-MHz proton-decoupled ^{13}C NMR spectra of a mixture of the dianions of phenylcyclooctatetraene and phenylcyclooctatetraene-d_7 in deuteriated THF. Expanded-scale versions of the ortho and para carbon resonances are shown as insets. Note that the peak positions of the ortho and para carbons are slightly upfield in the deuteriated system. Since both dianions are in the same sample, the apparent isotope effects upon chemical shift cannot be due to environmental effects. The diamagnetic ring current in the [8]annulene dianion has a diminishing effect upon the benzene carbons as we get further from the eight-membered ring (ortho to meta to para).

In the case of the phenylcyclooctatetraenes, an additional significant contribution to the observed deuterium isotope effect may be due to different degrees of twist between the COT and phenyl rings. Since there is more zero-point energy in the coplanar arrangement and the force constant for C–D or C–H stretching mode should be maximized in a coplanar arrangement, $[6]-[8]^{\bullet-}$ will tend to be more twisted than will $[6]-[8]-d_7^{\bullet-}$. Also, the "ortho" C–H on the COT moiety will be more compressed than the ortho C–H on the phenyl moiety due to the C–C–H bond angles. From this it would be predicted that the deviation from coplanarity will follow the order $[6]-[8]^{\bullet-} > [6]-d_5-[8]^{\bullet-} > [6]-[8]-d_7^{\bullet-}$. More spin density will be found in Ψ_s (Figure 1) for those systems with less coplanarity. This is consistent with the ratio of the ortho to para coupling constants ($a_{H(ortho)}/a_{H(para)} = a_{H(meta)}/a_{H(para)}$) decreasing from 2.3 for $[6]-[8]-d_7^{\bullet-}$ to 1.9 for $[6]-d_5-[8]^{\bullet-}$ to 1.5 for $[6]-[8]^{\bullet-}$.

In contrast to the effect that deuteriation of the cyclooctatetraenyl moiety has upon the spin distribution in the phenyl moiety, *deuteriation of the phenyl moiety has no significant effect* upon the spin distribution in the cyclooctatetraenyl moiety (structures IIB and IIC). This is the expected result, since the fraction of the spin density in the smaller ring is very small compared to that in the eight-membered ring.

In the anion radical of [6]–[8] deuteriation of the cyclooctatetraenyl ring system perturbs the *spin* distribution in phenyl ring system. Thus, an analogous perturbation is expected on the *charge* distribution in the *dianion* of [6]–[8].

NMR Study. Exhaustive reduction of [6]–[8] with potassium metal in tetrahydrofuran (THF-d_8) leads to the formation of the dianion ($[6]-[8]^{2-}$), which in the absence of anion radical yields a well-resolved ^{13}C NMR spectrum (Figure 3). In view of the fact that the two-electron reduction of [8]annulene is preferred over that of perdeuteriated cyclooctatetraene (reaction 5),[7] deuteriation of the [8]annulene moiety ($[6]-[8]-d_7^{2-}$) should result in a relative increase in the charge density in the six-membered ring (more leakage of charge from the eight-membered ring when it is deuteriated) with a subsequent upfield shift in the ortho and para carbon resonance positions relative to those in $[6]-[8]^{2-}$. Furthermore, the arguments in terms of the deviation from coplanarity used for the anion-radical systems lead to the prediction that $[6]-[8]-d_7^{2-}$ will be less twisted than $[6]-[8]^{2-}$ and therefore

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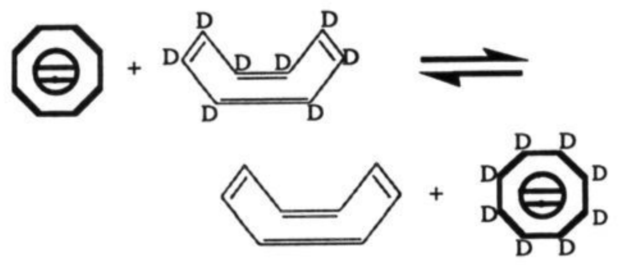
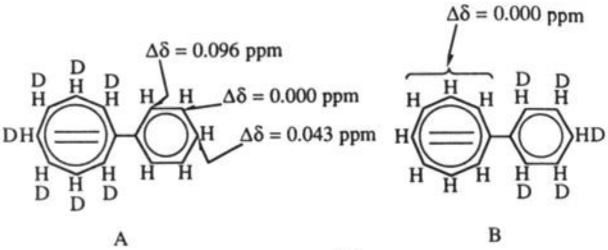
[7] (a) Stevenson, G. R.; Peters, S. J.; Reidy, K. A. *Tetrahedron Lett.* **1990**, *31*, 6151. (b) The fact that the second EA of C_8D_8 is smaller than that of C_8H_8 is a manifestation of the large destabilizing electron–electron repulsion energy in the dianion. Stevenson, G. R.; Peters, S. J. Unpublished results (see Experimental Section).



$$\Delta G^{o} = +142\ \mathrm{J/mol} \tag{5}$$

will donate more charge to the phenyl ring.

These expectations have been realized in these dianions, while the resonance frequencies of the phenyl carbons are the same in the two neutral molecules ([6]–[8] and [6]–[8]-d_7) (Figure 3). The chemical shift changes ($\Delta\delta$) resulting from deuteriation are shown on structure III. The chemical shifts of the cyclooctatetraenyl carbons do not change upon deuteriation of the phenyl moiety (structure IIIB). Even though it is known that the solution electron affinity of benzene is greater than that of perdeuteriated benzene,[8] the deuteriation of the phenyl moiety does not alter the chemical shifts in the cyclooctatetraenyl moiety. This is due to the fact that very little of the charge density resides in the smaller ring.



III

Conclusions

Deuteriation of the eight-membered ring of phenylcyclooctatetraene results in strong isotope effects upon spin distribution in the anion radical and upon charge distribution in the dianion. The observed spin distribution in the phenylcyclooctatetraene anion radical is best interpreted in terms of the two individual rings, each acting as a perturbation upon the spin density of the other. The assumed spin distribution in the phenyl moiety, which is consistent with simple MO theory, is incorrect. The fact that HMO prediction of $a_{\mathrm{H(ortho)}} = a_{\mathrm{H(meta)}} > a_{\mathrm{H(para)}}$ breaks down in twisted systems is consistent with the observations of Kurreck[9] regarding the 9-phenylanthracene anion radical.

In reality, the negatively charged cyclooctatetraenyl moiety acts as an electron-releasing substituent on the weakly charged benzene, which lifts the degeneracy of the antibonding benzene MO's and results in a larger spin density in the ortho and meta positions relative to that in the para position. This effect is stronger when the eight-membered ring is deuteriated due to the larger solution electron affinity of perdeuteriated [8]annulene relative to [8]-annulene and/or the larger deviation of the light isotopic analogues from planarity.

One might expect a Hückel treatment of the molecule as a whole to be more accurate than a treatment involving two Hückel type units perturbing each other. However, the Hückel assumption of coplanarity is incorrect here. Further, the Hückel assumption of identical π energy levels for molecules, and for corresponding anion radicals, is an oversimplification, which may be compensated for by this "perturbation" approach. Using ab initio calculations, the new σ–π separability criterion[10] suggests that the [8]annulene moiety is π-bond localized due to the large π energy that exists when the π system is delocalized. The addition of an electron lowers the π energy maximum, which allows the σ system to force bond equalization. It is logical that deuteriation of the ring results in even further lowering of this π energy maximum. A full ab initio treatment of the phenylcyclooctatetraene system would presumably show this and the interpretive separability of the two ring systems. However, this molecule is too large for such a calculation at this time.

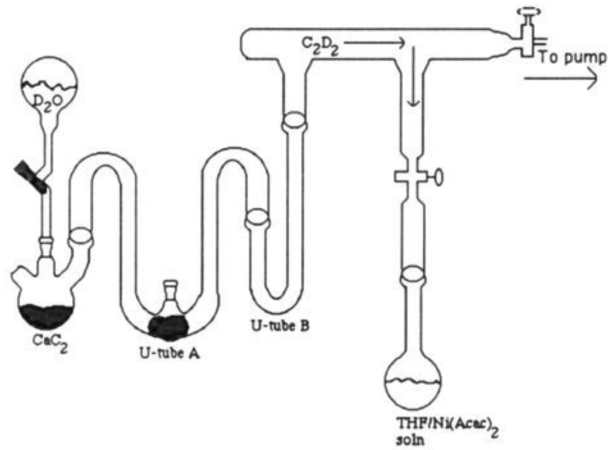


Figure 4. Apparatus used for the production of perdeuteriated cyclooctatetraene.

An upfield shift is observed for the ortho and para ^{13}C chemical shifts upon deuteriation of the cyclooctatetraenyl moiety due to an increased charge density in the phenyl moiety of the dianion when the cyclooctatetraenyl moiety is deuteriated. This observation is consistent with the fact that the two-electron-reduction potential of [8]annulene-d_8 is more negative than that of [8]-annulene, suggesting a greater leakage of charge density into the six-membered ring in [6]–[8]-d_7^{2-}. Following this most recent model,[10] the addition of the second electron increases the energy of the π system relative to that of the anion radical, but the energy still remains lower (in a solvated state) than that for the neutral system.

Experimental Section

Phenylcyclooctatetraenes. [6]–[8], [6]–[8]-d_7, and [6]-d_5–[8] were all prepared from the appropriately isotopically substituted cyclooctatetraene and phenyllithium reagent as previously described in detail.[2c]

Perdeuteriated Cyclooctatetraene. The procedures for the production of COT have been widely (Reppe synthesis) published.[11] However, there were some differences in the procedures used in our laboratory to generate the isotopically labeled materials.

A 50-mL round-bottom bulb was charged with about 0.85 g of Ni(Acac)$_2$, and the bulb was connected to the vacuum line and evacuated. A 30-mL portion of dry THF was then distilled into the round-bottom bulb using a dry ice/acetone solution (−78 °C). The bulb was then kept in the dry ice/acetone solution so that the acetylene would condense into the THF solution. The production of deuteriated acetylene was performed on the same vacuum line by dripping approximately 50 mL of D_2O onto 100 g of CaC_2, resulting in the production of 1.25 mol of acetylene which was condensed into the 50-mL bulb. The apparatus used for the production of deuteriated acetylene is shown in Figure 4. The chemical reaction between water and calcium carbide is very exothermic. Therefore, some unreacted water will vaporize and possibly condense in the reaction bulb. To eliminate this possibility, two U-tubes were placed between the reaction bulb and the three-neck flask where the CaC_2/D_2O reaction was taking place. U-tube A was submerged in an ice bath and was charged with CaC_2 to convert any vaporized D_2O to acetylene. To condense any residual D_2O, U-tube B was submerged in an acetone bath

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(8) Stevenson, G. R.; Espe, M. P.; Reiter, R. C. *J. Am. Chem. Soc.* **1986**, *108*, 5760.

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which had been cooled to approximately −50 °C. When the THF solution became saturated with acetylene, the bulb was submerged in liquid N_2 to condense any residual acetylene. Once all the acetylene was condensed and the solution frozen solid, the bulb was sealed from the line and enclosed in a 500-mL steel bomb. The bomb was submerged in a 90 °C oil bath for 15 h and shaken periodically. The bomb was then cooled in an ice bath and opened. The materials in the bomb were removed and dissolved in about 300 mL of diethyl ether. The solution was dried with magnesium sulfate and gravity filtered. The ether was evaporated under a stream of dry nitrogen. The remaining dark liquid was then vacuum distilled at 30 Torr. A yellow liquid was collected over the temperature range 40–50 °C. Mass spectral analysis is consistent with perdeuteriated [8]annulene (93% isotopic purity) mixed with heptadeuteriated [8]annulene (7% isotopic purity).

Instrumentation. The EPR spectra were recorded at 27 °C on an IBM (Bruker) ER-200D spectrometer equipped with an IBM variable-temperature unit. The 300-MHz NMR spectra of these samples were recorded on a Varian (Gemini) 300-MHz NMR spectrometer. Mass spectral data were collected using a Hewlett-Packard Model 5970 spectrometer connected with a 5790A gas chromatograph. All ^{13}C NMR spectra were recorded at 27 °C with a Varian (Gemini) 300-MHz wide-band spectrometer.

Reductions. Portions of [6]–[8], [6]–[8]-d_7, or [6]-d_5–[8] were placed into separate capillary tubes which were in turn sealed. The tubes containing the substrates were placed into glass apparatuses. After evacuation of an entire apparatus, a freshly distilled alkali-metal mirror was deposited and the portion of the apparatus from which it came was subsequently sealed from the apparatus. Dry THF (with 10% THF-d_8 for NMR lock) or HMPA was then distilled from a storage bulb containing NaK_2, directly into the apparatus. The entire apparatus was then sealed from the vacuum system. The apparatus was then shaken to break the tube containing the substrate and expose the solution to the metal mirror. Samples of the resulting anion-radical or dianion solutions were then poured into side tubes, which were then sealed from the apparatuses and submitted to analysis. NMR samples of the dianions were not sealed from the apparatus until complete reduction to the dianion was indicated by the absence of an EPR signal.

Reaction 5. The reduction of a mixture of C_8H_8 and C_8D_8 with 1 mol of potassium metal/mol of total [8]annulene in THF yields a solution that contains mostly neutral and dianionic materials. Due to the very large equilibrium constant for disproportionation (ca. 10^9),[12] there is very little anion radical present in solution. Thus, any separation of the anionic materials from the neutral materials is in net effect a separation of the dianionic and neutral materials. Further, the ratio of isotopic isomers in the two phases (α) is controlled by the equilibrium constant for reaction 5. A mixture of 2.40 mmol of C_8H_8 and 6.66 mmol of C_8D_8 was reduced by about 7 mmol of potassium metal at room temperature in THF. The solvent and neutral [8]annulenes were removed under reduced pressure (phase 1), and the remaining solid dianion salt was reoxidized with iodine (i.e., $I_2 + K^+{}_2C_8H_8{}^{2-} \rightarrow C_8H_8 + 2K^+I^-$) and labeled phase 2. The [8]annulenes from both phases were distilled under vacuum and submitted to NMR and mass spectral analysis, which are consistent with an equilibrium constant of 0.92 at 205 K. The details of this experiment and the confirmation of the equilibrium constant via the techniques discussed in ref 7a will appear in a future communication.

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Registry No. [6]-[8]$^{\bullet-}$, 53318-48-2; [6]-[8]-$d_5{}^{\bullet-}$, 53318-49-3; [6]-[8]-$d_7{}^{\bullet-}$, 137516-36-0; [6]-[8], 50277-25-3; [6]-[8]-$d_5{}^{2-}$, 137516-38-2; [6]-[8]-$d_7{}^{2-}$, 137516-37-1; deuterium, 7782-39-0.

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Solvation of Aggregates of Lithium Phenolates by Hexamethylphosphoric Triamide. HMPA Causes Both Aggregation and Deaggregation

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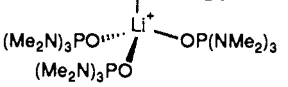
Abstract: The tetramer of lithium 3,5-dimethylphenolate in diethyl ether undergoes sequential solvation by HMPA and is fully converted to the HMPA tetrasolvate by 1 equiv of the cosolvent. Addition of 8 equiv of HMPA does not cause dissociation of the tetramer. Addition of HMPA to lithium *p*-bromo- and *p*-(trifluoromethyl)phenolates in THF results in conversion of their dimers to tetramers and, at high cosolvent ratios, monomers. Two equivalents of HMPA in either THF or diethyl ether converts dimeric lithium 2,6-dimethylphenolate to the monomer. ^{13}C, ^7Li, and ^{31}P chemical shifts for the various HMPA solvates are reported. The ^7Li quadrupole splitting constant for tetrameric lithium 3,5-dimethylphenolate HMPA tetrasolvate is 35 kHz. Lithium *p*-bromophenolate in THF at −120 °C forms a small quantity of a trimer together with the dimer and tetramer.

Hexamethylphosphoric triamide (HMPA)[1,2] and *N*,*N'*-dimethyl-*N*,*N'*-propyleneurea[2] are known to catalyze the reactions of lithium salts of carbon acids with electrophiles and often, if the anion is ambident, to result in dramatically altered regiochemistry.[3] The usual protocol calls for the addition of 4 equiv of the cosolvent to solutions of the salts in solvents such as diethyl ether, THF, etc., the idea being that this will lead to the formation of the tetrasolvated lithium cation, e.g. **1**, and an essentially free anion in place of a contact ion pair or an aggregate thereof. Direct evidence that this does occur in the case of certain organolithium



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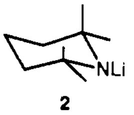

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