Perturbations in Aromatic and Antiaromatic Characters Due to Deuteration: The Case of [16]Annulene

Cheryl D. Stevenson* and Todd L. Kurth

*Department of Chemistry, Illinois State University
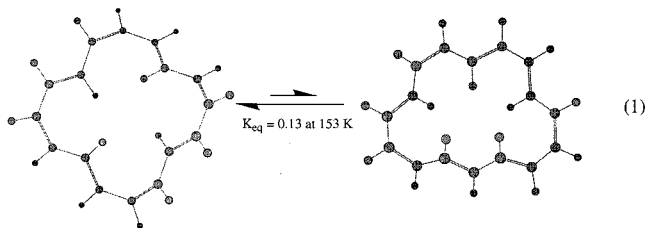Normal, Illinois 61790-4160*

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The addition or subtraction of π-electrons to or from conjugated organic systems can have a profound effect upon their structures and energies. Significant examples are the cases of [8]annulene[1a,b,c] and, to a lesser degree, [6]annulene.[1c,d] The extensive interest in structural perturbations due to π-electron addition is accounted for by their importance in understanding conjugation and aromaticity.[1] To extend our ongoing work concerning electron-transfer equilibrium isotope effects,[2] we synthesized samples of perdeuterated [16]annulene[3] and found that the paramagnetic ring current in the neutral molecule and the diamagnetic ring current in the dianion are significantly augmented upon deuteration.

There have been a number of empirical and theoretical definitions of aromaticity.[2] However, the one concept that all theoretical models and experimental tests are ultimately compared to is Huckel's $4n + 2$ rule.[4] Aromaticity in a Huckel sense[4] is based upon the number of π-electrons that exist in a conjugated system, while the predominant empirical test for aromaticity is based upon ^{1}H NMR chemical shift indications of paramagnetic or diamagnetic ring currents.[5]

The most basic prediction of the $4n + 2$ rule is that the aromatic and antiaromatic (diatropic and paratropic) characteristics of the annulenes can be interchanged via the addition or subtraction of two π-electrons. However, the steric interactions of the internal protons, present in all of the annulenes larger than [8]annulene, dominate both their structures and stabilities.[6] Unlike the [8]-annulene system, and despite the sterically interacting protons, the thermodynamically most stable configuration of neutral [16]-annulene (reaction 1) exhibits a paratropic ring current, as

$$K_{eq} = 0.13 \text{ at } 153 \text{ K} \qquad (1)$$

evidenced by the internal protons which have a chemical shift at δ 10.58 at -110 °C.[7]

Our synthesis of perdeuterated [16]annulene produced material that is 95 atom % deuterated.[8] The presence of [16]annulene-d_{15}

Figure 1. 400 MHz ^{1}H NMR of [16]annulene and [16]annulene-d_{15} at 153 K. The internal protons of [16]annulene (upper right) are split into a triplet due to the two vicinal hydrogens. The gyromagnetic ratio of the nearby deuteriums is too small to split the signal for the internal proton of [16]annulene-d_{15} (upper left). Note the augmented paratropic shift of the internal proton(s) caused by deuteration. The small peaks at the base of the [16]annulene-d_{15} internal proton resonance are due to [16]annulene-d_{14} impurity. The resonances shown below exhibit the augmented paratropic shift for the external protons caused by deuteration. In this case, the single resonance for the [16]annulene-d_{15} system appears upfield from the resonances of the perprotonated [16]annulene. The pattern from the eight equivalent hydrogens is split into a doublet of doublets, since the internal and external vicinal coupling constants are different.

allows comparison, by ^{1}H NMR analysis, of the isomeric systems. Integration of the ^{1}H NMR peaks revealed only the statistical distribution of the lone proton in the [16]annulene-d_{15} system. The chemical shifts of the lone proton in [16]annulene-d_{15} and the 16 protons in [16]annulene allowed the measurement of the relative paratropicity of the two systems. The analysis (Figure 1) reveals that the lone internal proton of [16]annulene-d_{15} (δ 10.82) is shifted downfield by 0.24 ppm relative to the internal protons of [16]annulene. This isotope effect is an order of magnitude larger than, and in the opposite direction of, the expected upfield shift due to zero point energy effects.[9] The resonances from the external protons shift upfield. These oppositely directed shifts result in an increased separation of the extreme upfield and downfield

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(2) For example, see: (a) Stevenson C. D.; McElheny, D. J.; Kage, D. E.; Ciszewski, J. T. Reiter, R. C. *Anal. Chem.* **1998**, *70*, 3880. (b) Hrovat, D. A.; Hammons, J. A.; Stevenson, C. D.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 9523. (c) Stevenson, C. D.; Halvorsen T. D.; Reiter, R. C. *J. Am. Chem. Soc.* **1993**, *115*, 12405. (d) Stevenson, C. D.; Rice, C. V. *J. Am. Chem. Soc.* **1995**, *117*, 10551.

(3) The [16]annulene was previously synthesized in our laboratory, see: Stevenson, C. D.; Forch, B. E. *J. Am. Chem. Soc.* **1980**, *102*, 5985.

(4) Huckel, E. Z. *Physik.* **1931**, *70*, 20. (b) Huckel, E. Z. *Electrokhim.* **1937**, *43*, 752.
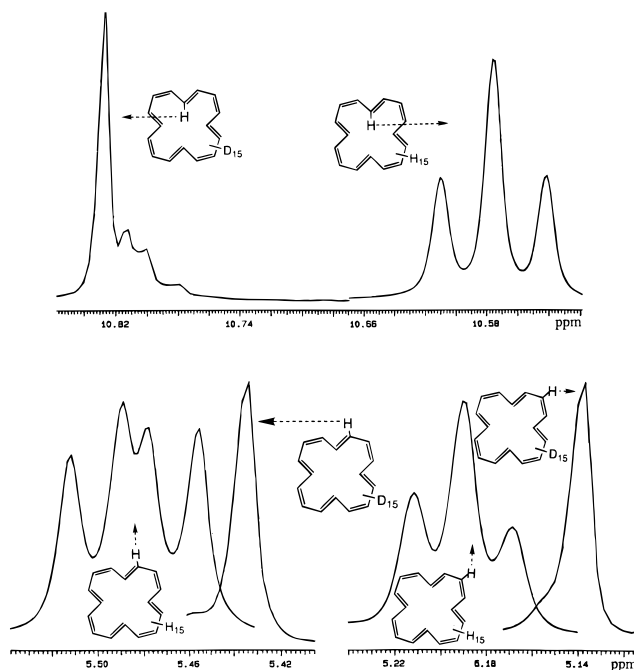
(5) (a) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Y. *Aromaticity and Antiaromaticity Electronic and Structural Aspects*; John Wiley and Sons: New York, 1994. (b) Gunther, H. *NMR Spectroscopy, An Introduction*; Wiley: New York, 1980. (c) Stevenson, C. D. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1986; Vol. 3.

(6) Garratt, P. J. *Aromaticity*; McGraw-Hill: London, 1971.

(7) At -140 °C Oth measured chemical shifts of 10.61 ppm for the internal protons, and 5.3 ppm for the external protons at 60 MHz, see: (a) Oth, J. F. M. *Pure Appl. Chem.* **1971**, *25*, 573. (b) Oth, J. F. M.; Baumann, H.; Gilles, J.-M.; Schroder, G. *J. Am. Chem. Soc.* **1972**, *94*, 3498.

(8) (a) Perdeuterated cyclooctatetraene was prepared as described in: Stevenson, C. D.; Burton, R. D.; Reiter, R. C. *J. Am. Chem. Soc.* **1992**, *114*, 399. (b) Cyclooctatetraene was dimerized to form the 2 + 2 dimer, which was in turn photolyzed to yield [16]annulene as described in: Schroder, G.; Kirsch, G.; Oth, F, M. *Chem. Ber.* **1974**, *107*, 460.

(9) In our hands, the change in the ^{1}H chemical shift of cyclooctatetraene due to heptadeuteration is -0.010 ppm.
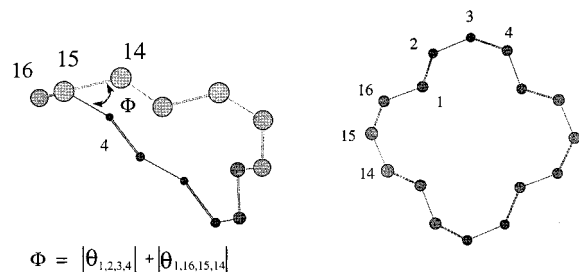
$$\Phi = |\theta_{1,2,3,4}| + |\theta_{1,16,15,14}|$$

Figure 2. The divergence from planarity of the [16]annulene system is depicted by the angle Φ, which represents the sum of the absolute values of dihedral angles $\theta_{1,2,3,4}$ and $\theta_{1,16,15,14}$. On the left the molecule is illustrated with carbons 15, 16, 1, 2, and 3 in the same plane.

peaks by more than 0.3 ppm. The changes of the various proton chemical shifts (experimental error is less than ±0.005 ppm) due to deuteration are shown in structure **I**, and they suggest a greater
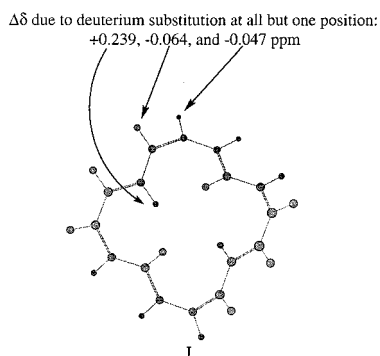
degree of planarity with a consequent augmentation of the paratropic ring current in the system with internal deuterium atoms.

Neutral [16]annulene, although nonplanar, is known to exhibit a paramagnetic ring current.[7a,b] Much of the nonplanarity is a consequence of the sterically interacting four internal protons. Consequently, these NMR data can be logically explained in terms of the shorter C−D as compared to the C−H bond lengths.[10] The shorter internal C−D bond alleviates a little of the steric crowding of the internal atoms, which allows the system to acquire a greater degree of planarity. This, in turn, results in a more paramagnetic ring current shifting the internal protons downfield.

Indeed, ab initio calculations carried out using the Spartan 4.0 program from Wave function Inc.[11] suggest that the dihedral angels, 1, 2, 3, 4 and 1, 16, 15, 14, shown in Figure 2, are slightly smaller (by a total of 0.083°) for the perdeuterated system. Geometry optimization on the [16]annulene system was carried out using the PM3 protocol. The resulting C−H bonds were then constrained to these values, after which the geometry was further optimized using the HF/6-31G* basis set. For the [16]annulene-d_{16} system, the C−D bond lengths were constrained to be 0.01 Å shorter than the PM3 predicted C−H bond lengths. The resulting structure was then optimized in the same manner.[11]

Given that deuteration augments the paramagnetic ring current in the neutral [16]annulene, it might seem reasonable that deuteration would increase the diamagnetic ring current in the dianionic form of this annulene. The HF/6-31G* calculations support the prediction and suggest that the dihedral angles, as
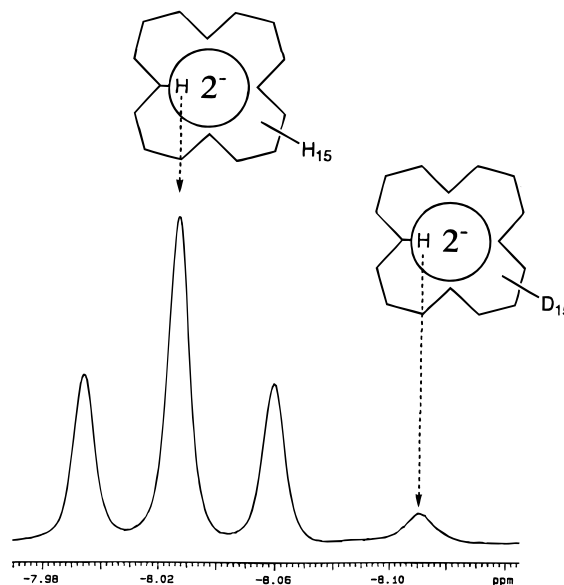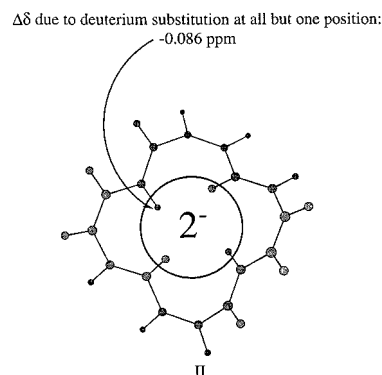
(10) (a) For naphthalene, X-ray crystallography reveals a reduction of the C−L (L = H or D) bond length from 1.085 (C−H) to 1.073 (C−D) Å see: Berger, S.; Kunzer, H. *Tetrahedron* **1983**, *39*, 1327. (b) For another cases of isotopic bond length reduction, see: Bartell, L. S.; Roth, E. A.; Hollowell, C. D. *J. Chem. Phys.* **1965**, *42*, 2683 and Melander, L.; Saunders, W. H. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980; pp 189−197.

(11) This treatment of deuterated systems is similar to that used by: Zuilhof, H.; Lodder, G.; van Mill, R. P.; Mulder, P. P. J.; Kage, D. E.; Reiter, R. C.; Stevenson, C. D. *J. Phys. Chem.* **1995**, *99*, 3461.

Figure 3. Expanded scale versions of the 400 MHz ^{1}H NMR spectrum of a mixture of Li$^+_2$,[16]annulene^{2-} and Li$^+_2$,[16]annulene-d_{15}^{2-} in THF-d_8. Note that the peak position of the internal protons are shifted upfield in the deuterated system. The external proton resonances are unperturbed and are not shown. Since both dianions are in the same sample tube, the apparent isotope effects upon chemical shift cannot be due to environmental effects. The diamagnetic ring current in the [16]annulene dianion is clearly increased by replacing the internal protons with deuteriums.

described above, are smaller by a total of 1.67° for the deuterated dianion system, see Figure 2.

Exhaustive reduction of samples of the [16]annulene and deuterated [16]annulene in tetrahydrofuran-d_8 with lithium metal under high vacuum resulted in the formation of the respective dianions. ^{1}H NMR analysis of these solutions reveals that the chemical shift of the internal protons for [16]annulene is δ −8.03 ppm, while the spectrum of the dianion of [16]annulene-d_{15} shows that the internal protons resonate at δ -8.11 ppm. To verify the validity of these results a mixture of [16]annulene and [16]-annulene-d_{15} was likewise reduced. ^{1}H NMR analysis clearly shows that the resonance for the internal protons is shifted upfield by 0.086 ppm, Figure 3. The perturbations in the chemical shifts of the external protons of the dianion are not larger than experimental error (see structure **II**).

Deuteration apparently allows flattening of the 16-membered ring. Further, the actual aromatic and antiaromatic characters of the neutral and dianionic systems are measurably increased via deuteration. Deuteration should, in principle, analogously affect all of the annulenes larger than [8]annulene. Work is currently in progress to verify this prediction.