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Isotopic Perturbations in Aromatic Character and New Closely Related Conformers Found in [16]- and [18]Annulene

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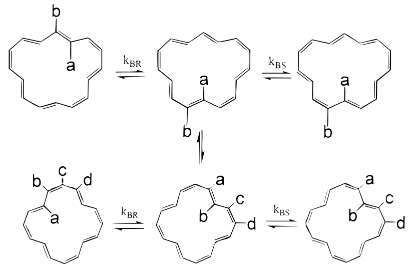
No series of compounds have contributed more to the study of aromaticity than have the annulenes. Considering only the number of π-electrons, the Hückel $4n + 2$ rule successfully predicts the aromatic character, and other properties of many of these monocyclic systems, despite the fact that this theory was developed without consideration of the effects of attached protons.[1] However, the importance of this electron count rule has been challenged.[2] It has been theorized that the σ-framework imposes the relative delocalization and thus aromaticity of a particular system. Here, we present evidence for the existence of previously unobserved, nearly degenerate isomeric forms of [16]-annulene and [18]annulene that differ in the spatial arrangement of the internal hydrogens and their internal $\mathrm{C{-}C{=}C}$ bond angles. The existence of these new isomers supports the relatively new theories coming from Shaik's and Jug's groups,[2] and it explains low-temperature chemical shift dependence, of the [16]- and [18]-annulene ^{1}H NMR spectra, that are not explained by the previously studied exchange mechanisms described in Schemes 1 and 2.[3]

The first (smallest) thermodynamically stable annulenes (at ambient temperatures) with internal protons are [16]- and [18]-annulene. Unlike the [6]- and [8]annulene systems, these two larger systems are effected by the steric interactions of internal protons. Indeed, recent ^{1}H NMR results suggest that these steric interactions, which have a profound effect on the planarity of the [16]annulene system, can be attenuated by replacing the internal protons with deuteriums.[3] Specifically, deuteriation results in increased paratropic shifts of the low temperature ^{1}H NMR resonances of [16]annulene-d_{15} relative to those of [16]annulene-h_{16}.[4a]

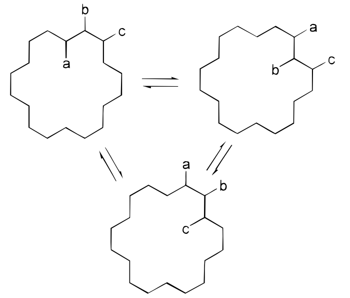
At temperatures above 163 K, consideration of the intramolecular proton exchange between the possible conformations (Scheme 1) is required for the simulation of the 400 MHz ^{1}H NMR spectra.[3] This exchange accounts for the broadening and ultimate coalescence of resonances as the temperature is raised.

Since the C−D bond is known to be shorter than the C−H bond, the increased paratropic shifts of the deuteriated [16]annulene has been accounted for in terms of the increased planarity and consequent increased paratropic (anti-aromatic) ring current (π-delocalization).[4] However, Shaik and Jug with their collaborators[2] have presented evidence indicating that delocalization of π electrons, and bond equalization, is enforced by the σ framework ($\mathrm{C{-}C{=}C}$ bond angles). Consequently, it is also possible that σ-framework changes, which occur upon deuteriation, may contribute to the increased level of delocalization. To further examine this effect, we sought to observe the analogous isotopic perturbation in a neutral, formally aromatic, $(4n + 2)$ π-electron system, which also contains internal protons ([18]annulene).

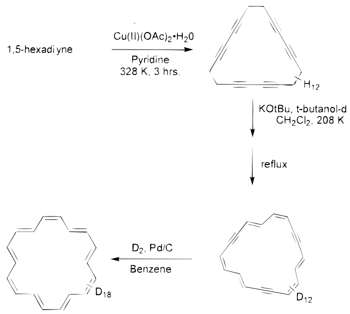
Scheme 1



Scheme 2



Scheme 3



It was found that [18]annulene-d_{18} can be synthesized using the synthetic scheme described by Sondheimer[5] but replacing the *tert*-butyl alcohol in the second step with *tert*-butyl alcohol-*d* and the H_2 in the third step with D_2 (Scheme 3).

The 400 MHz ^{1}H NMR spectrum of [18]annulene, in $CDCl_3$ at 213 K, is characterized by a quartet at δ 9.17 and a pentet at δ −2.96 for the 12 external and 6 internal protons, respectively. The analogous spectrum of [18]annulene-d_{17} (plus further protic impurity, e.g., [18]annulene-d_{16}) reveals increased diatropic shifts of both the internal protons and external shifts due to deuteriation. The external protons are shifted downfield by 0.03 ppm, and the internal protons are shifted upfield by 0.12 ppm (Figure 1). NMR spectra of mixtures of the perprotiated and deuteriated materials in THF-d$_8$/ethanol-d_8 allow the perprotiated system to serve as an internal reference, and these spectra confirm the data presented in Figure 1. The shorter internal C−D bonds in the [18]annulene-d_{17} system allow relaxation of the σ framework and consequently more σ enforced delocalization of the π-electrons.

Similar to [16]annulene, [18]annulene is fluxional at more elevated temperatures.[3] In the spectra of the [16]- and [18]-annulenes, thermal dependence of the chemical shifts continues well below the temperature where resolution is maximized, and

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(1) Garrat, P. J. *Aromaticity*, Wiley: New York, 1986. (b) Minkin, V. I.; Glukhovtstev, M. N.; Simkin, B. Y. *Aromaticity and Anti-aromaticity*, Wiley: New York, 1994.

(2) Shaik, S. S.; Hiberty, P. C.; Ohanessian, G.; Lefour, J.-M.; *J. Phys. Chem.* **1988**, *92*, 5086. (b) Jug. K.; Koster, A. M. *J. Am. Chem. Soc*. **1990**, *112*, 6772.

(3) Oth, J. F. M. *Pure Appl. Chem.* **1971**, *25*, 573.

(4) Stevenson, C. D.; Kurth, T. L. *J. Am. Chem. Soc.* **1999**, *121*, 1623. (b) 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. (c) 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.

(5) Sondheimer, F.; Wolovsky, R. *J. Am. Chem. Soc.* **1962**, *84*, 260. (b) Sondheimer, F.; Wolovsky, R.; Amiel, Y. *J. Am. Chem. Soc.* **1962**, *84*, 274.

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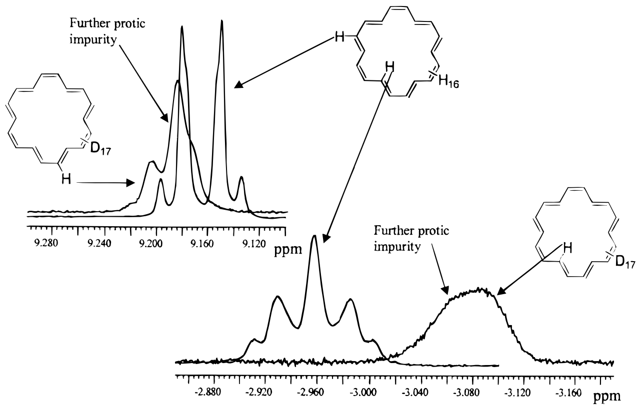

Figure 1. Overlaid 400 MHz ^{1}H NMR spectra of [18]annulene and [18]annulene-d_{17} (plus further protic impurity, e.g., [18]annulene-d_{16}), both in $CDCl_3$ at 213 K. The [18]annulene spectrum is characterized by a quartet at δ 9.17 and a pentet at δ −2.96 for the 12 external and 6 internal protons, respectively. In the spectrum of [18]annulene-d_{17}, singlets at δ 9.20 and −3.084 account for external and internal protons, respectively.

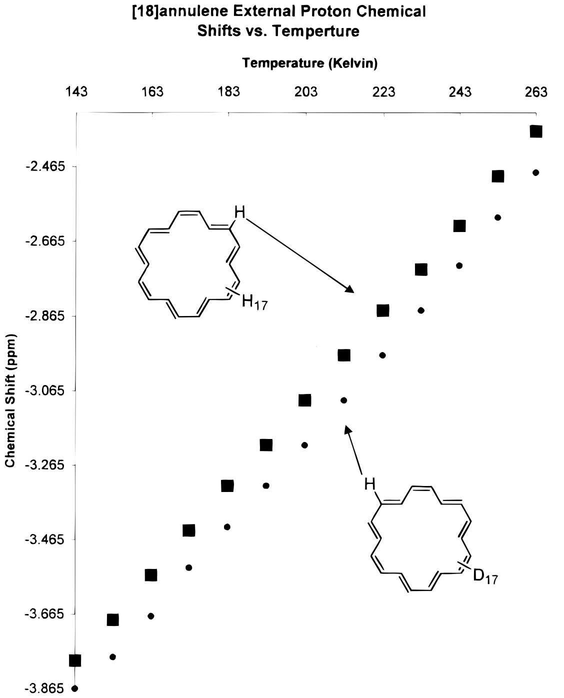

Figure 2. Plot of the chemical shift values (ppm) of the external proton resonances for the [18]annulene and [18]annulene-d_{17} systems vs temperature (K). The protiated and deuteriated data were taken from spectra of a mixed sample (deuteriated and protiated materials) in THF-d_8/ethanol-d_8 as well as data from a pure perprotiated sample in $CDCl_3$.

computer simulation no longer predicts chemical shift thermal dependency (Figure 2). At the working temperatures of the solvent (down to 153 K in a THF-d_8/ethanol-d_8 mixture), the exchange responsible for this chemical shift movement does not even begin to become slow on the NMR time scale. There clearly exists an exchange in both of these annulene systems that is not accounted for by the reactions shown in Schemes 1 and 2. The new exchange mechanisms must involve very similar molecular structures and very low energy barriers to exchange.

By observing simple models, it became apparent that the [16]annulene and [18]annulene systems can have two distinct arrangements of the internal protons (Figure 3), that would account for the structures involved in the proposed exchange. Confirming the intuitive observation, it was found that Hernando et al.,[6] using semiemperical calculations, had already predicted the existence of these isomers of [16]annulene. The aforementioned authors further indicate that the two isomers have slightly different energies, the most stable of each pair having relatively more ideal bond angles.[6] As the temperature of the [16]annulene system is lowered, the energetically allowed geometry of the σ-framework approaches ideality (120° C−C=C bond angles). The consequence of this is increased enforcement of π-delocalization[2] and augmented paratropicity of the annulene system. From the ^{1}H NMR data, it is apparent that in both the [16]- and [18]annulenes, there must exist such lower-energy structures having σ-frameworks that enforce greater π-delocalization and thus greater ring current (paratropic in the $4n$ π-electron system and diatropic in the $4n + 2$ π-electron system).

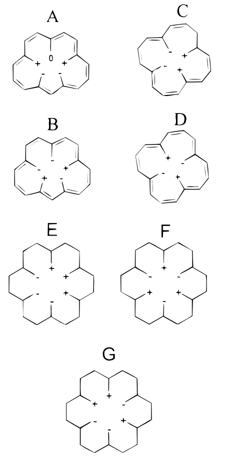

Figure 3. The conformers (A, B, C, and D) for [16]annulene that were proposed by Hernando are shown (ref 6). The plus signs indicate that the proton extends forward from the plane of the molecule, while a minus signifies that it extents back into the page. The zero indicates that the proton is in the plane of the ring (the plane containing the largest number of carbon atoms). According to Hernando, the most stable isomer of [16]annulene does not exist in conformations with protons lying in the plane of the ring. The analogous conformers for most table isomer of [18]annulene are also shown (E, F, and G).

Paratropicity and diatropicity in the [16]annulene and [18]annulene systems is quite sensitive to the steric interactions involving their respective internal protons. Alterations in these steric interactions via isotopic substitution or via changes in the stacking of the internal protons in the planes above and below the plane of the ring perturbs the aromaticity and antiaromaticiy (measured in terms of NMR chemical shift) exhibited by these two annulenes. Presumably this will prove to be the case in all but the largest annulenes that have internal hydrogens. Work is in progress to observe these differences via other analytical methods.

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Supporting Information Available: ^{1}H NMR of [18]annulene at 263, 243, and 213 K (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) Hernando, J. M.; Quirante, J. J.; Enríquez, F. *Collect. Czech. Chem. Commun.* **1992**, *57*, 1.