Annulenylenes, Annulynes, and Annulenes

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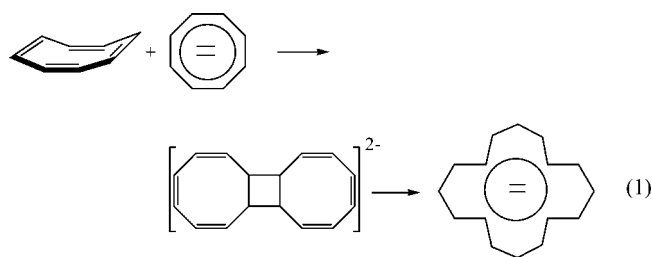
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ABSTRACT
A number of techniques have been found to generate annulynes. Some of the annulynes have been found to spontaneously dimerize to biannulenylenes and to form triannulenylenes. The reaction products, thermodynamics, and kinetic stabilities of the annulenylenes, annulynes, and their parent annulenes prove to be extremely dependent upon the number of π electrons. In fact, the addition of an extra electron can trap some "fugitive" systems and render them sufficiently stable for spectroscopic study. Even the number of neutrons can perturb the conjugation and, presumably, the stability of annulenes that have internal protons.

The structures and energies of conjugated organic systems are most profoundly perturbed by the simple addition or subtraction of π electrons. For example, naphthalene (a $4n + 2$ π-electron system) can be heated to over 1100 °C without noticeable decomposition, but the warming of its anion radical (considered a $4n + 3$ π-electron system) to just 100 °C results in the evolution of methane and hydrogen.[1] The extensive interest in structural perturbations because of π-electron addition is accounted for by its importance in understanding conjugation and aromaticity, and no series of compounds has contributed more to our quantum mechanical, thermodynamic, and kinetic understanding of the significance of the π-electron count rule than the family of annulenes, accounting for the "*renaissance of annulene chemistry*".[2]

In principle, the annulenes can be extended via [2 + 2] cycloaddition with other annulenes, followed by ring opening. However, because of the forbidden nature of the 2s + 2s addition and steric considerations, the vast majority of the alkene combinations cannot be forced to undergo this reaction thermally.[3] Despite this difficulty, the high reactivity of electron-rich alkenes with electron-deficient alkenes, in the (2 + 2) cyclo-addition reaction, has been of synthetic importance for a number of years (for example, tetrafluoroethylene preferentially adds to cyclopentadiene in the 2 + 2 mode rather than the 4 + 2 mode).[4] Consistent with this, the very electron-rich [8]annulene dianion reacts, over a period of several days at ambient temperature, with the electron-deficient [8]annulene to yield the dianion of [16]annulene (reaction 1).[5a] Surprisingly, this dimerization takes place only in hexamethylphosphoramide (HMPA), in the strict absence of ion association.[5]

Under analogous conditions, [8]annulene will add to the trianion radical of C_{60} and (likewise) the adduct

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$$\tag{1}$$

undergoes ring opening (reaction 2). The opening is sufficient to allow for the entry of an alkali metal cation (reaction 3),[6] as revealed by mass spectral analysis, which shows the appropriate *m/e* peaks using both positive and negative ion detection. One can simulate this passage by placing the K$^+$ near the orifice and minimizing the energy in a molecular-modeling program (e.g., Spartan without the inclusion of solvent effects).

$$\tag{2}$$

$$\tag{3}$$
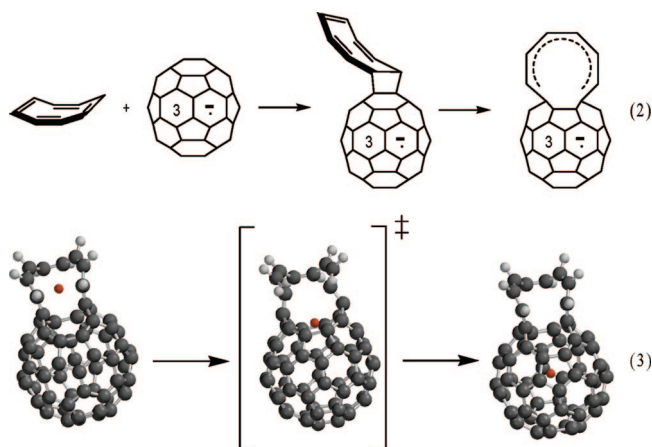
Neither [6]annulene (benzene) nor its anion radical are known to undergo any reaction analogous to those described (above) for the [8]annulene system. However, [6]annulyne (*o*-benzyne) is a very important reactive intermediate. It is used for the synthesis of a wide variety of materials and has been the subject of Accounts.[7] When it is not in the presence of a reactive substrate, it undergoes a 2 + 2 cycloaddition with itself, yielding biphenylene (reaction 4).[7b]

$$\tag{4}$$
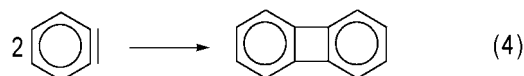
Despite the very intense theoretical[7a,c] and pragmatic[7b] interest in the [6]annulyne system, the next annulyne, in terms of size, ([8]annulyne) has been only very sparsely studied.[8] We found that [8]annulyne (C_8H_6) can be trapped as its corresponding anion radical (Figure 1), and it does undergo an analogous 2 + 2 cycloaddition with itself. The unstable cycloaddition product can be trapped as its anion radical, at low temperature [in tetrahydrofuran (THF)], for observation (Scheme 1).[9]

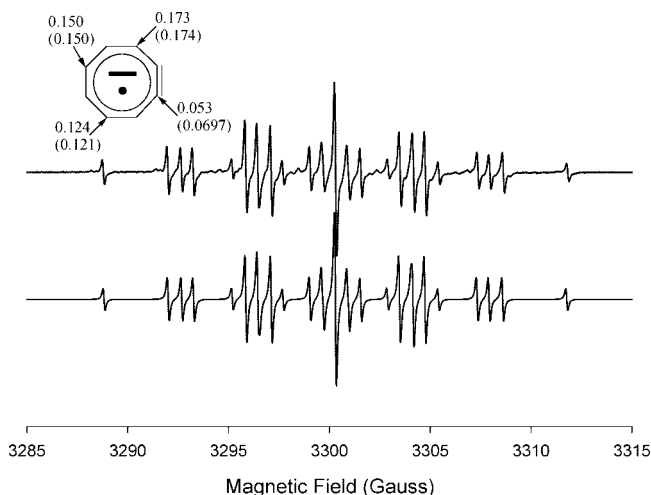* To whom correspondence should be addressed. E-mail: cdsteve@ilstu.edu.

FIGURE 1. (Top) X-band electron paramagnetic resonance (EPR) spectrum of a THF solution containing the sodium [8]annulyne anion radical salt at 150 K. (Bottom) Computer-generated EPR spectrum using a_H values of 3.18, 3.85, and 4.44 G, respectively, for three sets of two equivalent protons. The peak–peak intrinsic line width is 0.1 G. Note the agreement between the empirical p_z spin densities and those predicted via a B3LYP/6-31G* calculation, shown in parentheses.

Scheme 1
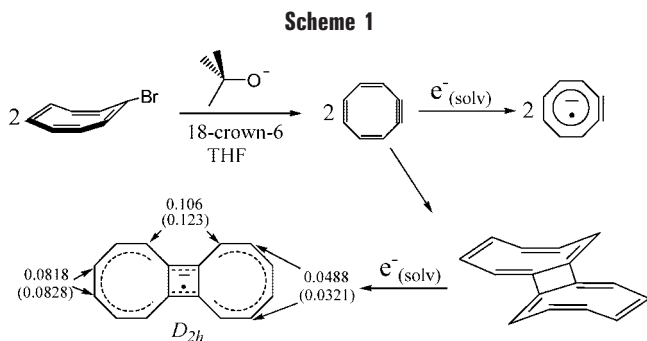
The cyclobutadienyl moiety, in the center of the bi-[8]annulenylene system, combined with the two cyclooctatetraenyl moieties produces instability because of their $4n$ π-electron count. This instability can be circumvented via the addition of a single electron. Hence, the second biannulenylene (bi-[8]annulenylene) was captured as its corresponding anion radical (as was C_8H_6) and observed by EPR spectroscopy (Scheme 1). The B3LYP/6-31G*-predicted p_z orbital spin densities and those observed are in excellent agreement.[10] Prior to this Account, biphenylene (now called bi-[6]annulenylene to allow for nomenclature needed to cover the other 2 + 2 annulyne–annulyne cycloadditions) remained the only example of a biannulenylene.

It is all about timing. If the alkoxide and bromo-[8]annulene, at 273 K, are mixed and immediately exposed to electrons (e.g., solvated electron), no dimerization takes place and the captured anion radical is that of [8]annulyne (Scheme 1). However, a few seconds delay in electron addition leads to the bi-[8]annulenylene anion radical. Surprisingly, the single electron exerts as much "flattening influence" on bi-[8]annulenylene as it does on [8]annulene (Scheme 1). The EPR spectra have proven both species to be planar ($Q = 25.6$ G).[9,10] The actual EPR-measured ($a_H = Q\rho$)[10] p_z spin densities (ρ values) are shown in Scheme 1 along with the B3LYP/6-31G*-predicted values in parentheses.

Scheme 2
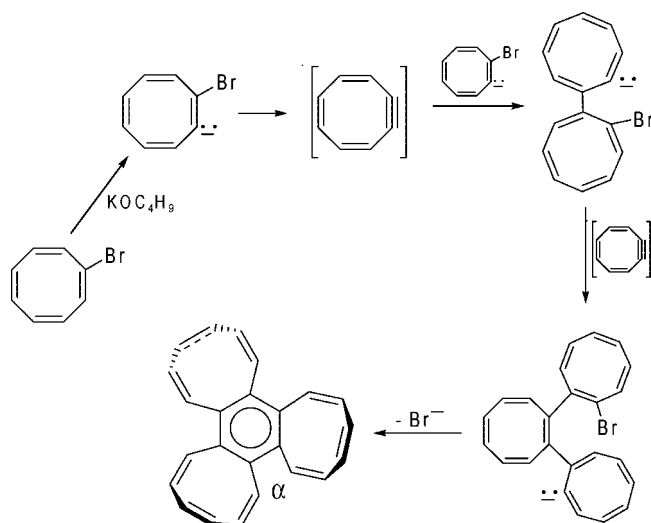
[6]Annulyne (from a bromobenzene source) is known to trimerize, leading to triphenylene. This is significant, because tri-[6]annulene has fascinated chemists since its discovery in 1867.[11] However, it has remained the only known triannulenylene for 140 years! To obtain a new triannulenylene, we built on the accepted mechanism for the formation of tri-[6]annulene and replaced all of the six-membered rings with eight-membered rings (Scheme 2). This suggested that, if the same protocol was employed as used for the formation of the bi-[8]annulene system but the alkoxide was added a bit more slowly, the anion radical of tri-[8]annulenylene ($C_{24}H_{18}$·⁻) might be revealed. This proved to be the case. Further, the triannulenylene lacks the cyclobutadienyl moiety in the center; therefore, it can be oxidized ($^1/_2I_2 + C_{24}H_{18}$·⁻ $\rightarrow C_{24}H_{18} + I^-$) to the neutral tri-[8]annulenylene, "the second triannulenylene" (Figure 2).[12]

Unlike the odd electron in the anion radical of bi-[8]-annulenylene, that in $C_{24}H_{18}$·⁻ is not delocalized over the entire molecule. The odd electron in ($C_{24}H_{18}$·⁻) resides predominantly in just one eight-membered ring.[12] Unlike the
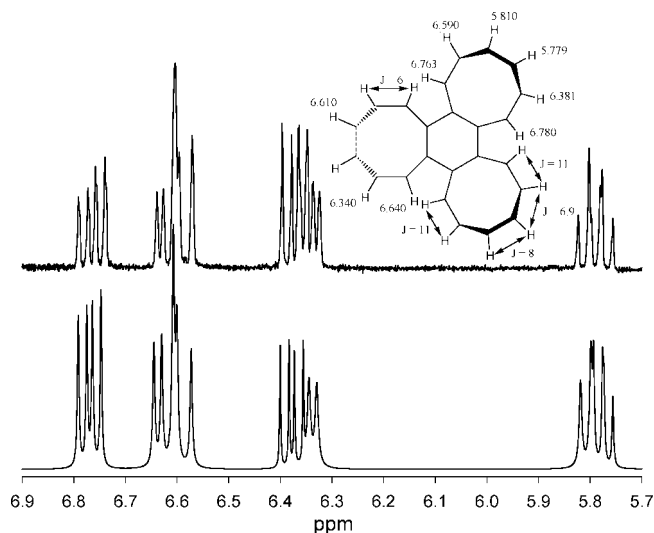

FIGURE 2. ¹H nuclear magnetic resonance (NMR) spectrum (400 MHz) of tri-[8]annulenylene. The simulation (bottom) was generated using the chemical shifts and the J couplings shown.
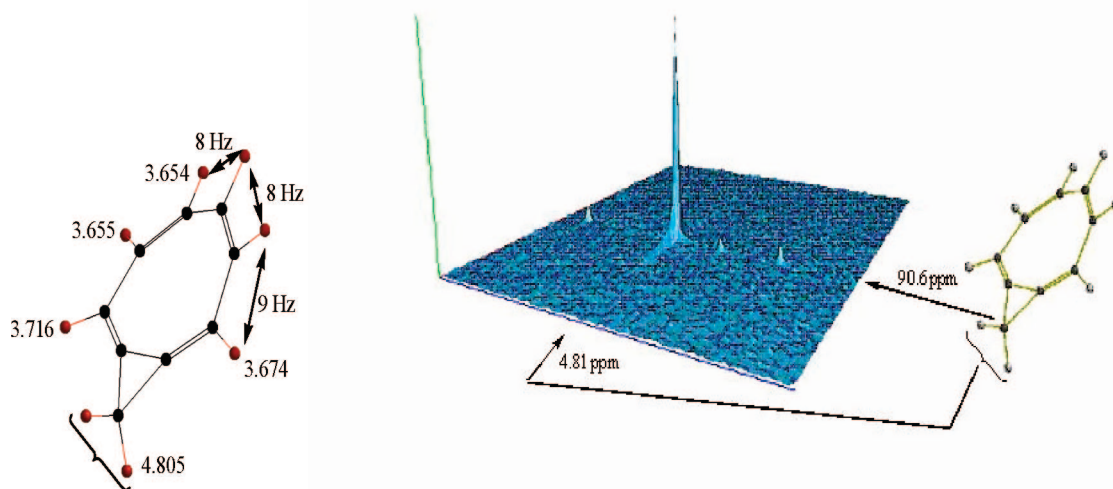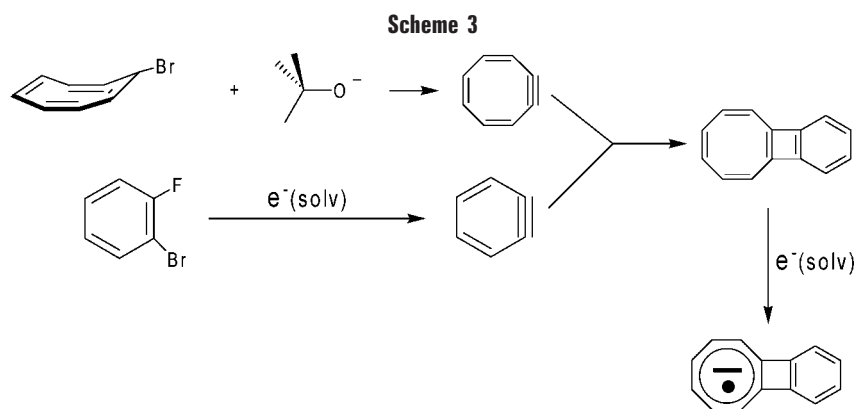
FIGURE 3. $^{13}C-^{1}H$ HETCORE of the sp³-hybridized carbon of ^{13}C-enriched cycloprop-[8]annulene and the ^{1}H NMR shifts and couplings with the DFT-predicted structure.

Scheme 3

planar fully conjugated anion radical of tri-[6]annulenylene, that of tri-[8]annulenylene has only one planar reduced ring, while the other two are puckered, one above and the other below the plane of the benzene moiety. The hopping of the odd electron from ring to ring is slow on the EPR time scale and represents a pseudorotation.[13] Complete analysis of the NMR spectrum of the neutral molecule[14,15] proves that all three rings are puckered, two above the plane of the benzene moiety and one below, so that the molecule has C_s symmetry, as depicted in the product of Scheme 2. Further, there is some steric interaction between the inside α protons on the two rings that are deflected in the same direction.
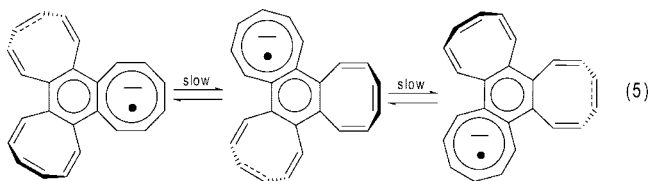

Spurred by our success with the observation of the second bi- and triannulenylenes, we went on to examine what other interesting annulyne–annulyne 2 + 2 cycloadditions could be realized. At room temperature, a mixture of Br-cyclooctatetraene (COT), *ortho*-bromofluorobenzene, and potassium *tert*-butoxide in HMPA yields an asymmetric annulenylene anion radical when exposed to

a potassium metal mirror (Scheme 3). The EPR spectrum reveals it to be that of [6]- and [8]annulenylene. As in the bi-[8]annulenylene system, the 25.6 G Q value and the measured spin densities reveal a planar fully conjugated anion radical. However, the odd electron, as expected, is primarily localized in the eight-membered ring.

The exposure of dichlorocyclobutene to the solvated electron in the presence of [8]annulyne presumably leads to the dewar benzeno-[8]annulene anion radical, which undergoes ring opening (analogous to that shown in reaction 1) to form [6]annuleno-[8]annulene (Scheme 4). The formation of benzocyclooctatetraene is not significant, but an analogous protocol could lead to a highly strained small ring system fused to [8]annulene with no possibility of ring opening.

Careful theoretical analysis had shown that the planar structure of [8]annulene is reasonable when the issue of strain is neglected. Indeed, the planar structure is preferred when the system is annelated with [2.1.1]hexeno moieties. Hence, annelation of [8]annulene with a strained cyclopropyl moiety might render the tub-shaped [8]annulene nearly planar and antiaromatic (paratropic).[16] Further, cycloprop-[6]annulene was the only existing member of the cyclopropannulene series. It has a strain energy greater than that of cylopropane and is very malodiferous (to the extent that extreme caution is war-

Scheme 4
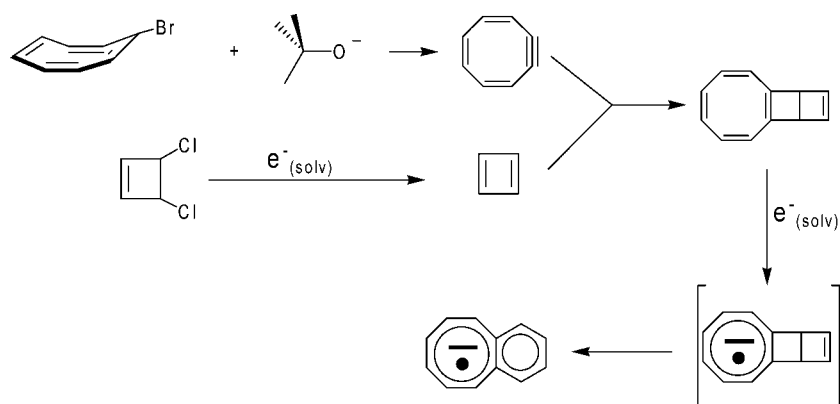
ranted), and it is the subject of a series of interesting reviews by Halton.[17] Would this dangerous odiferous nature extend to the next cyclopropannulene? The addition of carbene (:CH$_2$) to [8]annulyne (C$_8$H$_6$) should yield the desired annelated system, but :CH$_2$ is not at all selective toward triple over double bonds. A rather peculiar affinity of C$_8$H$_6^{\cdot-}$ for K$^+$ was noted that circumvented this selectivity problem.

Density functional theory (DFT) calculations predicted that the two alkynyl carbons in the highly strained $4n + 1$ π-electron annulyne (C$_8$H$_6^{\cdot-}$) are separated by a distance 1.23 Å. This distance is just right to bind a potassium cation (reaction 6), leading to a potassium organometallic complex (cyclooctatriene-η^2-ynyl potassium zwitterionic radical, C$_8$H$_6^{\cdot-}$K$^+$).[18] We were surprised to find that this very unusual overlap of the empty 4s orbital of the potassium cation with the p orbitals of the alkyne moiety is sufficiently strong to sequester K$^+$ from the grasp of 18-crown-6. An analogous affinity between C$_8$H$_6^{\cdot-}$ and Na$^+$ was not observed, because the ionic radius of Na$^+$ is only 0.95 Å, while that of K$^+$ is 1.33 Å.[19] Reaction 6, while interesting, in itself, proved valuable in our pursuit of cycloprop-[8]annulene.

$$(6)$$
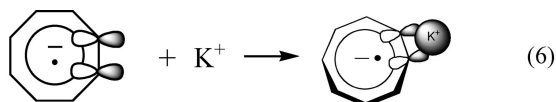
We have had some experience in the reaction of "chlorocarbene" and [8]annulene affording bicyclo[6,1,0]-nonatriene.[20] Hence, the reaction of "chlorocarbene", produced by the action of a strong base on methylene chloride,[21] with C$_8$H$_6^{\cdot-}$K$^+$ provided our cycloprop-[8]annulene, as anticipated. The K$^+$ ion appears to guide the attack of the CHCl$_2$ anion (prior to the loss of Cl$^-$ and the formation of "chlorocarbene") to the triple bond (Scheme 5).

The protons on the eight-membered ring of cycloprop-[6]annulene are shifted upfield by about 2 ppm, relative to those of [8]annulene,[22] to the 3.6–3.7 ppm region (see Figure 3), suggesting a paratropic ring current. Consistent with this, B3LYP/6-31G* calculations indicate that cycloprop-[8]annulene is much more planar than [8]annulene and that the structure with double bonds that are external (to the three-membered ring) is more stable than that with a cyclopropenyl moiety. Finally, the morphological and chemical

properties of cycloprop-[8]annulene leave it with the absence of the putrescence found in cycloprop-[6]annulene.[22]

The results with [8]annulyne suggested that the next $4n$ π-electron annulyne may also prove interesting. A synthetic approach to [12]annulyne could be envisioned because of the ready availability of an inexpensive possible precursor (the fire retardant: 1,2,5,6,9,10-hexabromocyclododecane, C$_{12}$H$_{18}$Br$_6$). The most striking difference that we anticipated, in this larger annulyne, was the probability of trans double bonds and, hence, internal protons.

Because C$_{12}$H$_{18}$Br$_6$ can be completely dehydrohalogenated to form [12]annulene (more about this later), we reasoned that C$_{12}$H$_{17}$Br$_7$ could be per-dehydrohalogenated to provide [12]annulyne. C$_{12}$H$_{18}$Br$_6$ was mono-dehydrohalogenated with 1 equiv of potassium *tert*-butoxide. The C$_{12}$H$_{17}$Br$_5$ product does not thermally incorporate Br$_2$ because of steric considerations. However, bromine does substitute allylically, in the presence of ultraviolet (UV) light, to afford the hexabromo-alkene, C$_{12}$H$_{16}$Br$_6$, with unknown placement of the double bond.[23]

The exact placement of the double bond relative to the bromines should not be an issue, if we just desire a [12]annulyne (C$_{12}$H$_{10}$), because this seems to be the only possible product from per-dehydrohalogenation (Scheme 6). When C$_{12}$H$_{16}$Br$_6$ was subjected to an excess of potassium *tert*-butoxide in THF containing 18-crown-6 at 173 K, per-dehydrohalogenation did take place. The hydrocarbon product could be trapped via one electron addition (exposure to a K metal mirror), and the EPR spectrum was recorded. The B3LYP/6-31G*-predicted spin densities (in parentheses below) for one of the anticipated [12]annulyne$^{\cdot-}$ structures agree extremely well with the empirical (EPR-measured) spin

**Scheme 5**

Scheme 6
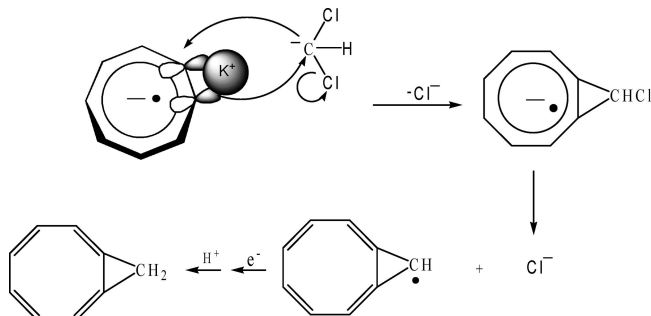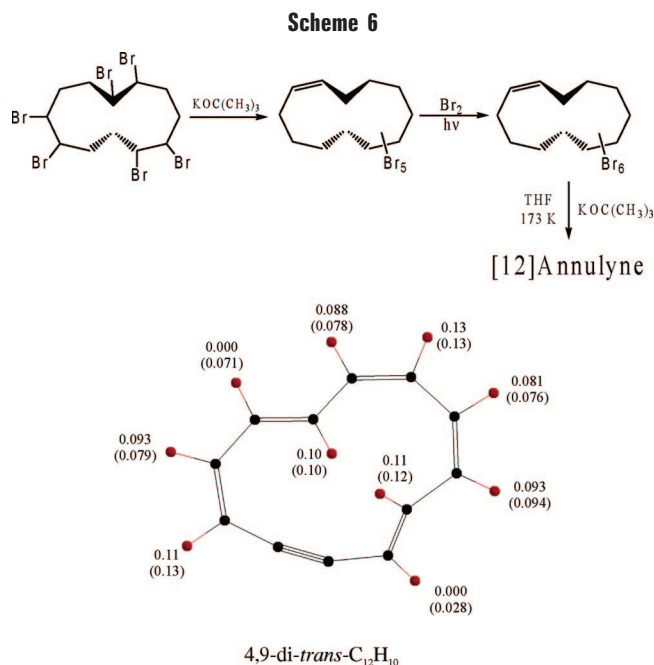
4,9-di-*trans*-$C_{12}H_{10}$

densities.[23] This left little doubt, in our minds, as to the presence of the 4,9-di-*trans*-[12]annulyne anion radical.

Prolonged exposure of the solution, containing 4,9-di-*trans*-$C_{12}H_{10}^{\cdot-}$, to a potassium mirror produces an EPR-silent solution that yields a very unusual ^{1}H NMR spectrum. At 298 K, the nonequivalent internal protons appear as a multiplet at δ −0.15 to −0.35 and a resonance for a single proton appears at δ +13.54.[23] This dianion can be observed for prolonged periods at this temperature. The anion radical also endures at 260 K. In the form of the dianion, the [12]annulyne "enjoys" some stability allowing for NMR observation at ambient temperature.

If the p_y orbitals of the 4,9-di-*trans*-cyclododecapentaene-η^2-ynyl potassium zwitterionic anion (4,9-di-*trans*-$C_{12}H_{10}^{2-}K^+$) and those of $C_8H_6^{\cdot-}K^+$ were interacting in an analogous fashion, perhaps one of the external protons adjacent to the cation could "feel" a sufficient positive charge (from the K^+) that, when acting synergistically with the diatropic ring current, a chemical shift of nearly δ 14 results (see the structure below). A lobe of the p_y orbital on carbon 1 overlapping with the back lobe of the σ bond to the hydrogen on carbon 12 could result from the forced nonlinearity of the alkyne moiety.


3,9-di-*trans*-$C_{12}H_{10}^{2-}K^+$
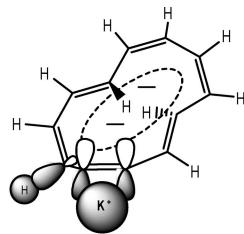
4,9-di-*trans*-cyclododecapenatene-η^2-ynyl potassium zwitterionic anion

Actually, while Matt Gard[23] and I were struggling with our attempts to unravel the NMR and EPR data resulting

from this per-dehydrohalogenation, Matt Kiesewetter,[23] while attempting to obtain octalene from [8]annulyne, found that commercially available 1,5-hexadiyne reacts with a suspension of potassium *tert*-butoxide in THF under vacuum to produce two isomers of our desired [12]annulyne. Under high-vacuum conditions, ^{1}H NMR spectra of this solution reveal only the presence of 4,11- and 5,10-di-*trans*-[12]annulyne. The proposed mechanism (Scheme 7) is based on that for the formation of [12]annuldiyne, which was proposed by Sondheimer some 20 years earlier.[24]

The isomers of [12]annulyne (shown below) do not spontaneously undergo the self-condensation observed with [6]- and [8]annulynes. Indeed, solutions of 4,11- and 5,10-di-*trans*-[12]annulyne have persisted for weeks without the observable formation of cycloaddition products. [12]Annulyne is the smallest of the annulynes for which different isomers are reasonable, and we have reported three of them.[23] However, two of them resulted unexpectedly from a simple one-pot reaction involving high vacuum, alkoxide, and 1,6-hexadiyne. This reaction proved to be even more bizarre when we realized that the simple addition of 18-crown-6 or HMPA to this mix turned the solution paramagnetic, yielding a strong well-resolved EPR signal. It comes from the anion radical of heptalene! In the absence of tight ion association, the dianion, shown in Scheme 7, proceeds to 1,7-di-*trans*-[12]annulene$^{\cdot-}$, which looses H_2.[25]

In principle, [12]annulyne can be partially hydrogenated to [12]annulene, but such hydrogenations at 173 K have eluded us. Sym-tri-*trans*-[12]annulene was, however, reported in 1970 by Oth and co-workers to be the product of the photochemical ring opening shown below. It was also shown to undergo photochemical and thermal ring closure to yield different isomers of [6.4.0]bicyclododecapentaene.[26a,b] We reproduced their synthesis and reduced the product to its corresponding anion radical (reaction 7). EPR analysis (EPR ρ values shown, B3LYP/6-31G*-predicted ρ values in parentheses) revealed a very narrow spectral width of less than 10 G, indicating an anion radical that is severely distorted from planarity.[26c] These three reports[26] did not convince everyone that an isomer of [12]annulene had indeed been created.[27] Consequently, we decided to use the per-dehydrohalogenation technique, to pursue new isomers of [12]annulene.


$$(7)$$
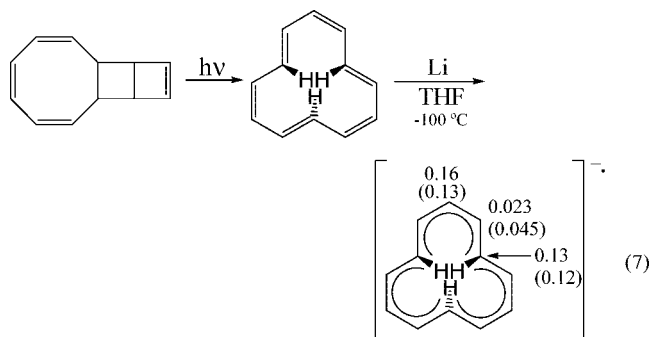
When a THF solution of $C_{12}H_{18}Br_6$ (containing 18-crown-6) was exposed to a large excess of potassium *tert*-butoxide at −100 °C, followed by contact of the solution with a freshly

Scheme 7
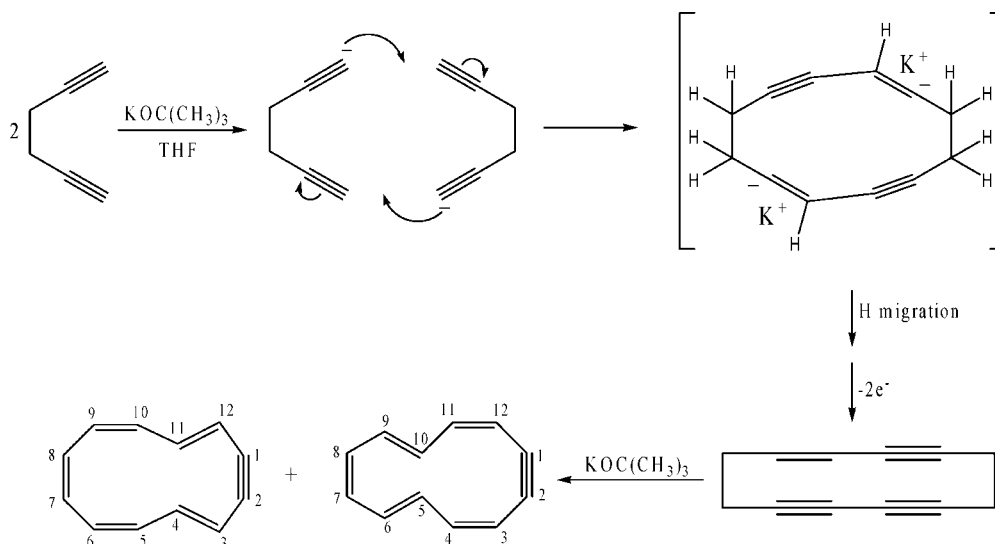
distilled potassium mirror, a dark purple solution resulted that yielded a well-resolved low-temperature EPR spectrum (Figure 4).[28] This spectrum reveals only proton splittings and, again, has an exceptionally narrow total spectral width, suggesting a nonplanar $C_{12}H_{12}$ ([12]annulene) anion radical. Warming the solution to ambient temperature causes the EPR pattern to change to a normal spectral width corresponding to a planar anion radical. Analysis of this new spectral pattern revealed that it comes from the anion radical of heptalene; therefore, reaction 8 must have occurred with the loss of molecular hydrogen.[28]

$$C_{12}H_{12}{}^{\bullet-} \longrightarrow \left[\vcenter{\hbox{(structure)}}\right]^{\bullet-} + H_2 \qquad (8)$$
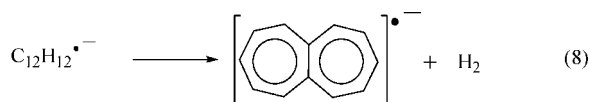
Consequently, it seemed reasonable that the appropriate isomer of the [12]annulene anion radical in reaction 8 is 1,5-di-*trans*-[12]annulene$^{\bullet-}$, depicted in Figure 2. Complete analysis of the rather complicated EPR spectrum was accomplished by my colleague, Dick Reiter.[28] EPR line-shape analysis revealed that one side of the 1,5-di-*trans*-$C_{12}H_{12}{}^{\bullet-}$ system is flat (containing most of the spin density) and the other is twisted. The system is involved in a dynamic pseudorotation equilibrium that interchanges these two sides (reaction 9). Most of the spin density and, of course, the larger coupling constants appear on the flatter side of the anion. B3LYP/6-31G* well reproduces this molecular morphology and spin distribution (as usual, DFT calculated ρ values are shown in parentheses below the empirical values).[28]

(9)
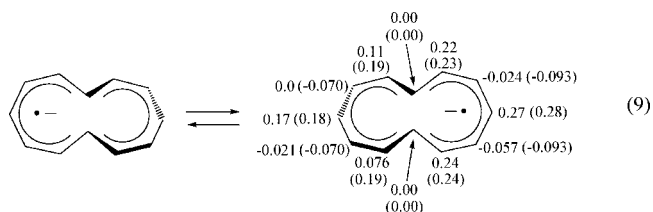
Shortly after our report,[28] Castro, Karney, and co-workers[29] published a nice rather complete theoretical

(DFT) analysis of the [12]annulene system. They concluded that their calculations leave almost no doubt that Oth and co-workers actually did synthesize sym-tri-*trans*-[12]annulene. They predict that 1,7-di-*trans*-[12]annulene is higher in energy than the sym-tri-*trans*-[12]annulene by about 1 kcal/mol, and the 1,5-di-*trans*-[12]annulene system is higher yet by about 4 kcal/mol. Our attempts to capture the anion radical of 1,5-di-*trans*-[12]annulene, via the per-dehydrohalogenation technique, have led only to anion-radical-containing solutions yielding EPR spectra with large total widths. The observed anion radical is consistent with that expected for the anion radical of *trans*-bicyclo[6,4,0]dodecapentaene (Scheme 8).[25]

The chemistry of [10]-, [12]-, and [14]annulene is dominated by strain and steric interactions involving the
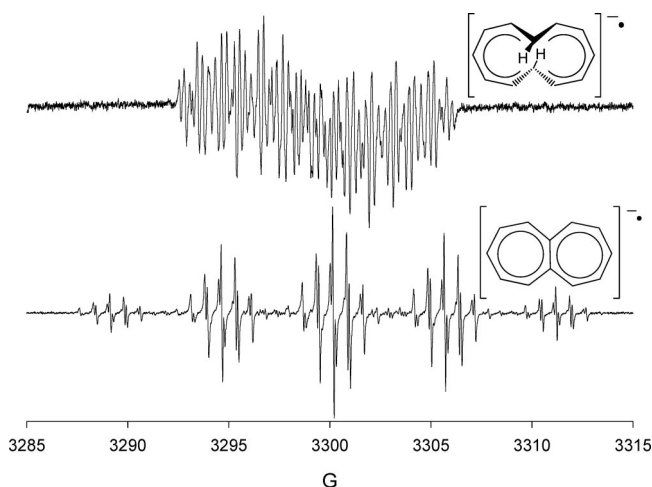

FIGURE 4. (Top) X-band EPR spectrum of di-*trans*-$C_{12}H_{12}{}^{\bullet-}$, recorded at 170 K, immediately after the potassium metal reduction of the potassium *tert*-butoxide dehydrohalogenation product of 1,2,5,6,9,10-hexabromocylododecane in THF containing 18-crown-6. (Bottom) EPR of the same solution after warming it to ambient temperature and recooling to 170 K. This spectrum is due to the anion radical of heptalene and is nicely simulated with a_H values of 5.52 G (4Hs), 0.69 G (4Hs), and 0.810 G (2 Hs). The peak–peak line width (Δw_{pp}) is 0.080 G.

Scheme 8
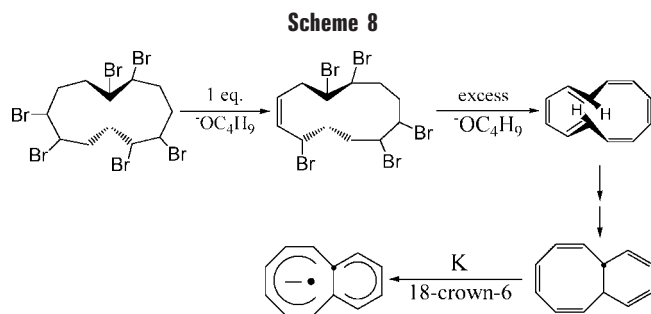
internal protons. It is these forces that induce the juxtapositions of the 1 and 7 carbons in 1,7-di-*trans*-$C_{12}H_{12}^{\cdot -}$, DFT-predicted to be 1.589 Å apart,[28] which leads to H_2 evolution.

The steric interactions involving the internal protons of the stable isomers of [16]- and [18]annulene are not so thermodynamically or kinetically important as to manifest themselves in chemical reactions or spectroscopic pa-

rameters. To gain some direct spectroscopic indication of the steric interactions of the internal protons of these larger annulenes, we prepared perdeuteriated samples of [16]- and [18]annulene. ^{1}H NMR data were collected on the $C_{16}D_{15}H$ and $C_{18}D_{17}H$ impurities in these samples, and their chemical shifts were compared to those of the perprotiated systems.[30]

We were aware that the C–D bond is just over 0.01 Å shorter than the C–H bond,[31] and we hoped that this very slight shortening of the C–H bond, induced by deuteriation, would be sufficient to cause an increase in the planarity of both [16]- and [18]annulene.[30] This, in turn, should increase the paratropicity of the former and the diatropicity of the latter. As can be seen in Figure 5, the internal protons of [16]annulene are shifted far downfield because of the paratropic ring current, and replacing all but one of the internal protons with deuterium shifts that internal proton further downfield
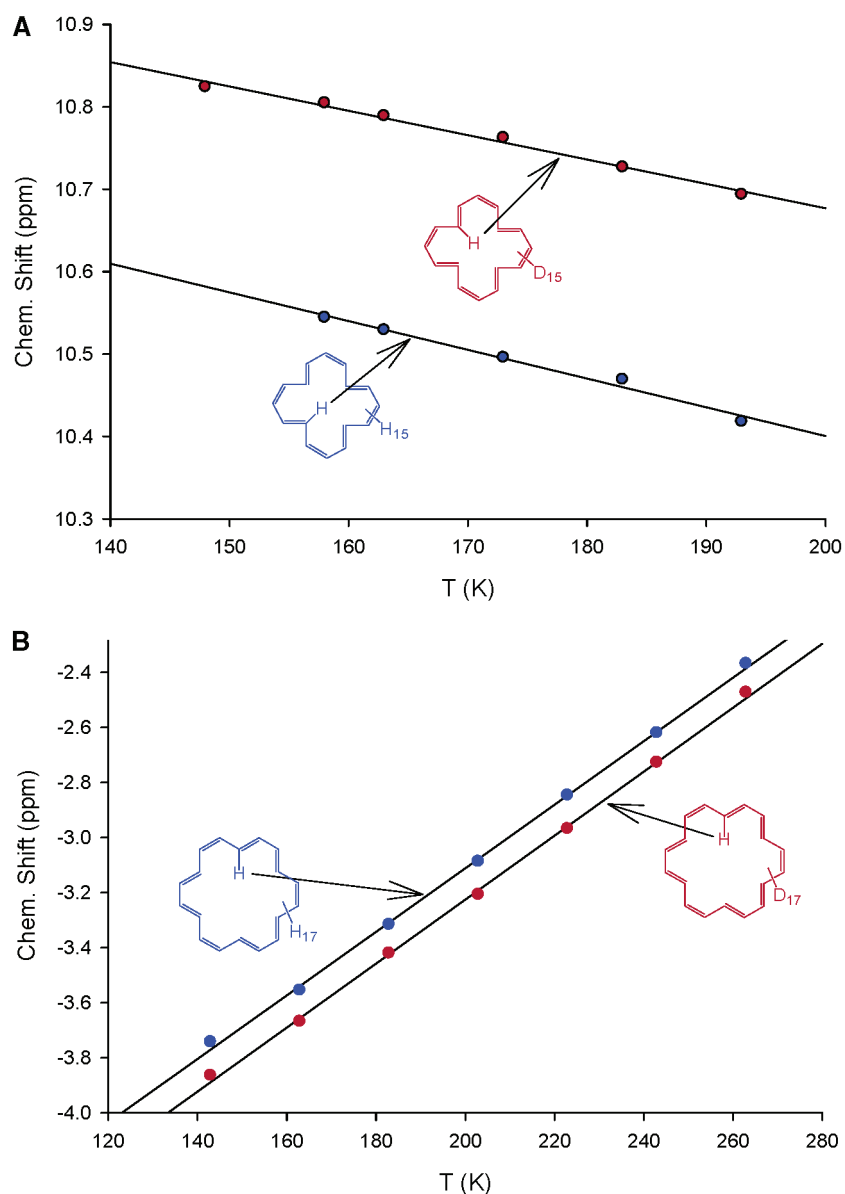

FIGURE 5. Plots of the 400 MHz ^{1}H-NMR-measured chemical shifts of the internal protons of mono- and perprotiated [16]- and [18]annulenes versus the temperature.

by more than $^2/_{10}$ of a ppm. An analogous effect is observed in the [18]annulene system, except that these internal protons are far upfield and are shifted further upfield, by more than $^1/_{10}$ of a ppm, by heptadeca-deuteration.[30b] Likewise, the internal protons of the dianion of [16]annulene are shifted upfield by 0.086 ppm upon pentadeca-deuteration.[30a]

Both annulenes reveal a linear dependence of the internal proton chemical shifts on temperature, reflecting the increasing paratropicity of [16]annulene and the increasing diatropicity of [18]annulene as the temperature is decreased. Extrapolation to absolute zero suggests zero-point chemical shifts of −5.42 and −5.55 ppm for $C_{18}H_{18}$ and $C_{18}D_{17}H$ and 11.11 and 11.27 ppm for $C_{16}H_{16}$ and $C_{16}D_{15}H$, respectively. Hence, on the basis of this empirical analysis, neither system is expected to be fully planar even at absolute zero.

The δ perturbations, because of deuteration, are much larger (and in the opposite direction for [18]annulene) than those expected from the normal zero-point energy effects. For example, the hepta-deuteration of [8]annulene results in a 0.010 ppm upfield shift of the ^1H resonance.[30a] The actual aromatic and antiaromatic characters of the neutral and dianionic systems are measurably increased, as detected by resonance frequency perturbations, via deuteration. On the other hand, perturbations in the EPR resonance frequencies of the anion radicals, produced via single-electron addition, could not be detected, even at high-field (in the W-band) EPR measurments.[30c] However, 20 years ago, we observed profound perturbations upon the thermodynamics of single- and double-electron addition because of deuteration.[32a]

These perturbations are represented by very large, secondary isotope effects on the equilibrium constant for electron transfer between the anion radical and the deuteriated neutral molecule.[32] For example, EPR measurements, at 173 K, of a mixture of [6]annulene and monodeuterio-[6]annulene reduced with a very deficient amount of K metal in THF allows for quantification of the ratio $[C_6H_5D^{\cdot-}]/[C_6H_6^{\cdot-}]$, which was found to be smaller than the ratio $[C_6H_5D]/[C_6H_6]$. Reduction was found to favor the formation of $C_6H_6^{\cdot-}$ over that of $C_6H_5D^{\cdot-}$, and $K_{eq} = 0.86$, at 173 K, for reaction 10, when the number of deuterium atoms (n) is 1. This corresponds to a 50 cal/mol smaller solution electron affinity (EA) for monodeuteriated benzene than for benzene. The solution EA was found to further decrease with each added deuterium (Figure 6). When $n = 6$, K_{eq} for reaction 10 is 0.26 at 173 K.

(10)
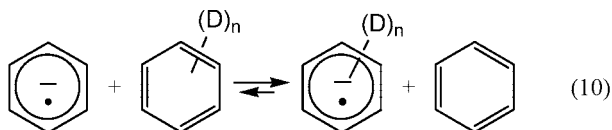
A very different result was found when a similar study was undertaken of the equilibrium isotope effect on the reduction of [8]annulene. At 173 K, the equilibrium constant for $C_8H_8^{\cdot-} + C_8D_8 \rightarrow C_8H_8 + C_8D_8^{\cdot-}$ was found
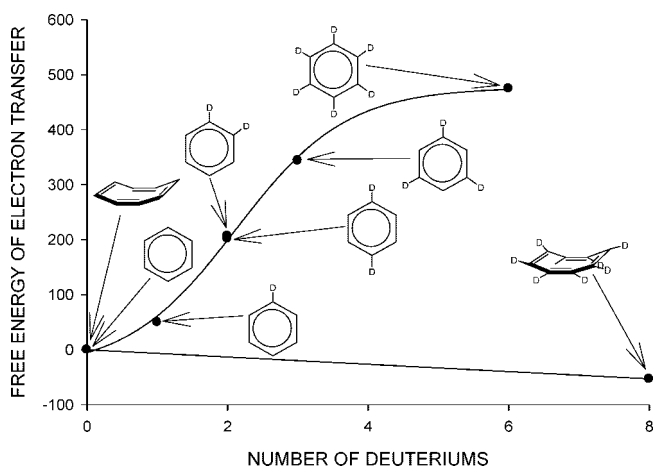
FIGURE 6. Plots of $\Delta G°$ of the electron transfer from [6]- or [8]annulene anion radical to the respective neutral molecule (indicated) versus the number of deuterium atoms (n) on the neutral system. $\Delta G°$ for reaction 10 versus n is fit to a sigmoidal curve, and $\Delta G°$ of $C_8H_8^{\cdot-} + C_8D_8 \rightarrow C_8H_8 + C_8D_8$ is represented by the lower line. It is opposite in sign and very small in magnitude ($\Delta G° = \Delta H° = -53$ cal/mol).

to 1.16. The very small, inverse equilibrium isotope effect found for the reduction of the C_8H_8/C_8D_8 system is in marked contrast to the large, normal, isotope effect found for the reduction of the C_6H_6/C_6D_6 system (see Figure 6). We explained this in terms of the divergence from the aromatic character that [6]annulene undergoes compared to the convergence toward aromaticity enjoyed by [8]annulene upon electron addition. It is clear that this was a bit of a "hand-waving" explanation of a controversial (at the time) measurement.

A chance meeting with Prof. Borden ultimately led to a collaborative project and the resolution of the apparent problem.[33] $C_8H_8^{\cdot-}$ has a planar, bond length alternating D_{4h} structure.[34] DFT calculations reveal that it is more facile to flatten C_8D_8 (than C_8H_8) into this D_{4h} configuration by about 500 cal/mol. The calculations confirm that the reduction of planar D_{4h} C_8H_8, such as that of planar benzene, has a substantial, normal equilibrium isotope effect. The inverse isotope effect observed in the reduction of [8]annulene results from a combination of the isotope effects for ring flattening and the electron transfer between the planar systems. These calculated predictions were subsequently verified, via dynamic ^1H NMR experiments, which reveal that ring inversion is faster for ring-d_7 isopropoxy-[8]annulene than it is for the perprotiated system.[35] The ring inversion has a D_{8h} planar transition state.

As pointed out over 37 years ago by Hoffman, orbital overlap, leading to conjugation, can take place through bonds or through space.[36] The annulenes represent the quintessential examples of the former, and spiro conjugation is the epitome of the latter. Our work regarding through-bond conjugation in the annulene systems is nearly over, but a new undergraduate student (Jordan Holloway) and I have developed a fascination with "spiro-conjugation"; for example, the $4n + 2$ π-electron fully conjugated *sym*-spiro[2.4]heptatriene[37] relates to benzene as *sym*-spiro[2.6]nonatetraene relates to [8]annulene.

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