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Article

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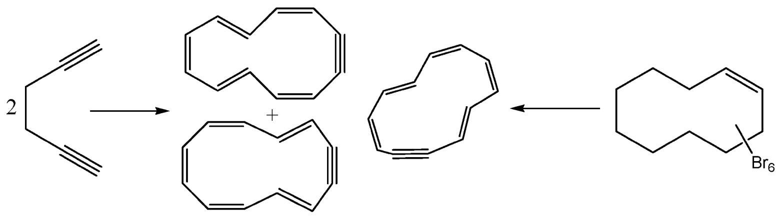

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[12]Annulynes

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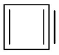
Abstract: Only one isomer of *o*-benzyne ([6]annulyne or 1,2-didehydrobenzene) exists, but the dehydro analogue of the "ring-opened double benzene", [12]annulyne, was generated in several isomeric forms. 1,5-Hexadiyne undergoes self-condensation in the presence of potassium *tert*-butoxide to yield two isomers of [12]annulyne (3,11-di-*trans*-[12]annulyne and 5,9-di-*trans*-[12]annulyne), both of which exhibit a weak paratropic ring current in their ^{1}H NMR spectra and are oxygen sensitive. They can be reduced to their respective dianions, which are diatropic. A third isomer (3,9-di-*trans*-[12]annulyne) was generated via the complete dehydrohalogenation of hexabromocyclododecene and found to be much less stable but can be tamed via one- or two-electron reduction. A tight association of the cation (K^+) with the p_y-orbitals within the alkyne moiety results in an unusually low-field resonance for an adjacent external proton.

Introduction

o-Benzyne is the quintessential, and most studied, member of the very reactive series of compounds known as the 1,2-didehydroannulenes or annulynes (see structures **1**−**4**). The extreme reactivity, coupled with the low thermodynamic stability of this $C_nH_{(n-2)}$ series, renders its members difficult to study.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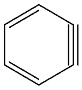
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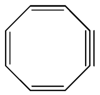
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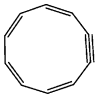
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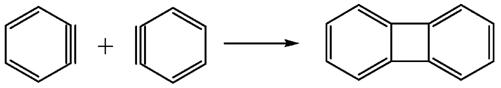
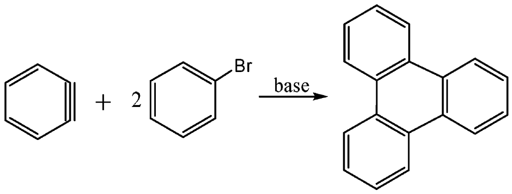
Well over 100 years ago, the first annulyne was undoubtedly produced as a reactive intermediate. The reaction simply involved the heating of bromobenzene and sodium amide with a Bunsen burner.[1] Although [6]annulyne or *o*-benzyne was surely the intermediate leading to the product (aniline), its structure was not proposed until 55 years later.[2] Neutral [6]annulyne was directly observed under cryogenic conditions (8 K) in 1973.[3] Since its proposed existence, [6]annulyne has been shown to be a versatile reaction intermediate that is involved in a host of noteworthy reactions.[4] Of particular note is its ability to react with itself to form its dimer (bi[6]annulenylene)[5] and with its precursor to form its trimer (tri[6]annulenylene), eqs 1 and 2.[6]

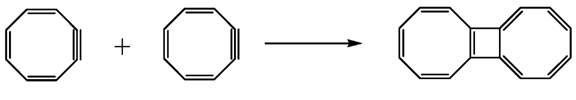


(1)



(2)

The special antiaromatic nature of the 4*n* π_z-electron systems, e.g. [4]annulyne, [8]annulyne, and [12]annulyne, renders them amiable to single electron entrapment. The added electron helps these systems escape from their antiaromatic π-electron count. The added electron is of minimal help in the case of [4]annulyne, which is racked by strain energy, and may even exist as a carbene.[7] Indeed, of the small neutral annulynes, **1**−**4**, only [6]-annulyne has been observed.[3] However, [8]annulyne, which also dimerizes and "trimerizes" in a manner that is analogous to that of [6]annulyne (eqs 3 and 4),[8] has been trapped as its corresponding anion radical and observed via EPR spectroscopy.[8,9]



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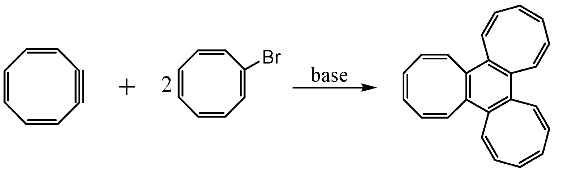

(4)

The next member of the annulynes ([12]annulyne) can be thought of as the dehydro analogue of the ring-expanded double benzene. It is, also, the first annulyne necessarily having internal protons. [12]Annulyne has, until now, escaped detection.

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(1) Haeussermann, C. *Ber. Dtsch. Chem. Ges.* **1899**, *32*, 1912.
(2) Huisgen, R.; Rist, H. *Naturwissenschaften* **1954**, *41*, 358.
(3) Chapman, O. L.; Mattes, K.; McIntosh, C. L.; Pacansky, J.; Calder, G. V.; Orr, G. *J. Am. Chem. Soc.* **1973**, *95*, 6134.
(4) For examples, see: (a) Heaney, H. *Chem. Rev.* **1962**, *62*, 81. (b) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047.
(5) Schafer, M. E.; Berry, R. S. *J. Am. Chem. Soc.* **1965**, *87*, 4497.
(6) Buess, C. M.; Lawson, D. D. *Chem. Rev.* **1960**, *60*, 313.

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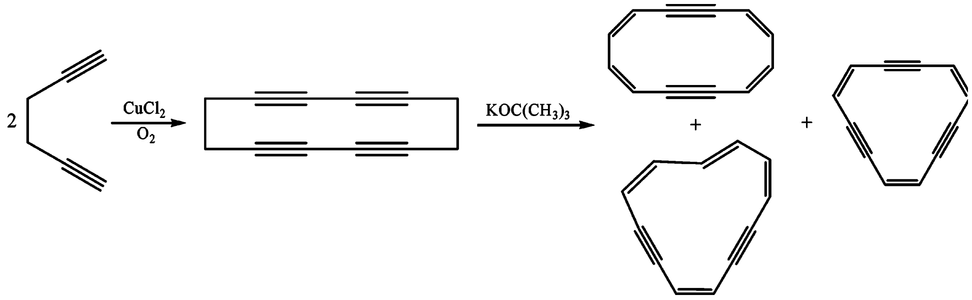
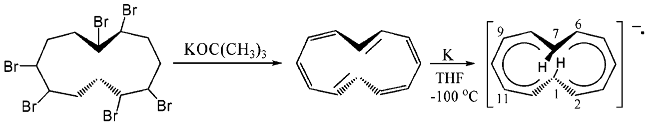
Scheme 1



Scheme 2



However, Sondheimer and Wolovsky[10a] were able to generate cyclododecatetraenediyne ([12]annuldiyne) via the oxidative dimerization of hexadiyne followed by treatment with potassium *tert*-butoxide (Scheme 1). Four years later, it was found that the action of *tert*-butoxide on the cyclododecatetrayne also yielded some cyclododecatrienetriyne (*sym*-[12]annultriyne) along with some mono-*trans*-[12]annuldiyne (Scheme 1).[10b]

We were motivated to generate [12]annulyne to gain insight as to its structure(s) and magnetic properties and to see if it undergoes self-condensations that are analogous to eqs 1−4. We anticipated that [12]annulyne, or at least reduced forms of [12]annulyne, would be available through a modification of our recently reported protocol for the synthesis of the [12]annulene anion radical (Scheme 2)[11] and/or through a modification of Sondheimer and Wolovsky's synthesis of [12]annuldiyne (Scheme 1). Both approaches met with some success, and the properties of the resulting $C_{12}H_{10}$ systems proved to be quite interesting.

Results and Discussion

[12]Annulyne from 1,5-Hexadiyne. Our very first attempts at the modification of Scheme 1 to synthesize a [12]annulyne were extremely simple and, quite surprisingly, led to the formation of two isomers of the desired product. When a sealed glass tube containing neat, commercially available 1,5-hexadiyne is ruptured in a suspension of potassium *tert*-butoxide in tetrahydrofuran (THF) under vacuum, an immediate reaction ensues that produces *tert*-butyl alcohol and two hydrocarbons (**5** and **6**), in a ratio of [**5**]/[**6**] = 1.1, as the only ^{1}H NMR observable products. Simply tilting the sealed apparatus to allow the resulting solution to pour into an attached NMR tube and subsequent flame sealing of the tube allows for NMR analysis of the two hydrocarbons.

The two simultaneously observed ^{1}H NMR spectra are each accounted for in terms of five pairs of proton spins, with chemical shifts of δ 5.167, 5.308, 5.642, 6.397, and 6.628 for hydrocarbon **6** and δ 5.259, 5.378, 5.463, 6.462, and 6.874 for **5**. Note that the proton resonances furthest downfield in both **5** and **6** are very close to the "traditional" aromatic region for benzenoid systems. The spectrum becomes better resolved after filtering, to remove the insoluble potassium salts, but both **5** and **6** are oxygen sensitive, extremely so in the presence of *tert*-butoxide, requiring any workup to be carried out under an inert atmosphere. Mass spectral analysis (parent peaks at m/z 154) suggests that **5** and **6** are $C_{12}H_{10}$ isomers, and COSY (Figure 1) assisted computer simulation of the spectrum (Figure 2) leaves no doubt as to the connectivity of the respective symmetrical spin systems.

The NMR data (Figures 1 and 2) require, on the ^{1}H NMR time scale, a symmetrical spin system. Empirically, a symmetrical spin system enforces an even number of internal protons, but structural limitations rule out any number but two internal protons. Structures with the internal protons on positions 9 and 6 or on 8 and 7 do not allow for the observed spin system (see Supporting Information), leaving possible only structures **5** and **6** (Scheme 3).

The relatively low-field resonances of the internal protons in both **5** and **6** indicate some paratropic ring current, more so in **5**. The B3LYP/6-31G* calculated geometries support the existence of the large H−C−C−H dihedral angles (see Figure 3) involving the proton pairs on positions 8 and 9 for both **5** and **6**, suggesting little or no coupling between these protons (as observed). Both **5** and **6** do have one $^3J_{\mathrm{H-H}}$ equal to 0. The special w-plan arrangements involving the protons on positions 10 and 8 (**5**) and those on 5 and 7 (**6**) suggest a measurable $^4J_{\mathrm{H-H}}$ in both isomers (as observed). The two products shown in Scheme 3, where the internal protons on carbons 5, 10 (**5**) and 4, 11 (**6**) are twisted above the ring systems, uniquely satisfy the chemical shifts and coupling patterns observed.

Details of the reaction mechanism leading to **5** and **6** are unclear, but we can arrive at a general mechanism based on Sondheimer's conjecture (Scheme 1).[10] Instead of Sondheimer's tetrayne intermediate that rearranges to two isomers of [12]-annuldiyne, a triyne intermediate rearranges to two isomers of [12]annulyne (Scheme 3). Certainly, the alkoxide removes a proton from two 1,5-hexadiynes, which condense to form a $C_{12}H_{10}$ dianion. Transannular hydrogen migration[12] and electron transfer would lead to a cyclododecenetriyne. In the presence of *tert*-butoxide, cyclododecatetrayne ($C_{12}H_8$) rearranges to [12]-annuldiyne ($C_{12}H_8$) (Scheme 1). Likewise, cyclododecenetriyne ($C_{12}H_{10}$) in the presence of *tert*-butoxide rearranges to [12]-annulyne ($C_{12}H_{10}$) (Scheme 3).

---

(7) Mabry J.; Johnson, R. P. *J. Am. Chem. Soc.* **2002**, *124*, 6497.

(8) (a) Peters, S. J.; Kiesewetter, M. K.; Turk, M. R.; Stevenson, C. D. *J. Am. Chem. Soc.* **2003**, *125*, 11264. (b) Kiesewetter, M. K.; Reiter, R. C.; Stevenson, C. D. *J. Am. Chem. Soc.* **2004**, *126*, 8884.

(9) Stevenson, C. D.; Colon, M.; Concepcion, J. G.; Block, A. *J. Am. Chem. Soc.* **1974**, *96*, 2283.

(10) (a) Sondheimer, F.; Wolovsky, R. *J. Am. Chem. Soc*. **1962**, *84*, 2844. (b) Sondheimer, F.; Wolovsky, R.; Garratt, P. J.; Calder, I. C. *J. Am. Chem. Soc.* **1966**, *88*, 2610.

(11) Gard, M. N.; Reiter, R. C.; Stevenson, C. D. *Org. Lett.* **2004**, *6*, 393.

(12) Verner, E. J.; Cohen, T. *J. Org. Chem.* **1992**, *57*, 1072.

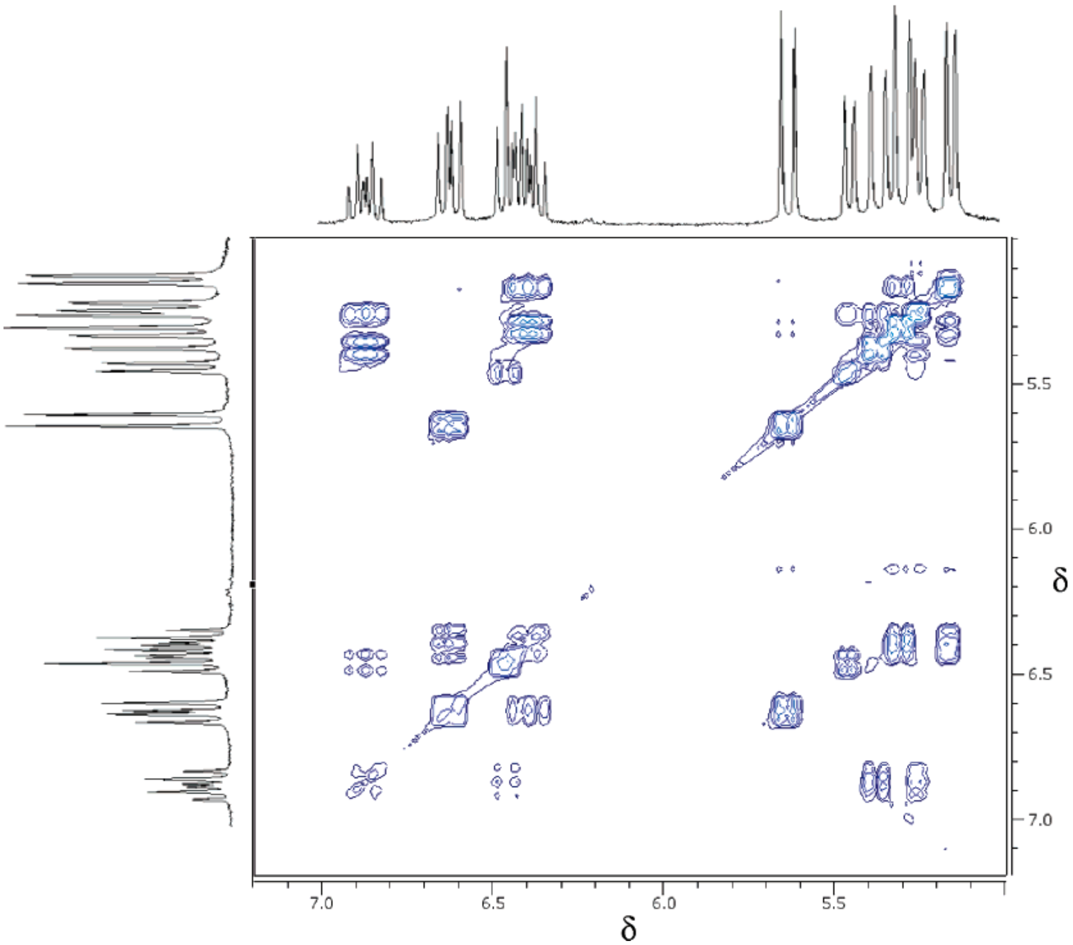
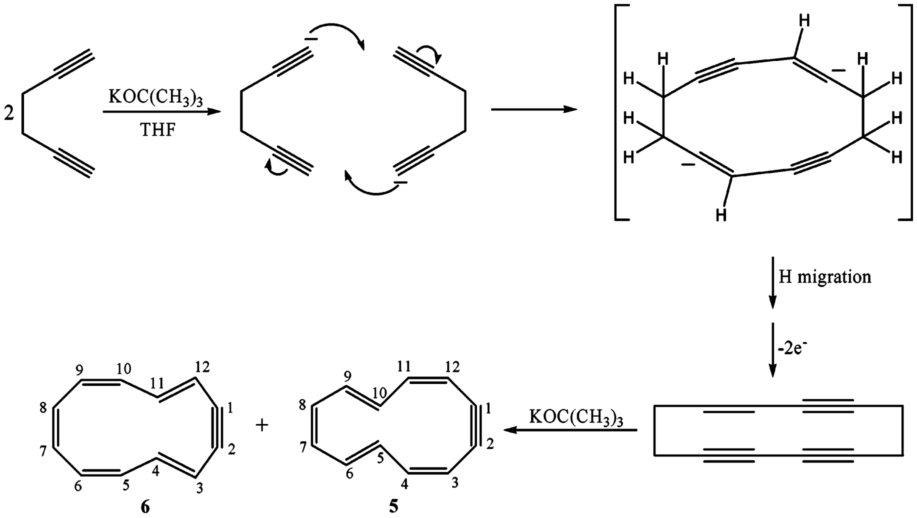


Figure 1. 400-MHz $^1H-^1H$ COSY spectrum of the hydrocarbons produced by mixing 1,5-hexadiyne with potassium *tert*-butoxide in THF-d_8.

Scheme 3



The ^{13}C NMR spectrum of isomers **5** and **6** reveals two resonances from the alkyne carbons (one for **5** and one for **6**) centered at δ 84.33 and 80.66. These are typical chemical shifts for alkyne carbons, as evident in Figure 4, where some 1,5-hexadiyne is also present. The resonances for each of the other five magnetically distinct carbons, for both isomers, are observed further downfield. The resonance for the internal carbons of one of the isomers is broadened to oblivion at room temperature, and it splits into two resonances separated by 0.33 ppm at −30 °C. BHandHLYP/6-31+G* calculations indicate that the two internal protons on **5** are too close in proximity to allow them to be equally distant from the plane of the ring. Hence, one lies slightly above the other. Interconversion of these hydrogens is fast enough on the ^1H NMR time scale to yield a single ^1H resonance, as in the case of [16]annulene.[13] It is, however, causing broadening on the ^{13}C NMR time scale.

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[13] Stevenson, C. D.; Kurth, T. L. *J. Am. Chem. Soc.* **1999**, *121*, 1623.

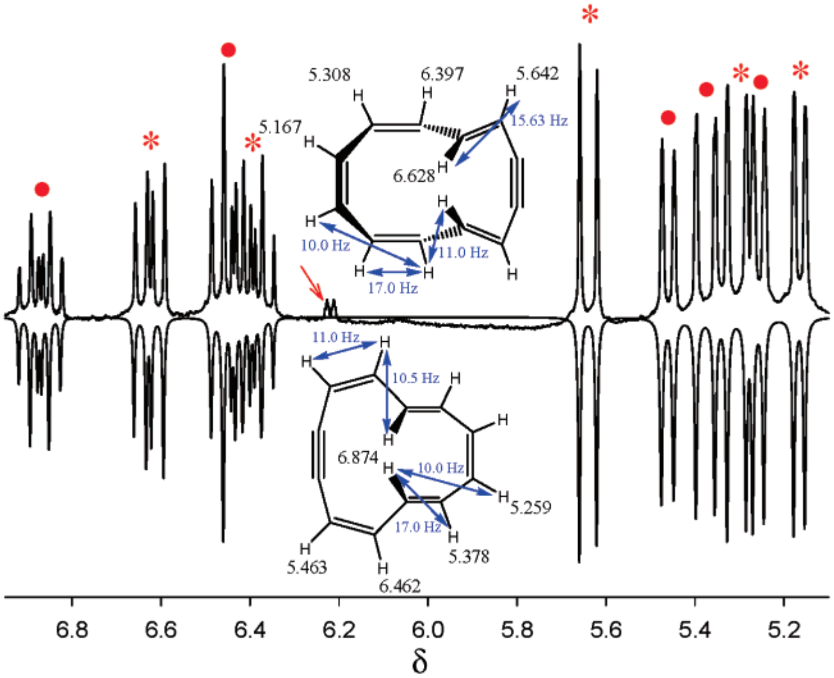

Figure 2. (Upper) 400-MHz ^{1}H NMR spectrum of the hydrocarbons produced by mixing 1,5-hexadiyne with potassium *tert*-butoxide in THF-d_8. The simulation (lower) was generated using the chemical shifts and the *J* couplings shown. The dots and stars indicate the multiplets due to **5** (lower structure) and **6**, respectively. The red arrow points to a small impurity resulting from brief exposure to oxygen during filtration of the sample.

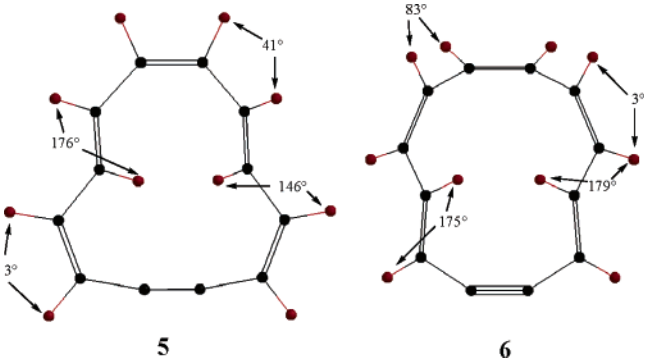

Figure 3. B3LYP/6-31G* (with imposed symmetry to show time-averaged geometry) calculated geometries of **5** and **6.** Some of the calculated H−C−C−H dihedral angles are indicated. The NMR data suggests that the 41° prediction in **5** might be a little small.

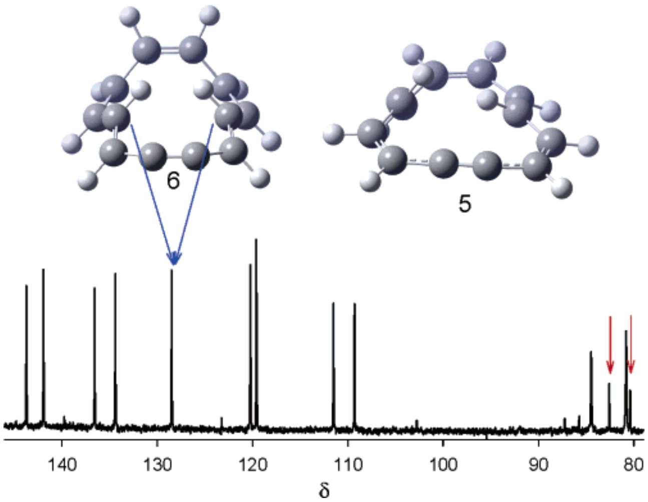

Figure 4. Ambient-temperature, 100-MHz ^{13}C NMR of a mixture of **5** and **6** produced by reacting 1,5-hexadiyne with potassium *tert*-butoxide in THF-d_8. The two signals marked with the vertical red arrows are due to the presence of residual hexadiyne and hexadiynide. The BHandHLYP calculated structures are shown above. Note that the internal carbons of **5** are not quite equivalent. They are interconverting on the ^{13}C NMR time scale to the extent that the resonances are broadened to oblivion.

Exposure of the THF solution (now containing 18-crown-6) of **5** and **6** to potassium metal leads to a strong but poorly resolved (broad) EPR spectrum, which, presumably, arises from $\mathbf{5}^{\bullet-}$ and $\mathbf{6}^{\bullet-}$. Continued exposure of the solution to the K metal leads to the formation of the dianions, which exhibit broad resonances for the internal protons at δ −2.683 and −1.804. These upfield resonance positions are well accounted for. They represent the internal protons shifted by diamagnetic ring currents acting synergistically with shielding from the added electrons in $\mathbf{5}^{2-}$ and $\mathbf{6}^{2-}$. The lowest field resonances are due to external protons and appear at δ 7.531 and 7.506. The remaining external proton resonances are obscured by the solvent, alkoxide, crown ether, etc. involved in the reaction. Nevertheless, the resonances on the high-field side of that for TMS and the resonances downfield of δ 7 make it clear that the dianions have been generated and that they possess diamagnetic ring currents ($4n + 2$ π_z-electrons, $n = 3$). For comparison, the internal protons in the dianion of tri-*trans*-[12]annulene, reported by Oth and co-workers,[14] appear at δ −1.34.

[12]Annulyne from Hexabromocyclododecene. Commercially available hexabromocyclododecane was treated with 1 equiv of potassium *tert*-butoxide in DMSO. The resulting pentabromocycloalkene was brominated in the allylic position by treating it with 1 mol of Br_2 under UV irradiation to give hexabromocyclododecene ($C_{12}H_{16}Br_6$), for which the tertiary geometry remains unclear (Scheme 4). Simple PM3 geometry optimizations of various $C_{12}H_{16}Br_6$ structures suggests that a

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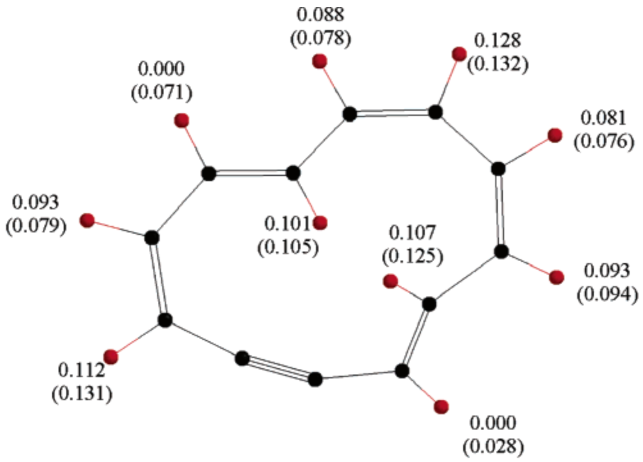
(14) Oth, J. F. M.; Röttele, H.; Schröder, G. *Tetrahedron Lett.* **1970**, 61.



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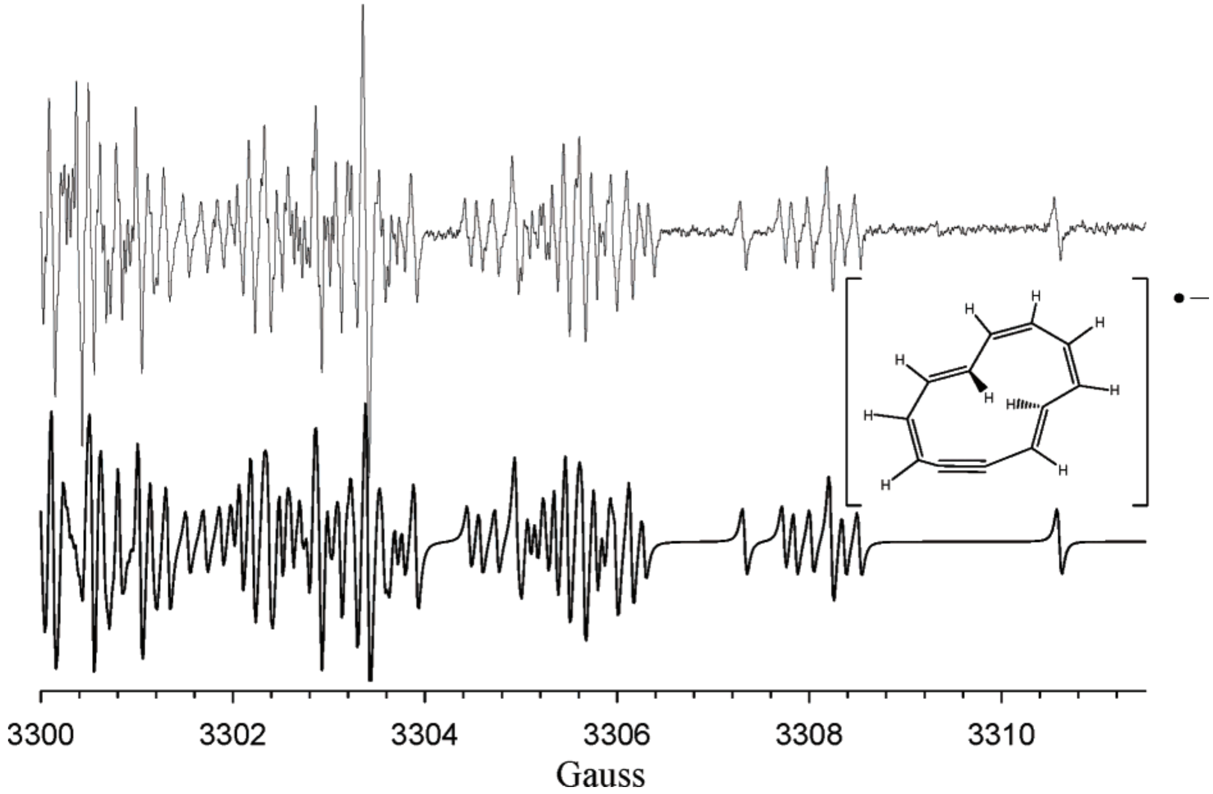
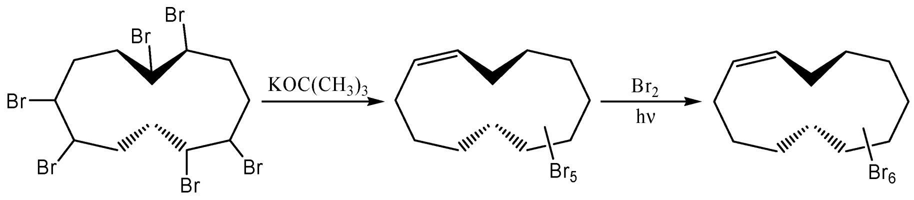


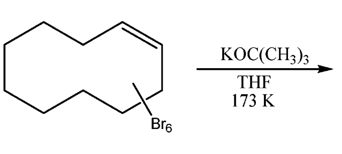
Figure 5. (Upper spectrum) High-field half of the X-band EPR spectrum of a THF solution containing the 3,9-di-*trans*-[12]annulyne anion radical (**7**) recorded at 260 K. (Lower spectrum) Computer-generated EPR spectrum using a_Hs of 3.276 G (1H), 2.866 G (1H), 2.748 G (1H), 2.58 G (1H), 2.374 G (2H), 2.242 G (1H), and 2.082 G (1H). The peak-to-peak line width is 0.05 G. The spin densities obtained from the a_Hs are in structure **7**.

Scheme 4



[12]annulyne that is less symmetric than either **5** or **6** will result from the complete dehydrohalogenation (eq 5).

In a sealed glass apparatus fitted with an EPR sample tube, a solution of our $C_{12}H_{16}Br_6$ in THF-d_8 containing an excess of 18-crown-6 was exposed to 20 equiv of potassium *tert*-butoxide at 173 K for 8 h. Due to the low concentration of desired product, and the plethora of "impurities" (*tert*-butyl alcohol, crown, THF-d_7, etc.), NMR analysis of this solution failed to clearly reveal a [12]annulyne. However, since a [12]annulyne is the only material in the sample capable of existing as its anion



(5)

radical after one-electron reduction, we hoped that EPR observation of the reduced solution would allow detection of the desired anion radical, the “tree in the forest.”

The dark solution resulting from the reaction described in eq 5 was exposed to a freshly distilled potassium metal mirror. A color change to deep purple was noted, the purple solution was submitted to EPR analysis, and a strong well-resolved EPR signal from a single anion radical was revealed. The signal can be nicely simulated with seven different coupling constants (Figure 5), mandating an asymmetrical structure. B3LYP/6-31G* calculations were used to find the spin densities for plausible [12]annulyne geometrical isomers.

Carbon p_z spin densities (ρ) have been very accurately predicted using B3LYP/6-31G* geometry optimization calculations for a host of analogous anion radicals.[8,15b] We were only able to find one structure (**7**) whose calculated and empirical spin densities are in agreement. Since the ρ values are directly proportional to EPR coupling constants ($a_H = Q\rho$),[8,15] we generated purely theoretical (DFT calculated) ρ values. Using a $Q = 25.6$ G, the Q value for [8]annulyne,[8] the experimental p_z spin densities were determined and are compared to the DFT calculated values (in parentheses) in structure **7**. The agreement between the empirical and theoretical ρ values indicates that **7** represents the correct structure of this [12]annulyne anion radical. However, the structure of the 5,9-di-trans isomer with internal protons at the 5 and 9 positions also is in reasonable agreement with experimental data.

Prolonged exposure of the solution, yielding the EPR spectrum shown in Figure 5, to the potassium mirror produces a diamagnetic solution that, upon NMR analysis, yields a very unusual spectrum. At 298 K, the internal protons appear as a multiplet (they are not equivalent) at δ -0.15 to -0.35, and a resonance for a single proton appears at δ $+13.54$ (Figure 6). This dianion can be observed for prolonged periods at this temperature. The anion radical also endures at 260 K. However, if the reaction mixture producing the neutral [12]annulyne is allowed to warm above ca. 200 K, this strained isomer is lost to decomposition. Electron addition provides stability and an escape from the $4n$ π_z-electron count. Upon the addition of I_2, the dianion and anion radical are irreversibly lost due to electron transfer and formation of iodide, as expected.

The very low-field resonance must be due to external protons in a strong diamagnetic ring current, but its position is much further downfield than those of any analogous hydrocarbon.[16] This extreme downfield shift is unprecedented in annulene dianion chemistry.[16] By way of a possible explanation, we remember that the anion radical of [8]annulyne ($C_8H_6^{\bullet-}$) features a very unusual overlap of the empty 4s orbital of the potassium cation with the p_y-orbitals of the alkyne moiety (structure **8**).[4a]

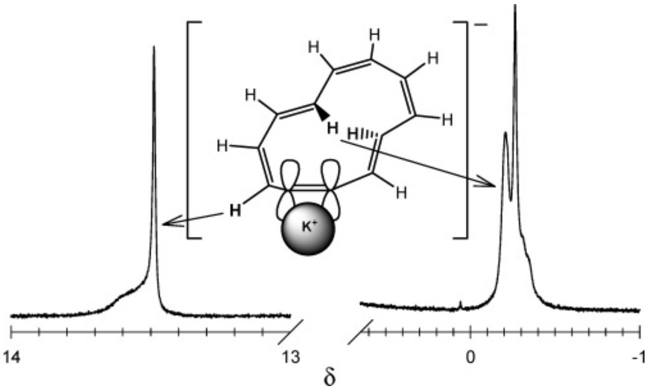
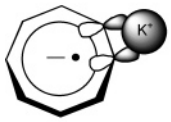


Figure 6. Low-field and high-field portions of the ^{1}H NMR spectrum of the potassium dianion salt of 3,9-di-*trans*-[12]annulyne in THF-d_8 at 298 K. The “up” and “down” internal protons can be interchanged. This spectrum disappears upon the addition of I_2 ($\pi^{2-} + I_2 \rightarrow \pi + 2I^-$).



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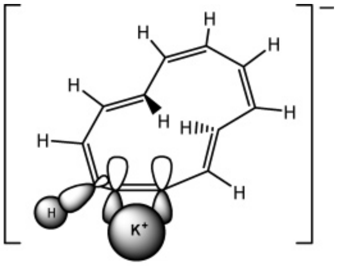

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If the dianion of the 3,9-di-*trans*-[12]annulyne were involved in a similar interaction with the potassium cation (structure **9**), perhaps one of the external protons adjacent to the cation could “feel” sufficient positive charge (from the K^+) that, when acting synergistically with the diatropicity, a chemical shift of nearly δ 14 results. Indeed, due to the nonlinearity of the alkyne moiety, a lobe of the p_y orbital on carbon 1 may overlap with the back lobe of the σ bond to the hydrogen on carbon 12 (see structure **9**). Such interactions have previously been proposed to significantly perturb spin and charge densities.[17] The dianions of neither **5** nor **6** exhibit such a phenomenon, but they do not have as much strain in their respective alkyne units.

Conclusions

Three geometric isomers of the fugitive [12]annulyne have been formed. Two were formed via a base-assisted self-condensation of 1,5-hexadiyne. They are relatively strain free and persist at ambient temperature. They are completely delineated via ^{1}H and ^{13}C NMR spectroscopy and exhibit a weak paratropic ring current. They are assigned as 5,9-di-*trans*-[12]-annulyne (**5**) and 3,11-di-*trans*-[12]annulyne (**6**). These two [12]-annulynes lack the destabilizing steric interaction caused by the internal protons that are present in both 1,5,9-tri-*trans*-[12]-annulene[14,18] and 1,7-di-*trans*-[12]annulene systems.[11] Both of these [12]annulynes can be reduced to their respective dianions that, in turn, exhibit diamagnetic ring currents.

3,9-Di-*trans*-[12]annulyne results from the dehydrohalogenation of hexabromocyclododecene. We were able to observe the dianion (NMR) and anion radical (EPR) of this isomer. The dianion exhibits a very unusual low-field resonance for one of

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(15) (a) Weil, J. A.; Bolton, J. R.; Wertz, J. E. *Electron Paramagnetic Resonance*; John Wiley and Sons: New York, 1994; p 241. (b) Stevenson, C. D.; Kim, Y. S. *J. Am. Chem. Soc.* **2000**, *122*, 3211.

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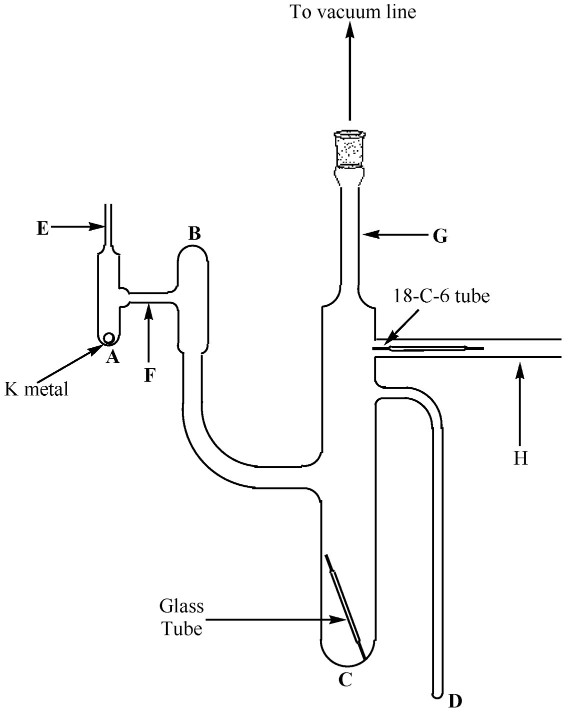

Figure 7. Apparatus used for the generation of the [12]annulyne anion radicals. Tube D can be either an EPR or NMR sample tube.

the external protons. This is attributed to a strong interaction between the potassium cation and the p_y-orbitals of the alkyne dianion acting synergistically with the diamagnetic ring current. The anion radical exhibits spin densities that agree very well with those calculated by the B3LYP/6-31G* protocol. This anion radical (**7**) as well as the two neutral [12]annulyne systems (**5** and **6**), formed via the condensation of 1,5-hexadiyne, do not necessarily represent the isomers at the global energy minima. The morphologies of **5**−**7** do, however, represent the reaction products and uniquely fit the empirical data.

Although only two of the three neutral isomers, observed herein, were produced in appreciable amounts, [12]annulyne appears to lack the propensity for self-condensation observed with the other annulynes. Solutions of neutral **5** and **6** have persisted for weeks without the observable formation of cycloaddition products (cf. eqs 1−4). Other than [10]annulyne, whose existence is purely theoretical,[19] [12]annulyne represents the smallest of the annulynes for which different isomers are reasonable, and we have found three of them.

Experimental Section

Formation of [12]Annulyne from 1,5-Hexadiyne. A glass tube was charged with 0.15 mmol of neat 1,5-hexadiyne and sealed (with fragile ends). This tube, in addition to 0.23 mmol of potassium *tert*-butoxide, was placed into bulb C of the Pyrex glass apparatus shown in Figure 7. A second glass tube was charged with 0.60 mmol of 18-crown-6, sealed with fragile ends, and placed in the sidearm as indicated; the sidearm was sealed at point H. A small amount of potassium metal was placed into bulb A, which was then sealed at point E. The entire apparatus was evacuated, and the potassium metal was sublimed into bulb B to form a potassium mirror. Bulb A was then sealed from the apparatus at point F. THF (~4 mL) was distilled from a separate flask, containing sodium−potassium eutectic, directly into bulb C, and the evacuated apparatus was subsequently sealed from the vacuum line at point G. After the apparatus was cooled to 0 °C and shaken gently to suspend the *tert*-butoxide in the solvent, it was vigorously agitated to break the glass tube containing the hexadiyne followed by (after a couple of minutes) the tube containing the 18-crown-6. The apparatus was then quickly rotated so the solution could come into contact with the K metal mirror.

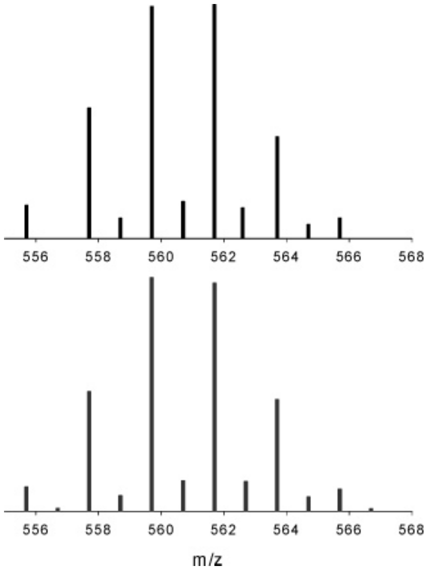

Figure 8. (Upper) Field desorption mass spectrum of pentabromocyclododecene. (Lower) The theoretical isotopic distribution pattern for $C_{12}H_{17}Br_5$.

The EPR spectrum was immediately recorded by placing the 3-mm tube D into the X-band EPR cavity. The apparatus could be removed from the EPR, the solution exposed to more metal, and the spectrum recorded again. This process was continued until the best signal-to-noise ratio for the [12]annulyne anion radicals was obtained. To generate the dianions, the contact time of the THF solution with the K mirror was increased until a deep blue color persisted, and the solution became EPR silent.

To collect NMR spectra of the neutral molecules, an apparatus absent tube B and the 18-crown-6 sidearm was employed, and the experiment was set up with minor modifications: no crown ether or K metal was used and THF-d_8 (~3 mL) served as the solvent system. No immediate color change was apparent when the hexadiyne was exposed to the base, but an insoluble suspension eventually formed (after several minutes). The NMR tube D was sealed from the apparatus. The NMR tube containing the clear and very light yellow [12]annulyne solution was placed into the probe of a 400 MHz ^1H NMR spectrometer, and ^{13}C and ^1H NMR spectra were recorded.

Synthesis of Hexabromocyclododecene. A round-bottom flask, purged with argon, was charged with 3.14 mmol of hexabromocyclododecane. An addition funnel was charged with 3.57 mmol of potassium *tert*-butoxide in approximately 45 mL of dry DMSO. The *tert*-butoxide solution, slightly pink in color, indicating the presence of dimsyl anion, was added dropwise over 40 min, and the resulting solution was stirred for 3 h and turned yellow. The reaction was quenched with approximately 150 mL of 1% acetic acid in water at 0 °C. An ether extraction was performed, residual DMSO removed, and the ether was removed under reduced pressure to yield a brown powder.

The brown powder was washed with cold ether to separate product from starting material. The solvent was stripped, resulting in a brown oil, which was then separated via silica gel column chromatography using a 2% ethyl acetate solution in pentane. A yellow band was collected, which proved to be the pentabromocyclododecene. Due to steric crowding about the double bond, the pentabromocyclododecene, which exhibits ^1H NMR olefinic resonances between δ 5.6−6.1, does not

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[19] Nevaro-Vazques, A.; Schreiner, P. R. *J. Am. Chem. Soc*. **2005**, *127*, 8150.

readily take up Br_2. The mass spectral isotopic distribution pattern is essentially identical to the theoretical pattern for $C_{12}H_{17}Br_5$ (Figure 8).

In 100 mL of deoxygenated carbon tetrachloride, 0.196 mmol of our pentabromocyclododecene was added to an argon-purged 250-mL three-neck round-bottom equipped with a long-wave UV pencil. An addition funnel was charged with 0.195 mmol of bromine (10 μL) in 30 mL of CCl_4. The apparatus was wrapped in aluminum foil, and the UV pencil was turned on while the bromine solution was added in small aliquots over 1 h. The solution was stirred, while being irradiated, for 2 h more. The bright orange solution was quenched with water and sodium thiosulfate at 0 °C. The organic layer was dried with magnesium sulfate, and the CCl_4 was removed under reduced pressure. The resulting green oil was purified via column chromatography using a silica gel column and a 10% ethyl acetate solution in pentane. A single green band was collected and submitted to a second chromatographic separation (silica gel column and a 2% ethyl acetate solution in pentane). Three yellowish green bands were collected, the first of which proved to be hexabromocyclododecene. ^{1}H NMR reveals a complex multiplet for the olifinic peaks between δ 5.7 and 6.3.

Formation of [12]Annulyne from Hexabromocyclododecene. In a typical reaction, bulb C of the apparatus shown in Figure 5 was charged with 0.100 mmol of potassium *tert*-butoxide, 0.277 mmol of 18-crown-6, and a glass tube containing 0.00527 mmol of $C_{12}H_{16}Br_6$ (note: here, the sidearm is not used). A small amount of potassium metal was placed into bulb A, which was then sealed at point E. The entire apparatus was evacuated, and while bulb C was cooled in liquid nitrogen, the potassium metal was sublimed into bulb B to form a potassium mirror. Bulb A was then sealed from the apparatus at point F. THF (∼4 mL) was distilled from a separate flask, containing sodium−potassium amalgam, directly into bulb C (cooled with acetone slush), and the evacuated apparatus was subsequently sealed from the vacuum line at point G. The apparatus was cooled in acetone slush (173 K) and agitated to expose the $C_{12}H_{16}Br_6$ to the base and start the reaction. The reaction was allowed to proceed at 173 K for 8 h.

The reduction and magnetic resonance observation methods were identical to those described above.

Acknowledgment. We thank the National Science Foundation and the donors of the American Chemical Society Petroleum Research Fund.

Supporting Information Available: Calculated atomic coordinates for various isomers of [12]annulyne, EPR data, NMR data, and calculated spin densities for several isomers of the [12]annulyne anion radical. This material is available free of charge via the Internet at http://pubs.acs.org.

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