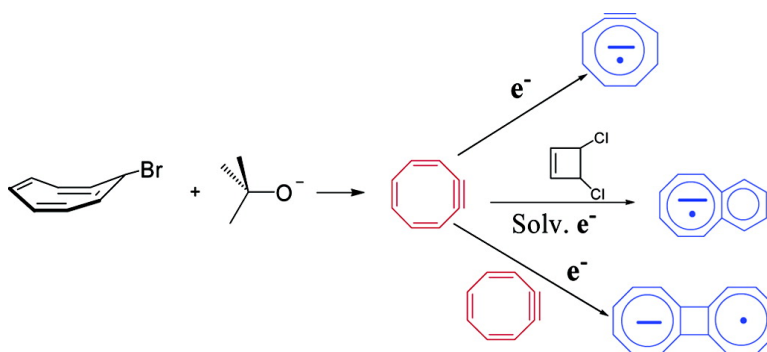


## Single-Electron Entrapment of [8]Annulyne, Biannulenylenes, and an Annulenoannulene

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## Single-Electron Entrapment of [8]Annulyne, Biannulenylenes, and an Annulenoannulene

Steven J. Peters,<sup>†</sup> Matthew R. Turk, Matthew K. Kiesewetter, and Cheryl D. Stevenson\*<sup>‡</sup>

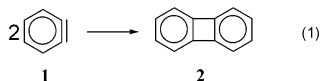
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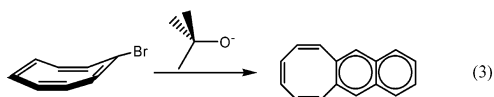
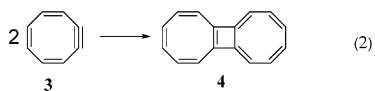
**Abstract:** The low-temperature (−100 °C) dehydrohalogenation of bromocyclooctatetraene followed by immediate electron-transfer yields a stable solution of the [8]annulyne anion radical. If the unstable [8]annulyne is reacted with itself, cyclobutadiene, or benzyne, the respective bi-[8]annulenylene, [6]annuleno[8]annulene, or [6]-[8]annulenylene can be trapped as their anion radicals via one-electron transfer. These condensation products were all obtained from simple [2 + 2] cycloaddition reactions. B3LYP/6-31G\* geometry optimizations were carried out, and the calculated spin densities were compared to the EPR spectral results obtained for the anion radicals of [6]annuleno[8]annulene, [8]annulyne, bi[8]annulenylene, and [6]-[8]annulenylene, and excellent agreement has been realized. This simple “one-pot” approach should be applicable to a wide range of such systems.

### Introduction

[6]Annulyne (*o*-benzyne, **1**) represents the only commonly used annulyne. It is used as a reactive intermediate for the synthesis of a variety of materials, and when left to react with itself, undergoes a [2 + 2] cycloaddition to produce biphenylene (**2**), reaction 1.<sup>1</sup>

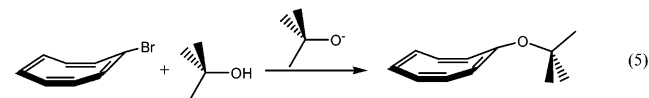
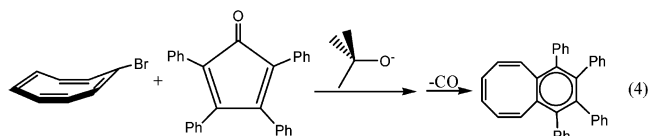


In terms of size, the next annulyne is [8]annulyne (cyclooctatrienyne, **3**), which (by analogy to reaction 1) should dimerize to bi[8]annulenylene (**4**), reaction 2. It is thought that **3** is actually the reactive intermediate following the dehydrohalogenation of bromocyclooctatetraene (Br-COT) which leads to naphthocyclooctatetraene, reaction 3.<sup>2</sup>



Furthermore, **3** is believed to be the intermediate in several condensation reactions where Br-COT is treated with potassium

*tert*-butoxide in the presence of a reactive substrate like tetraphenylcyclopentadienone (reaction 4) or *tert*-butyl alcohol (reaction 5).<sup>2</sup>



Over 20 years ago, Haug and Sondheimer reasoned that the introduction of the triple bond into COT would cause a splitting of the degenerate MOs of COT and result in “a fully conjugated eight-membered carbocycle.”<sup>3a</sup> This prediction proved to be prophetic. Wenthold and Lineberger reacted O<sup>−</sup> ions with COT in a liquid nitrogen-cooled flowing afterglow apparatus to yield the [8]annulyne anion radical.<sup>4a</sup> Considerable insight into the nature of the [8]annulyne system was obtained via photoelectron spectroscopy (PES). Their experimental studies coupled with density functional theory showed that [8]annulyne is indeed planar or pseudoplanar, and it has an electron affinity of +24 kcal/mol.<sup>4</sup>

We have carried out the dehydrohalogenation of Br-COT under conditions where fast one electron-transfer traps **3** and **4**

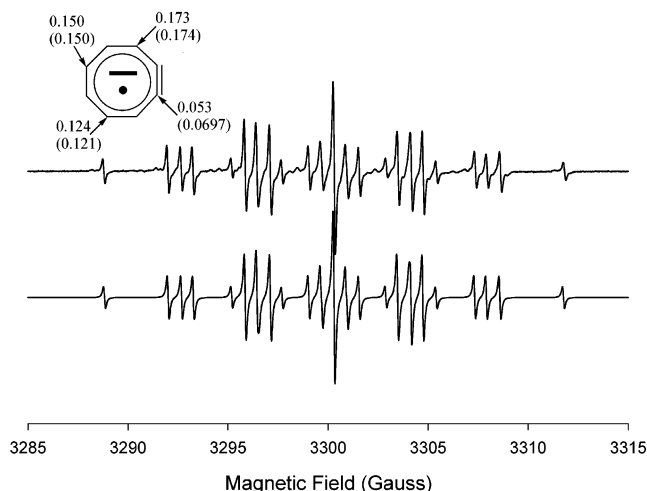
- (3) (a) Haug, N. Z.; Sondheimer, F. *Acc. Chem. Res.* **1982**, *15*, 96. (b) The [8]annulyne anion radical was observed as a tight ion pair, see: Stevenson, C. D.; Colon, M.; Concepcion, J. G.; Block, A. *J. Am. Chem. Soc.* **1974**, *96*, 2283.
- (4) (a) Wenthold, P. G.; Lineberger, W. C. *J. Am. Chem. Soc.* **1997**, *119*, 7772. (b) Kato, S.; Lee, H. S.; Gareyev, R.; Wenthold, P. G.; Lineberger, W. C.; DePuy, C. H.; Bierbaum, V. M. *J. Am. Chem. Soc.* **1997**, *119*, 7863.

<sup>†</sup> Camille and Henry Dreyfus Foundation Fellow.

<sup>‡</sup> Camille and Henry Dreyfus Foundation Scholar.

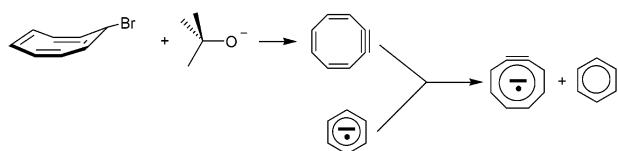
(1) Schafer, M. E.; Berry, R. S. *J. Am. Chem. Soc.* **1965**, *87*, 4497.

(2) (a) Krebs, A. *Angew. Chem.* **1965**, *77*, 1966. (b) Krebs, A.; Byrd, D. *Liebigs Ann. Chem.* **1967**, *707*, 66. (c) Stevenson, C. D.; Colon, M.; Ocasio, I.; Concepcion, J. J. *J. Phys. Chem.* **1975**, *79*, 1685.



**Figure 1.** (Upper) X-band EPR spectrum of a THF solution containing the [8]annulyne anion radical ( $3^{\bullet-}$ ) recorded at a temperature of 150 K. (Lower) Computer generated EPR spectrum using  $a_{\text{H}}$ 's of 3.18 G, 3.85, and 4.44 G for three sets of two equivalent protons. The peak-to-peak line width is 0.1 G. The B3LYP spin densities are given in parentheses, and the empirical spin densities are shown above them.

#### Scheme 1

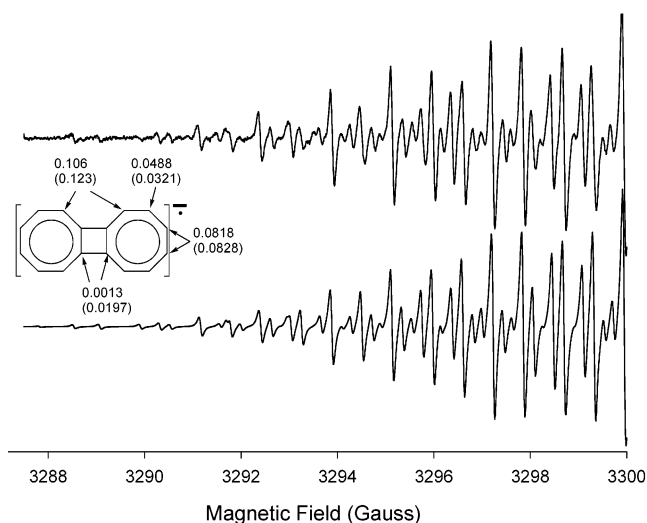


as their respective anion radicals, allowing expedient EPR observation of  $3^{\bullet-}$  and  $4^{\bullet-}$ . Further, **3** was reacted with other reactive intermediates, such as cyclobutadiene and benzyne, in the presence of an electron source to yield the EPR-detected anion radicals of [6]annuleno[8]annulene and [6]-[8]annulenyne.

## Results and Discussion

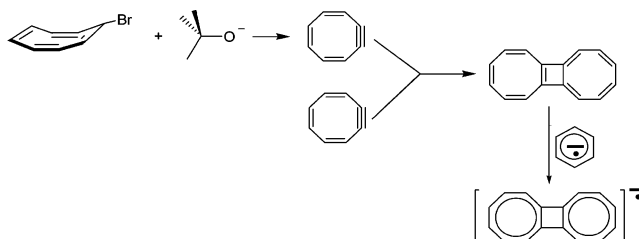
The low temperature ( $-100\text{ }^{\circ}\text{C}$ ) dehydrohalogenation of Br-COT with potassium *tert*-butoxide in a tetrahydrofuran (THF) solution containing 1 mol of 18-crown-6 per mol of Br-COT yields [8]annulyne (**3**). Immediate exposure of this solution to the solvated electron or benzene anion radical results in the one-electron transfer to **3** and consequent generation of the kinetically stable (for hours)  $3^{\bullet-}$  (Scheme 1). The presence of the crown ether prevents spin delocalization into the potassium metal cation and allows the first EPR observation of the uncomplexed anion radical.<sup>3b</sup> The odd electron in  $3^{\bullet-}$  exhibits coupling to three sets of proton pairs, Figure 1, where there is no  $\text{K}^+$  splitting, and the  $a_{\text{H}}$ 's are 9% larger than those in the absence of crown ether.

Theory predicts that  $3^{\bullet-}$  is completely planar, consistent with PES studies.<sup>4a</sup> The B3LYP/6-31G\* predicted carbon  $p_z$  spin densities (shown in parentheses in Figure 1) are in extraordinary agreement with the experimental spin densities (upper numbers) obtained from the  $a_{\text{H}}$ 's (Figure 1) and the McConnell relationship<sup>5</sup> ( $a_{\text{H}} = Q\rho$  with  $Q = 25.6\text{ G}$ ).<sup>6</sup> The spin densities on the sp carbons are obtained by requiring the total spin density to be unity. Just as [6]annulyne spontaneously dimerizes to



**Figure 2.** (Upper) Downfield half of an X-band EPR spectrum of  $4^{\bullet-}$  in THF at 150 K. A small amount of  $3^{\bullet-}$  is present as an impurity. (Lower) The computer simulation generated using  $a_{\text{H}}$ 's of 1.25, 2.094, and 2.72 G for three sets of four equivalent protons for  $4^{\bullet-}$  ( $\Delta w_{\text{pp}} = 0.07\text{ G}$ ). The impurity ( $3^{\bullet-}$ ) has been added in a ratio:  $[4^{\bullet-}]/[3^{\bullet-}]$  of 20. The spectrum for  $3^{\bullet-}$  is shifted 0.05 G upfield relative to that for  $4^{\bullet-}$ . The B3LYP spin densities are given in parentheses, and the empirical spin densities are shown above them.

#### Scheme 2



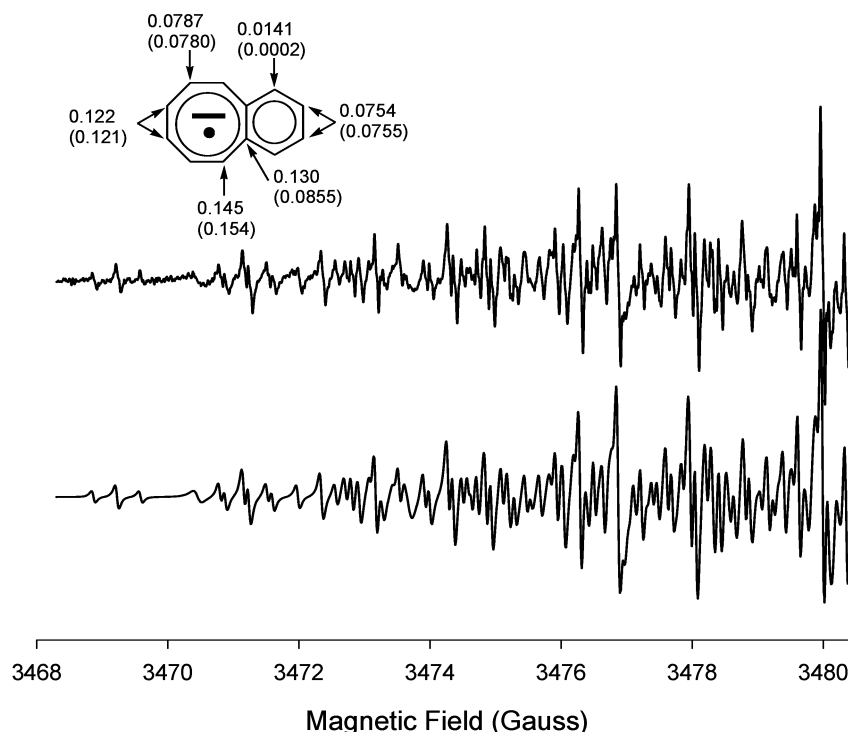
biphenylene,<sup>1</sup> **3** is expected to dimerize to form the “fugitive” bi[8]annulenyne (**4**). When the neutral [8]annulyne solution (described above) is kept below 173 K and not immediately exposed to a source of electrons, **3** undergoes the expected [2 + 2] dimerization. When the dimer (**4**) is exposed to a freshly distilled potassium metal mirror, it too is trapped (Scheme 2) as its anion radical (Figure 2).<sup>7</sup>

These results are in agreement with B3LYP/6-31G\* predictions where  $4^{\bullet-}$  has a planar  $D_{2h}$  symmetry, and again, there is excellent spin density agreement between theory and experiment, Figure 2. Other than the formation of naphthocyclooctatetraene, the EPR spectrum of  $4^{\bullet-}$  represents the first actual evidence for the dimerization of **3**.

The empirical and calculated spin densities suggest that the odd electron avoids the four-membered ring. This spin density profile in  $4^{\bullet-}$  is in stark contrast with that found in the biphenylene (bi[6]annulenyne) anion radical where spin localizes on the cyclobutadienyl moiety.<sup>8,9</sup> These two ( $2^{\bullet-}$  and  $4^{\bullet-}$ ) comprise the only biannulenyne anion radical systems to be

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(6) (a) Strauss, H. L.; Katz, T. J.; Fraenkel, G. K. *J. Am. Chem. Soc.* **1963**, *85*, 2360. (b) The successful theoretical interpretation appears in: Hammons, J. H.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1991**, *113*, 4500. (c)  $Q$  for the cyclooctatetraene anion radical is 25.6 G. (7) The use of an electron to stabilize a reactive intermediate is established, see: (a) Broadus, K. M.; Kass, S. R. *J. Am. Chem. Soc.* **2000**, *122*, 10697. (b) Broadus, K. M.; Kass, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 4189. (8) McDowell, C. A.; Rowlands, J. R. *Can. J. Chem.* **1960**, *38*, 503. (9) Bauld, N. L.; Banks, D. *J. Am. Chem. Soc.* **1965**, *87*, 128.



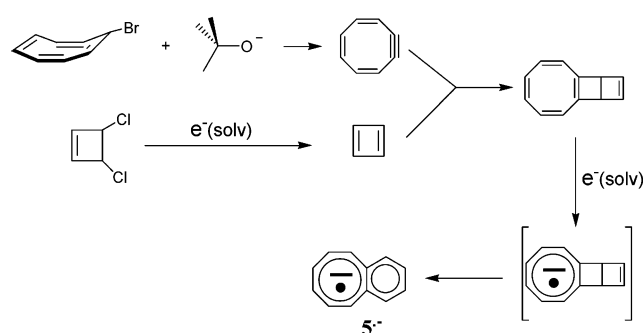
**Figure 3.** (Upper) Downfield half of an X-band EPR spectrum of benzocyclooctatetraene anion radical ( $5^{\bullet-}$ ) in HMPA recorded at 298 K. A small amount of cyclooctatetraene anion radical ( $COT^{\bullet-}$ ) is present as an impurity. (Lower) Computer-generated simulation using  $a_H$ 's of 0.36, 1.93, 2.015, 3.12, and 3.7 G for five sets of two equivalent protons ( $\Delta w_{pp} = 0.13$  G). The  $COT^{\bullet-}$  impurity has been added using an  $a_H$  of 3.215 G for the eight protons, and the ratio,  $[5^{\bullet-}]/[COT^{\bullet-}]$ , is 6.7. The B3LYP spin densities are given in parentheses, and the empirical spin densities are shown above them.

reported. However, many more annulenylenes can be envisioned and presumably trapped using the technique described above. It occurred to us that if the reactive [8]annulyne were allowed to react with itself or a series of other ring systems, a simple one-step route to a series of annulenoannulenes would also become available. This might be significant, since the annulenoannulenes represent the most fundamental extension of the annulenes, and no series of compounds has contributed more to our quantum mechanical understanding of aromaticity than have the annulenes.<sup>5</sup>

Exposure of a mixture of Br-COT, *cis*-3,4-dichlorocyclobutene and potassium *tert*-butoxide in hexamethylphosphoramide (HMPA)<sup>10</sup> to a potassium metal mirror at room temperature results in the formation of a dark viscous solution that exhibits a strong EPR spectrum, Figure 3. This spectrum is clearly that of the previously published [6]annuleno[8]annulene anion radical ( $5^{\bullet-}$ ).<sup>11</sup> The strong base dehydrohalogenates the Br-COT to form [8]annulyne; simultaneously, the solvated electron dehalogenates the *cis*-3,4-dichlorocyclobutene to form cyclobutadiene. The strained alkyne traps the unstable cyclobutadiene via a [2 + 2] cycloaddition, leading to the formation of (Dewar[6]annuleno[8]annulene). Upon exposure to potassium metal, the system undergoes ring opening to yield the persistent and thermodynamically stable anion radical of [6]annuleno[8]annulene ( $5^{\bullet-}$  in Scheme 3).

Very few experimental studies have been performed on  $5^{\bullet-}$ , because its synthesis is cumbersome.<sup>12a-e</sup> Anderson and Paquette suggested that the anion radical is nonplanar and that the odd

#### Scheme 3



electron resides only in the hexatriene moiety.<sup>13</sup> However, previous INDO calculations coupled with EPR data indicated that the anion radical is planar.<sup>11,14</sup> Our simple one-step procedure for the synthesis and direct EPR observation of  $5^{\bullet-}$  coupled with our B3LYP/6-31G\* calculations also reveals a planar system. Further, remarkable agreement between experiment and B3LYP-predicted spin densities for  $5^{\bullet-}$  is achieved, Figure 3.

When the same room-temperature experiment is carried out in the absence of dichlorocyclobutene, the [8]annulyne can only condense with itself, forming **4**, which is known to rearrange to naphthaleno[8]annulene.<sup>2</sup> Exposure of this solution to potassium metal yields a strong well-resolved EPR spectrum of the known<sup>14</sup> anion radical of naphthaleno[8]annulene.

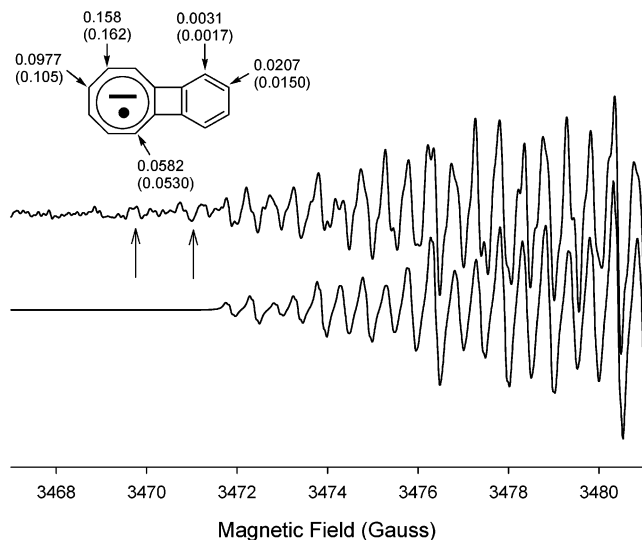
(10) Ion association is absent with anion radicals in HMPA, see: (a) Levin, G.; Jagur-Grodzinski, J.; Szwarc, M. *J. Am. Chem. Soc.* **1970**, *92*, 2268. (b) Stevenson, C. D.; Echegoyen, L.; Lizardi, L. R. *J. Phys. Chem.* **1972**, *76*, 1439.

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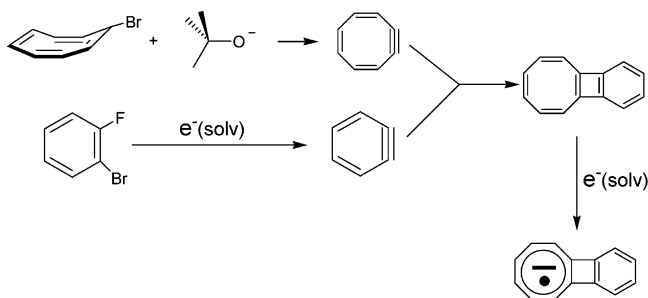
(13) Anderson, L. B.; Paquette, L. A. *J. Am. Chem. Soc.* **1972**, *94*, 4915.

(14) Stevenson, C. D.; Colon, M.; Ocasio, I.; Concepcion, F. J. *J. Phys. Chem.* **1975**, *79*, 1685.



**Figure 4.** (Upper) Downfield half of an X-band EPR spectrum of [6]-[8]-annulenyne anion radical in HMPA recorded at 298 K. A small amount of an impurity radical is present (see vertical arrows). (Lower) A computer-generated simulation using  $a_{\text{H}}$ 's of 0.08, 0.53, 1.49, 2.50, and 4.05 G for five sets of two equivalent protons ( $\Delta w_{\text{pp}} = 0.08$  G). The B3LYP spin densities are given in parentheses, and the empirical spin densities are shown above them on the structure.

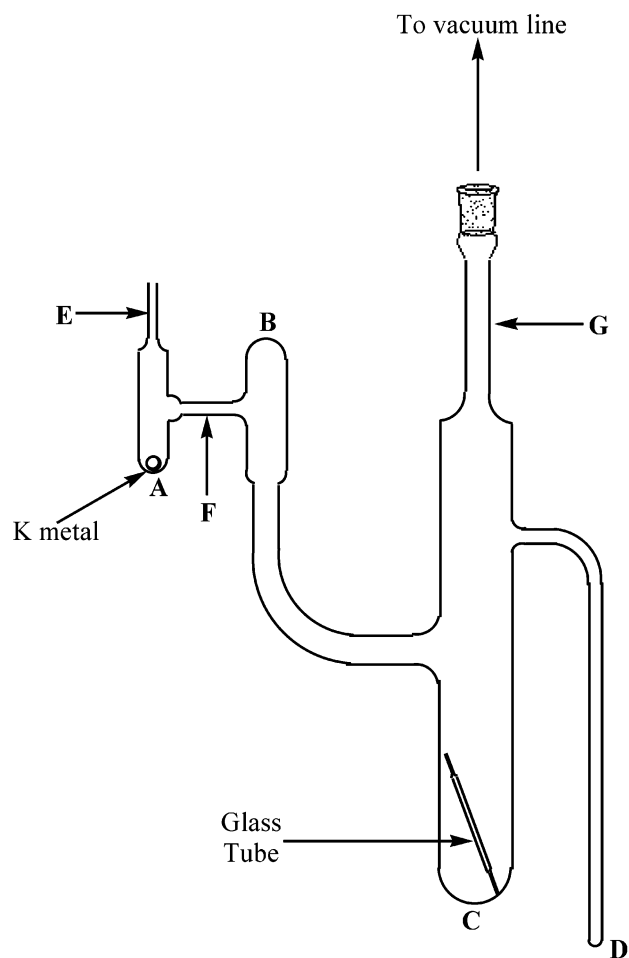
#### Scheme 4



The successful condensation of [8]annulyne with itself and with cyclobutadiene prompted us to attempt the formation of [6]-[8]annulenyne anion radical via the condensation of [6]-annulyne and [8]annulyne. When a room temperature mixture of Br-COT, *o*-bromofluorobenzene, and potassium *tert*-butoxide in HMPA is exposed to a potassium metal mirror, Scheme 4, the resulting solution exhibits a somewhat noisy EPR spectrum, Figure 4. This spectrum is due to a primary anion radical and a small radical impurity. Computer simulation reveals that the major component comes from a species exhibiting splittings from five pairs of protons. Using 25.6 G as the  $Q$  value, these splittings reveal the spin densities shown in Figure 4.

The empirical spin densities are quite close to those predicted by the B3LYP calculation for the anion radical of [6]-[8]-annulenyne, Figure 4. In view of the remarkable predictive ability of the B3LYP protocol in the other systems, the similarities between the predicted and empirical spin densities strongly suggest that [6]-[8]annulenyne has, indeed, been trapped as its anion radical.

The experimental techniques described above should be applicable to the synthesis and observation of a wide variety of annulyne, biannulenyne, and annulenoannulene anion radicals in one procedural step from the halogenated annulenes. Since the EPR "sees" only the doublets, most side products do not



**Figure 5.** Apparatus used for the generation of annulyne, biannulenyne, and annulenoannulene anion radicals.

interfere with the EPR observation. A plethora of such reactions await empirical observation.

#### Experimental Section

**Materials.** The synthesis of Br-COT was carried out as described by Krebs.<sup>2a</sup> The *o*-bromofluorobenzene ( $\text{C}_6\text{H}_4\text{FBr}$ ) was obtained from Aldrich Chemical Co., and *cis*-3,4-dichlorocyclobutene ( $\text{C}_4\text{H}_4\text{Cl}_2$ ) was purchased from Fluka Chemical Co.

**Reductions in HMPA.** A sealed glass tube (with fragile ends) was charged with a mixture of 0.1 mmol each of Br-COT and  $\text{C}_4\text{H}_4\text{Cl}_2$ . This tube was then placed into bulb C of the Pyrex glass apparatus shown in Figure 5. Bulb C was also charged with 0.1 mmol of potassium *tert*-butoxide. 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 distilled into bulb B to form a potassium mirror. Bulb A was sealed from the apparatus at point F. HMPA (4 mL) was distilled from a separate flask, containing potassium metal, directly into bulb C, and the evacuated apparatus was subsequently sealed from the vacuum line at point G. After dissolution of the *tert*-butoxide, the solution was exposed to the potassium mirror to generate the blue color, indicating the presence of solvated electron. The apparatus was then shaken to break the glass tube containing the mixture of Br-COT and  $\text{C}_4\text{H}_4\text{Cl}_2$ .

The EPR spectrum was immediately recorded by placing the 3-mm tube D into the EPR cavity. The apparatus could be removed from the EPR and the solution exposed to more metal and the spectrum recorded again. This process was continued until the best signal-to-noise ratio for the anion radical of [6]annuleno[8]annulene was obtained. This same procedure was carried out in the absence of the  $\text{C}_4\text{H}_4\text{Cl}_2$  to obtain the

anion radical of naphthocyclooctatetraene. When the  $C_4H_4Cl_2$  was replaced with  $C_6H_4FBr$  the anion radical of [6]-[8]annulenyne was obtained.

**Reductions in THF.** The anion radicals of bi-[8]annulenyne and [8]annulyne were obtained by replacing the HMPA with THF and placing only Br-COT in the sealed tube. In addition, 0.1 mmol of 18-crown-6 was mixed with the *tert*-butoxide in bulb C. Further, the whole apparatus was immersed in acetone slush at  $-100\text{ }^\circ\text{C}$  during the entire procedure. Immediate exposure of the THF solution (after breaking of the sealed tube) to the metal mirror yielded  $C_8H_6^{\bullet-}$ . However, when a delay of ca. 1 min was inserted between the rupture of the sealed tube

and exposure to the metal mirror, the anion radical of bi-[8]annulenyne was obtained. The choice of the solvent system was pragmatic in nature because we were unable to obtain the [6]-[8]annulenyne system in THF at any temperature.

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