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# Influence of Annulation on the Electron Spin within the 1,2,3-Triazole Ring in Annulenotriazole Anion Radicals

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#### ABSTRACT

The low temperature (-100°C) single electron reduction of N1-phenyl benzotriazole in liquid ammonia, and the room temperature reduction of N1-phenyl cyclooctatetraenotriazole in hexamethylphosphoramide, yields stable solutions of both anion radicals, which were studied via EPR spectroscopy. The amount of electron spin localized within the triazole ring, and how spin is distributed within this ring, is greatly influenced by the size of the annulene ring attached. UB3LYP/6-31++G(d,p) geometry optimizations using DFT methods were carried out for both anion radicals, and the calculated coupling constants (and electron spin densities) are in good agreement with the EPR spectroscopic results. Both theory and experiment show that much of the unpaired electron spin in the N1-phenyl benzotriazole anion radical is delocalized over the entire  $\pi$  system of benzotriazole ring including the phenyl ring attached, but that a significant percentage of total spin is found to reside within triazole ring with much of it centered on the second nitrogen (N2). With the N1-phenyl cyclooctatetraenotriazole anion radical, the majority of spin is localized over the  $\pi$  system of the COT ring, however a relatively small amount of total spin, found within the triazole moiety, is largely concentrated on two of the nitrogens (N1 and N3) within the ring.

#### **INTRODUCTION**

Aromatic N1-Benzotriazole (**Bt**) has been extensively studied for its broad range of synthetic applications and biological/medicinal activity.<sup>1-12</sup> For example, in the area of pharmacology, **Bt** derivatives have shown useful activity as antimicrobial, antitumor and cholesterol lowering agents.<sup>1-5</sup> The aromatic character of the **Bt** fused ring in these molecular species is key to their stability in drugs. In addition, the hydrogen bonding capability and the dipole moment associated with the **Bt** ring are important factors related to its biological utility.<sup>4</sup> For example, some N1-substituted benzotriazoles have shown promise as biological inhibitors of certain dioxygenases,<sup>3,5</sup> which are an important target for the treatment of cancer, as well as inhibition of phosphatases and intercellular ion exchangers.<sup>1,2</sup>

The application of **Bt** derivatives to organic synthesis has been realized for decades, where they have been uses as synthetic auxiliaries for the introduction of diverse functional groups into molecules. <sup>6-12</sup> Katritzky research group has investigated the chemistry involving **Bt** derivatives and has published much in this area.<sup>7-11</sup> There are a number of important functional roles that benzotriazole has in organic transformations, and two of these include its ability to function as an electron-donor or an electron-acceptor under certain conditions.<sup>11</sup> As an electron acceptor, **Bz** 

becomes a good leaving group in elimination reactions, with the formation of a stable benzotriazolate (**Bt**<sup>-</sup>) anion. For example, Scheme 1 depicts such an elimination of **Bt**<sup>-</sup> after the one electron reduction of N1-benzotriazolyl-alkylamines with Samarium (II) iodide (SmI<sub>2</sub>).<sup>8,9,11</sup> The resulting alkylamine



**Scheme 1**. Synthesis of pyrrolidine via the one electron reduction of N1-benzotriazolylalkylamine with SmI<sub>2</sub>.

radical intermediate will undergo a rapid intramolecular cyclization to generate a pyrrolidine ring.<sup>9</sup> The use of benzotriazole derivatives in such radical cyclization reactions has been shown to be a viable method to generate other nitrogen containing heterocycles, which are key ingredients in alkaloids.<sup>9,10,11</sup>

Given the myriad chemical studies performed on N1-benzotriazole derivatives, we find it interesting that studies involving N1-substituted derivatives of other annulenotriazole systems have largely been unexplored. The only other known system is that of the N1-phenylcyclo-octatetraenotriazole (**COTt-Ph**), which was first synthesized by Krebs in 1967.<sup>13</sup> However,



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the chemical properties of this non-aromatic (with respect to the [8]annulene ring) triazole are largely unknown. Having a viable method for generating **COTt-Ph**, we have chosen to compare the one electron reduction chemistry of this system with the fully aromatic N1phenylbenzotriazole (**Bt-Ph**). Our interest lies in exploring how different annulene rings will influence electron spin distribution within the triazole ring (e.g., within the three bonded nitrogens) attached. Since these annulene rings are quantum mechanically different from one another (e.g., [6]annulene is fully aromatic (4n+2  $\pi$ e<sup>-</sup>) while [8]annulene is non-aromatic (4n  $\pi$ e<sup>-</sup>), the difference in spin distributions should be profound. Upon reduction of **COTt-Ph**, we anticipate that much of electron density will be drawn into the COT ring. This is a consequence of the expected high electron affinity (EA) of the [8]annulenyl moiety in **COTt-Ph**.<sup>14,15</sup> However, it is unclear to what degree the fused triazole will attenuate the spin distribution throughout this system. On the other hand, benzene has a negative electron affinity due to loss of aromatic character upon addition of an electron,<sup>16</sup> therefore we anticipate the triazole moiety will have a considerable influence on spin distribution within the anion radical of **Bt-Ph**.

To the best of our knowledge, no spectroscopic investigations involving the anion radical of N1-substituted benzotriazoles have been published prior to these studies. We have successfully generated, and detected via EPR spectroscopy, the anion radicals of both **Bt-Ph** and **COTt-Ph**, and a complete assessment of spin density has been performed on both of these annulenotriazole systems. These studies will help with the understanding of differences in the electronic structures of these anion radicals as compared to those of the unreduced species, and will add to the important understanding of the structure and reactivity of annulenotriazole compounds.

### **RESULTS AND DISCUSSION**

The one electron reduction of **Bt-Ph** was carried out by exposing a liquid ammonia solution to a freshly distilled sodium metal surface under low temperature (-100°C) and high vacuum conditions. The resulting light blue solutions exhibited a strong, somewhat broad, EPR signal (Figure 1). The solution must be kept cold or the blue color fades rapidly with loss of the



**Figure 1**. (Upper) X-band EPR spectrum of a liquid ammonia solution containing the N1phenylbenzotriazole anion radical (**Bt-Ph'**<sup>-</sup>) recorded at a temperature of 190 K. (Lower) Computer generated EPR spectrum using  $a_{H}$ 's for nine unique protons: 4.30 G, 3.80 G, 3.55 G, 1.05 G, 0.83 G, 0.63 G, 0.55 G, 0.30 G, and 0.25 G and  $a_{N}$ 's for three nitrogen-14 atoms: 8.00 G, 1.36 G and 0.90 G. The peak-to-peak linewidth ( $\Delta w_{pp}$ ) is 0.35 G.

EPR signal, signifying loss of the anion radical. The rapid loss of anion radical upon warming or

within a few hours of it formation may explain why others were unable to detect **Bt-Ph<sup>•-</sup>**.<sup>17</sup>

Attempts were made to reduce the observed peak-to-peak linewidth in the spectral data by lowering the solution concentration of **Bt-Ph'**<sup>--</sup>. These experiments did show some improvement in linewidth although the spectrum was still broad. These low concentration experiments resulted in poor EPR signal strength for meaningful analysis. We conclude that the broadening in likely due to rapid spin-spin exchange due to the planarity of the **Bt-Ph** system. The computer simulation of this spectrum reveals that the odd electron exhibits coupling to nine unique protons and three nitrogen atoms, see Figure 1. The magnitude of the observed coupling to the three nitrogens reveals that a substantial amount of spin is localized within the triazole ring. While these EPR results suggest the presence of **Bt-Ph'**<sup>--</sup> in solution, theoretical calculations were needed to correctly assign the hyperfine coupling constants (hfccs) to the respective nuclei throughout the system.

Density Functional Theory (DFT) methodologies have been shown to predict isotropic hfccs exceptionally well for annulene anion radicals,<sup>18-20</sup> and have also proven to adequately predict coupling constants observed in organic radicals that contain nitrogen nuclei.<sup>21,22</sup> The geometry for **Bt-Ph'** was optimized using the UB3LYP/6-31++G(d,p) level of theory along with the theoretical hfccs.<sup>23</sup> Table 1 gives these results along with the experimentally determined hfcc values. Although these calculations were performed for the gas-phase **Bz-Ph** anion radical, we find that there is remarkably good agreement between theory and experiment especially for the  $a_{HS}$  and  $a_{NS}$  associated with the benzotriazole ring. Additional calculations were performed that included the polarizable continuum model (PCM) and mimic the solvation properties of liquid ammonia. In these calculations, the solvent choice was ethanol since the dielectric constant of this solvent is nearly the same as that for liquid ammonia at -74°C.<sup>23</sup> Table 1S in Supporting

Table 1. UB3LYP/6-31++G(d,p) Calculated and Experimental Coupling Constants (Gauss)
with Mulliken Calculated Spin Densities ( $\rho_N$ and $\rho_C$ ) for the Gas-Phase Bt-Ph <sup>*-</sup>

<b>Position</b> <sup><i>a</i></sup>	Expt <sup>b</sup>	Calc	$\rho_N$ and $\rho_C$
1(N)	0.90	-0.72	-0.0084
2(N)	8.00	7.46	0.40
3(N)	1.36	2.38	0.11
4	4.30	-4.45	0.20
5	1.05	1.37	0.083
6	3.80	-4.46	0.19
7	0.83	-1.03	0.002
8	-	-	0.021
9	-	-	-0.17
10	-	-	-0.026
11	0.55	-0.82	0.024
12	0.25	0.043	-0.010
13	3.55	-2.26	0.16
14	0.30	0.27	0.013
15	0.63	-1.32	0.028

<sup>*a*</sup>Position assignments are shown in Figure 1. <sup>*b*</sup>The sign for each of the measured coupling constants was not determined, but is assumed to be the same as the calculated values.

Information gives the calculated values for  $a_{Hs}$  and  $a_{Ns}$ . We find that these values are close to those obtained for the gas-phase system. The one noticeable difference is with the coupling constant determined for N1 ( $a_{N1} = -0.72$  G for the calculated gas-phase anion radical while the PCM model gives a value that is an order of magnitude smaller,  $a_{N1} = 0.073$  G). Comparison with the experimentally determined values suggest that the calculated gas-phase values are in better agreement with the measured values.

Included in Table 1 are the calculated Mulliken spin densities throughout the  $\pi$  system of **Bt**-

**Ph<sup>•–</sup>**. The predicted carbon  $p_z$  spin densities ( $\rho_C$ ) are given, since it is known that  $a_H$  is

proportional to the spin density on the adjacent  $sp^2$  carbon.<sup>24</sup> We see from both the calculated

spin densities, and magnitude of the experimentally determined hfccs, that the majority of electron spin in **Bt-Ph'** is concentrated within the fused benzotriazole ring, and that a relatively small amount of spin resides in the phenyl ring attached to N1. We also find a substantial amount of electron spin residing on the 3 Ns (total  $\rho_N > 0.50$ ) with the largest density on N2 ( $\rho_{N2} = 0.40$ ). This localization of spin on N2 is supported by the large coupling observed in the EPR spectrum where  $a_{N2} = 8.00$  G. With over half of the total spin residing in this portion of the **Bt** ring, the strong electron withdrawing nature of the fused triazole ring is realized. The ability of the 3 Ns to pull much unpaired electron density away from an annulene ring, and into the adjacent triazole moiety, can be further tested through exploring the one electron reduction of **COTt-Ph**.

The synthesis of **COTt-Ph** was necessary before reduction studies could be performed, and was carried out using the method developed by Krebs.<sup>13</sup> The preparation involves the reaction of monobromocyclooctatetraene ( $C_8H_7Br$ ) with potassium *tert*-butoxide in the presence of phenyl azide, reaction 1. The dehydrohalogenation of  $C_8H_7Br$  generates the reactive cyclooctatrienyne ([8]annulyne), which undergoes a [2+3] cycloaddition with the azide resulting in the formation of a stable triazole ring. The formation of **COTt-Ph** was confirmed via mass spectrometry (ESI-MS) and NMR spectroscopy (see Supporting Information). The <sup>1</sup>H-NMR analysis suggests that



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the COT ring retains its tub shaped geometry with  $D_{2h}$  symmetry upon formation of **COTt-Ph**. (The protons on the eight-membered ring appear from 6.4-5.7 ppm, which is close to the chemical shift for the protons on [8]annulene ( $\delta$  = 5.68 ppm).<sup>25</sup>)

The one electron reduction of **COTt-Ph** was carried out with sodium metal under vacuum conditions at room temperature in hexamethylphosphoramide (HMPA). The resulting green solution exhibits a strong EPR signal; however, attempts to simulate this very complex spectrum proved to be difficult due to the many unique couplings observed from the interaction of the free electron with many magnetically non-equivalent nuclei. (There are at least 11 unique proton and 3 unique nitrogen couplings possible; see Supporting Information for the entire EPR spectrum.<sup>26</sup>) We expect that no hyperfine coupling from the counter ion (Na<sup>+</sup>) will be observed since ion association is typically not detected when HMPA is the solvent.<sup>27,28</sup> We surmised that the smallest couplings observed come from the small amount of unpaired electron spin residing in the  $\pi$  system of the phenyl ring attached to N1. Therefore, efforts were undertaken to simplify the EPR spectrum through replacement of this phenyl ring with the perdeuteriated analog.

It was anticipated that the EPR signal from the anion radical of this perdeuteriated isotopamer (e.g, **COTt-PhD**<sub>5</sub><sup>•-</sup>) would not exhibit any hyperfine coupling associated with the phenyl ring since the ratio of gyromagnetic ratios is,  $\gamma_D/\gamma_H = 0.154$ .<sup>24</sup> Any hyperfine coupling associated with these deuterium atoms will be lost in the spectral linewidth and the spectrum obtained will be less complex and easier to simulate. In addition, any electron-hydrogen coupling now observed for **COTt-PhD**<sub>5</sub><sup>•-</sup> must come from the 6 Hs on the COT ring.

The formation of **COTt-PhD**<sub>5</sub> first required the synthesis of the perdeuterophenyl azide  $(C_6D_5N_3)$  precursor. This was carried out by reacting deuteroaniline  $(C_6D_5NH_2)$  with *tert*-butyl nitrite (*t*-BuONO) and azidotrimethylsilane (TMSN<sub>3</sub>) in acetonitrile, reaction 2.<sup>29</sup> Upon



(2)

purification of  $C_6D_5N_3$ , its structure was confirmed via <sup>13</sup>C-NMR spectroscopy (All Cs bonded to deuterium are now split into triplets). With the  $C_6D_5N_3$  in hand, the synthesis of **COTt-PhD**<sub>5</sub> was carried out in the same manner as already described, reaction 1. The <sup>1</sup>H-NMR spectrum exhibits resonances only associated with the COT ring protons (all resonances associated with the phenyl ring hydrogens are absent) and the <sup>13</sup>C-NMR spectrum shows coupling to the deuterium atoms attached to the five phenyl ring carbons; see Supporting Information.

The reduction of **COTt-PhD**<sub>5</sub> was performed using the same conditions as for the perprotiated analog, and the resulting EPR spectrum was indeed considerably less complex, with significantly less coupling observed (Figure 2). A computer simulation was generated using hyperfine couplings associated with six protons and three nitrogens, which again must be associated with only the **COTt** ring in **COTt-PhD**<sub>5</sub><sup>••</sup> (see Figure 2). As hoped, the coupling between the unpaired electron and the deuterium atoms on the phenyl ring is buried in the EPR linewidth. (A small  $a_D = 0.06$  G was used to improve line-shape.) With these electron-nuclear couplings now determined, the simulations of the complex spectrum obtained for **COTt-Ph**<sup>••</sup> becomes achievable, since all remaining hyperfine coupling observed must come from the phenyl ring protons. Incorporation of these five  $a_{HS}$  produced a simulation that is remarkably similar to that of the recorded spectrum, Figure 3. These results reveal that the odd electron is no longer concentrated within the triazole moiety, as in the case of **Bt-Ph**<sup>••</sup>, but resides mostly within the [8]annulenyl ring where the three nitrogens now simply attenuate the spin distribution.



**Figure 2**. (Upper) X-band EPR spectrum of a HMPA solution containing the N1-phenyl(D<sub>5</sub>)cyclooctatetraenotriazole anion radical (**COTt-PhD<sub>5</sub>**<sup>•–</sup>) recorded at 295 K. (Lower) Computer generated EPR spectrum using  $a_{\rm H}$ 's for six protons: 5.26 G, 5.16 G, 4.12 G, 2.87 G, 1.61 G, and 0.72 G and  $a_{\rm N}$ 's for three nitrogen-14 atoms: 2.02 G, 0.32 G and 0.10 G and a small  $a_{\rm D} = 0.06$  G (<sup>2</sup>H). The peak-to-peak linewidth ( $\Delta w_{\rm pp}$ ) is 0.11 G.

As with the **Bt-Ph<sup>·-</sup>** system, DFT calculations were performed to assign the hyperfine

couplings to the respective hydrogens and nitrogens in COTt-Ph<sup>•-</sup>. The geometry optimization

and the gas-phase theoretical hyperfine couplings and Mulliken spin densities ( $\rho_N$  and  $\rho_C$ ) were





**Figure 3**. (Upper) X-band EPR spectrum (downfield half) of a HMPA solution containing the N1-phenylcyclooctatetraenotriazole anion radical (**COTt-Ph'**<sup>-</sup>) recorded at 295 K. (Lower) Computer generated EPR spectrum using  $a_{\rm H}$ 's for 11 protons: 5.24 G, 5.14 G, 4.10 G, 2.84 G, 1.60 G, 0.73 G, 0.325 G, 0.315 G, 0.17 G, 0.12 G and 0.030 G and  $a_{\rm N}$ 's for three nitrogen-14 atoms: 2.00 G, 0.315 G and 0.095 G. The peak-to-peak linewidth ( $\Delta w_{pp}$ ) is 0.05 G.

calculated using the same DFT protocol. These calculated results along with the measured coupling constants are shown in Table 2. Calculations on the neutral **COTt-Ph** predict that the COT ring has a tub ( $D_{2h}$ ) conformation (in agreement with our experimental results), but for **COTt-Ph**<sup>•-</sup> the ring is planar with the expected  $D_{4h}$  geometry.<sup>30</sup> Comparison between the theoretical and experimental  $a_{HS}$  and  $a_{NS}$  indicate that there is good agreement especially for

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Table 2. UB3LYP/6-31++G(d,p) Calculated and Experimental Coupling Constants (Gauss)and Mulliken Calculated Spin Densities ( $\rho_N$  and  $\rho_C$ ) for the Gas-Phase COTt-Ph<sup>•–</sup>.

<b>Position</b> <sup><i>a</i></sup>	Expt <sup>b</sup>	Calc	$\rho_N$ and $\rho_C$
N(1)	2.00	1.34	0.056
N(2)	0.095	0.064	0.002
N(3)	0.315	0.080	-0.002
4	5.24	-5.97	0.25
5	0.73	-0.15	-0.036
6	5.15	-5.88	0.24
7	1.60	-0.75	-0.0015
8	4.10	-4.98	0.22
9	2.84	2.02	0.036
10	-	-	0.16
11	-	-	0.013
12	-	-	-0.046
13	0.17	-0.69	0.051
14	0.12	0.37	-0.006
15	0.325	-1.01	0.044
16	0.030	0.28	-0.016
17	0.315	-0.74	0.037

<sup>*a*</sup>Position assignments are shown in Figure 3. <sup>*b*</sup>The sign for each of the measured coupling constants was not determined, but is assumed to be the same as the calculated values.

those coupling constants associated with the COT ring and with  $a_{N1}$  (2.00 G vs 1.34 G). However, there is less agreement between the calculated and measured  $a_{N2}$  and  $a_{N3}$  values. Theory predicts similar electron coupling to both these nitrogens, although with  $a_{N2}$  slightly smaller than  $a_{N3}$ , while the experimental results reveal that the couplings are quite different. ( $a_{N3}$ is nearly four times larger than that predicted by theory.) The DFT calculation also predict larger  $a_{H}$ 's for the phenyl ring protons than those found experimentally (see Table 2). Additional calculations were performed on **COTt-Ph'**<sup>-</sup> that including PCM modeling. As with the **Bt-Ph'**<sup>-</sup> system, the solvent chosen was ethanol and the results of these calculations can be found in

Table 2S in Supporting Information. Interestingly, these calculations do show better agreement with the experimental values for N1 and N3 (theory gives  $a_{N1} = 1.91$  G and  $a_{N3} = 0.44$  G and the experimental values are  $a_{N1} = 2.00$  G and  $a_{N3} = 0.315$  G). The PCM predicted value for N2 ( $a_{N2} = -0.27$  G) however is in worse agreement than that for the gas-phase value ( $a_{N2} = 0.064$  G) while the experimental value for N2 is  $a_{N2} = 0.095$  G. The EPR results reveal that far less electron spin resides within the  $\pi$  system of this ring.

The two annulenotriazole anion radicals we have investigated here exhibit considerable differences in the location of the unpaired electron within the triazole ring (see Tables 1 and 2). The results indicate that the electron spin residing in the heterocyclic portion of **COTt-Ph'** is concentrated almost entirely on N1 and N3 ( $a_{N1}$  and  $a_{N3} \gg a_{N2}$ ) whereas the largest portion of spin in **Bt-Ph'** is clearly found on N2. These findings suggest a significant difference in the electronic structure of the triazole moiety, depending on whether COT or benzene is present in these annulenotriazole systems. These differences can be visualized by first comparing the changes to the molecular orbital plots associated with the neutral 1,2,3-triazole and annulenotriazoles (e.g., HOMOs) and then comparing these HOMO plots with the spin density plots for the respective annulenotriazole anion radicals.

Neutral 1,2,3-triazole (**Trz**) is known to undergo a significant change to its HOMO  $\pi$  electronic structure upon benzannulation.<sup>31</sup> As seen in Figure 4, the B3LYP generated HOMO plots of both **Trz** and 1H-benzotriazole (**Bt-H**) show the extent of this change and the quantum mechanical "location" of  $\pi$  electrons.<sup>31,32</sup> Notably, the charge density in **Trz** is concentrated on N2 while there is a node that persists on N2 in the benzotriazole system (see Figure 4). It becomes clear from these molecular orbital plots that the fused benzene ring has a profound

effect on the location of the  $\pi$  electrons within the triazole moiety. We also see for the latter system that much of the charge density now populates the N1 and N3 sites.<sup>31</sup> Theory also reveals that annulation of the triazole ring with COT (e.g., **COTt-H**) generates a HOMO  $\pi$ electronic structure that is qualitatively similar to **Trz** in that much of the charge density is



**Figure 4**. B3LYP HOMO  $\pi$ -electron charge density plots **Trz** (left) and **Bt-H** and **COTt-H** (center) and unpaired electron spin density plots for **Bt-H**<sup>•-</sup> and **COTt-H**<sup>•-</sup> (right).

present on N2, see Figure 4.<sup>33</sup> The similarity is somewhat expected, because the tub conformation of the COT ring results in a molecular system that is essentially olefinic,<sup>25</sup> and therefore the  $\pi$  electrons within the ethylene bond shared by the COT and the triazole moiety can contribute in the same way to the aromatic character of the heterocycle.<sup>34</sup>

Figure 4 also contains the B3LYP calculated spin density plots for the anion radicals of **Bt-H** and **COTt-H**. (Replacement of the phenyl ring on N1 in **Bt-Ph<sup>·-</sup>** and **COTt-Ph<sup>·-</sup>** with a hydrogen atom (e.g., **Bt-H<sup>·-</sup>** and **COTt-H<sup>·-</sup>**) shows no major change to the spin density distribution and gives a plot that still agrees qualitatively with the magnitude of the  $a_N$ 's

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observed for the nitrogens within the triazole moiety, see Tables 1 and 2. The calculated Mulliken charges have also been determined for these anion radicals and these results can be found in Supporting Information. We find that a considerable about of negative charge does reside within the triazole ring for both anion radical systems with the majority of charge residing on N2 and N3 in both systems.

The unpaired electron density plots obtained are indicative of the SOMO  $\pi$  electronic structures (see Supporting Information) and reveal how different these molecular orbitals are from the HOMO plots associated with the neutral annulenotriazole. Remarkably, we see that the portion of the spin density plot (and therefore the SOMO) associated with the triazole moiety in **Bt-H'** is reminiscent of the HOMO plot for **COTt-H** (and **Trz**) in that a node is no longer present on N2, whereas the electron density plot for **COTt-H'** and the HOMO plot for **Bt-H** are alike in that the electron density (spin and charge, respectively) tends to populate the N1 and N3 sites at the expense of N2 site. The similarity in these electronic structures may result from **COTt-H'** exhibiting more aromatic character with the addition of the single electron, whereas **Bt-H'** exhibits more anti-aromatic character with the addition of an electron. These two (**Bt-Ph'** and **COTt-Ph'**) represent the only N1-annulenotriazole anion radicals reported, but there are many other annulenoazoles that await further study as anion radicals. We are currently exploring the reduction chemistry of these interesting heterocycles.

#### **EXPERIMENTAL SECTION**

**Materials**. Deuteriated analine ( $C_6D_5NH_2$ ) was purchased from Cambridge Isotopes, Inc. and used in the synthesis of deuteriated phenyl azide ( $C_6D_5N_3$ ).

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Synthesis of N1-Phenyl-[8]annulenotriazole (COTt-Ph and COTt-PhD<sub>5</sub>). The synthesis of monobromocyclooctatetraene (BrCOT) was first carried out based on Kreb's preparation, <sup>13,35</sup> and is already described elsewhere.<sup>36</sup> Once the BrCOT was generated, the synthesis of COTt-Ph was carried out using the procedure also described by Krebs.<sup>13</sup> An ether solution (20 mL) charged with 0.40 g BrCOT (2.4 mmol), 0.3 g phenyl azide (2.5 mmol) and 0.3 g potassium *tert*-butoxide (2.3 mmol) was stirred for 72 hrs under ambient conditions. After this time, a dilute aqueous solution of acetic acid was added to the orange/brown turbid solution. The ether layer was dried with anhydrous MgSO<sub>4</sub> and filtered. The ether was removed leaving behind the crude solid product. Purification of COTt-Ph was performed via flash chromatography using silica gel as the stationary phase. Chloroform was used first as the mobile phase to remove all unwanted side products from the synthesis, followed by a 1:1 mixture of chloroform and ethyl acetate, which was used to remove the desired product from the column. Removal of the solvent mixture left behind a yellow solid, and NMR and ESI-MS analysis confirm the formation of COTt-Ph (see Supporting Information for spectral data).

Synthesis of perdeuteriated phenyl azide ( $C_6D_5N_3$ ) from deuteriated aniline  $C_6D_5NH_2$ . The synthesis of  $C_6D_5N_3$  was carried out using the procedure developed by Barral et al.<sup>29</sup> A solution containing 1.0 g  $C_6D_5NH_2$  (10 mmol) in 20 mL CH<sub>3</sub>CN was cooled to 0°C, after which was added 1.70 g *t*-BuONO (16.5 mmol) followed by 1.50 g TMSN<sub>3</sub> (13 mmol) dropwise. The resulting solution was warmed slowly to room temperature and stirred for 1 hr. The CH<sub>3</sub>CN was removed under vacuum and the crude product was purified via silica gel flash chromatography with hexanes as the mobile phase. <sup>13</sup>C-NMR analysis confirmed that  $C_6D_5N_3$  was generated. This azide was then used in the synthesis of **COTt-PhD**<sub>5</sub>. See Supporting Information for <sup>1</sup>H-

NMR and for <sup>13</sup>C-NMR spectral data. All <sup>1</sup>H-NMR and <sup>13</sup>C{<sup>1</sup>H}-NMR spectroscopic data were collected using a Bruker Avance III 400 MHz NMR spectrometer.

#### **Reduction of N1-Phenyl Benzotriazole in Liquid Ammonia for EPR Experiments.**

A Pyrex glass apparatus (see Supporting Information for schematic) was charged with 0.084 mmol of **Bt-Ph** in bulb A. A small amount of sodium metal was placed into bulb B, which was then sealed at point C, and the entire apparatus was evacuated. The sodium metal was distilled into bulb D to form a pristine metal mirror, after this, bulb B was sealed at point E. Approximately 2.0 mL of anhydrous liquid ammonia (dried with a small piece of potassium metal) was distilled through the vacuum manifold directly into bulb A using a liquid nitrogen/acetone slurry. The evacuated apparatus was sealed from the vacuum line at point F. The **Bt-Ph** was mildly soluble in the liquid ammonia, but upon addition of metal, it became clear that the **Bt-Ph'** dissolved nicely into solution. All reductions were carried out at -100°C. A series of EPR tubes were harvested from the apparatus as the solution was exposed to more and more metal. Each sample was interrogated via EPR spectroscopy until the sample with the best signal-to-noise ratio was found for the anion radical in solution. All spectroscopic data were collected at -100°C.

# **Reductions of N1-Phenyl Cyclooctatetraenotriazole** (**COTt-Ph and COTt-PhD**<sub>5</sub>) in **HMPA**. The reductions were carried out by allowing a HMPA solution of either **COTt-Ph** or **COTt-PhD**<sub>5</sub> to come into contact with a sodium metal mirror at room temperature in vacuo as previously described.<sup>37</sup>

All spectra were recorded using a Bruker EMX X-band EPR spectrometer equipped with a variable-temperature unit. Data was collected with the following EPR parameters: microwave power = 25 dB, modulation amplitude = 0.1 G, time constant and conversion times = 655.36 ms.

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In the case of spectra collected for the **Bt-Ph** anion radical, once it was determined that the peakto-peak linewidth was greater than 0.3 G, the spectra were then re-collected with a modulation amplitude of 0.25 G for the purpose of improving the signal strength.

**Computational Methodology.** Both **Bt-Ph'** and **COTt-Ph'** geometry optimizations were carried out via DFT calculations at the UB3LYP/6-31++G(d,p) level of theory as were the theoretically determined coupling constants and spin densities. All calculations were implemented in Gaussian 09, Revision D01,<sup>23</sup> and were done for the gas-phase molecules. In the case of the PCM modelling, the solvent used was ethanol since it has a dielectric constant similar to that for ammonia.<sup>23</sup> The optimized gas-phase structures were used and a single-point UB3LYP/6-31++G(d,p) calculation was performed to determine the coupling constants and spin densities. The calculated Mulliken spin densities were used and are the difference between the alpha and beta spin occupancies. All optimizations did converge and stability in the calculated structures was determined by performing a vibrational analysis on all structures; no imaginary frequencies were found.

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#### SUPPORTING INFORMATION

EPR spectrum obtained from the reduction of **COTt-Ph** and the <sup>1</sup>H- and <sup>13</sup>C-NMR spectra and ESI-MS from the synthesis of **COTt-Ph**. Further information regarding the DFT calculations for **Bt-Ph<sup>·-</sup>** and **COTt-Ph<sup>·-</sup>**. This material is available free of charge via the Internet at http://pubs.acs.org.

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