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Tris-[8]annulenyl Isocyanurate Trianion Triradical and Hexa-anion from the Alkali Metal Reduction of [8]Annulenyl Isocyanate

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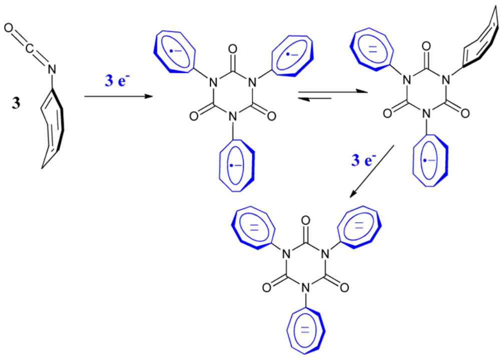
Supporting Information



ABSTRACT: The solution phase alkali metal reduction of [8]annulenyl isocyanate (C_8H_7NCO) yields an EPR spectrum, which reveals electron couplings to seven protons and only one nitrogen. Although this strongly suggested that the C_8H_7NCO anion radical was generated, experiments on the oxidized product reveal the actual reduced species to be tris-[8]annulenyl isocyanurate. Unlike the previously studied phenyl isocyanurate anion radical, the unpaired electron(s) is now localized within an [8]annulenyl moiety. Further exposure to metal results in the formation of an equilibrium mixture of trianion triradical and trianion radical species. The cyclotrimerization to form the isocyanurate is proposed to be driven by a reactive C_8H_7NCO dianion, which is produced from the large equilibrium disproportionation of the anion radical. Exhaustive reduction of the tris-[8]annulenyl isocyanurate with potassium in THF generates the first-ever observed hexa-anion of an isocyanurate. NMR analysis reveals that the polarity of the carbonyl bonds within this hexa-anion is augmented and is caused by the close proximity of K^+ ions, which are tightly ion paired to the three [8]annulenyl dianion rings. These preliminary studies on the reduction of C_8H_7NCO suggest that polymeric materials (e.g., polyisocyanates) made from this isocyanate might exhibit unique properties.

INTRODUCTION

The remarkable utility of isocyanates (R—N═C═O) as building blocks for the production of more complex molecular systems has been recognized for well over 150 years.[1] Their greatest use has certainly been in the production of polyurethanes and polymer blends that contain cross-links of isocyanurate heterocycles,[2−5] where the latter is particularly important in making these polymers flame retardant and impact resistant.[4,5] Isocyanates are also widely used in the synthesis of biologically relevant compounds, including antibiotics as well as many newly discovered natural products.[2,6−12] In recent years, both alkyl- and aryl isocyanates have been used to generate materials that may be harnessed for their electronic and optical properties. For example, aryl urea based protophanes, synthesized from isocyanate precursors, exhibit unique electronic interactions in these π-stacked aromatic chromophores.[13,14] An alternative is the generation of polyisocyanates (e.g., 1-nylon polymers from isocyanate monomers), which are known to exhibit enhanced optical activity due to the extended helical conformation; these polymers have the potential to be used as linkers in optical materials and molecular switches.[15−20] Formation of these polyisocyanates commonly occurs at low temperatures, using an anion initiator such as the anion radical of an isocyanate monomer.[15−20]

Our motivation for exploring the chemistry of isocyanate anion radicals comes from the fact that studies investigating their structure and their reactivity are few. A greater understanding of these systems should lead to a more complete picture of how they can be used in syntheses. We recently investigated the alkali metal reductions of aryl isocyanates and determined that ion association plays an important role in the stability and reactivity of these anion radicals.[21] Under solvent conditions where ion association is typically absent (e.g., in hexamethylphosphoramide, HMPA),[22] we found it possible to generate the stable anion radical of phenyl isocyanate ($PhNCO^{\bullet-}$) and observe it via electron paramagnetic resonance (EPR) spectroscopy, reaction 1.[21] The measured EPR hyperfine coupling constants reveal that the electron spin density is delocalized throughout the molecular π system, and that the molecular structure of $PhNCO^{\bullet-}$ is similar to that of the neutral PhNCO, where the isocyanate moiety remains nearly linear.[21] However, when these reductions are performed under conditions where strong ion association occurs between the alkali metal cation and anion radical (e.g., in tetrahydrofuran, THF),[23−25] no $PhNCO^{\bullet-}$ is detected. Instead, the only anion radical observed is that of tris-phenyl isocyanurate formed via a rapid cyclotrimerization (reaction 2) where the electron is largely localized within one of the carbonyl bonds.[21] The expected Coulombic attraction between the metal cation and the NCO moiety in $PhNCO^{\bullet-}$ will augment the electron density within the NCO group resulting in a more reactive anion radical that propagates the cyclotrimerization.[26] A similar argument can be made for the reactivity of alkyl isocyanate anion radicals. Low temperature matrix isolation studies on the

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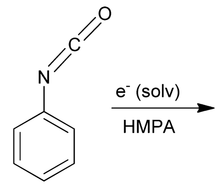

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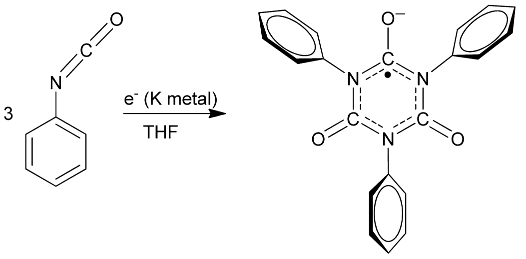
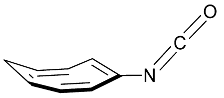


(2)

anion radical of CH_3NCO revealed that nearly all of the unpaired electron density resides within the π molecular system of the NCO group.[27] Apparently, these experimental conditions were necessary to capture $CH_3NCO^{\bullet-}$ and to prevent it from undergoing polymerization. Our group investigated the one electron reduction of alkyl isocyanates under ambient conditions in both HMPA and THF and found that it was not possible to detect the respective anion radicals in either of these solvents. Only solutions containing trialkyl isocyanurate anion radicals could be detected.[28]

To further our understanding of the stability and the reactivity of isocyanate anion radicals, we are motivated to investigate the reduction of [8]annulenyl isocyanate (C_8H_7NCO, **1**), which is a new isocyanate and its chemistry has yet to be explored. We believe this to be an ideal molecular system for further exploration of isocyanate reduction chemistry since we anticipate that much of electron density will reside within the [8]annulenyl ring upon addition of an electron. This is a consequence of the expected high electron affinity (EA) of the [8]annulenyl moiety in **1**. (The EA of [8]annulene (cyclooctatetraene, COT) is +63 kJ/mol.[29]) If substantial attenuation of spin density away from the NCO group occurs, how will this impact the reactivity of $\mathbf{1}^{\bullet-}$? Additionally, **1** is a particularly attractive system to explore due to the fundamental quantum mechanical differences between [8]annulene (4*n* π electrons) and [6]annulene (4*n* + 2 π electrons). Therefore, the reduction chemistry of C_8H_7NCO is an interesting choice to compare with that of the already explored PhNCO.[21]



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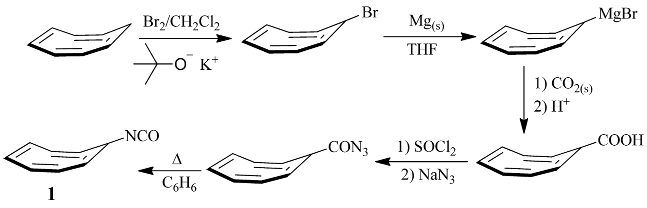
RESULTS AND DISCUSSION

Before reduction studies on C_8H_7NCO could be performed, it was necessary to develop a synthetic route to this new isocyanate starting from cyclooctatetraene, Scheme 1. The monobromo-COT (C_8H_7Br) was synthesized as described by Krebs.[30] Exposure of C_8H_7Br to Mg metal generated a deep blue-green colored solution indicating the formation of the Grignard, C_8H_7MgBr. This solution was quenched with excess dry ice ($CO_2(s)$) and acidified to generate the carboxylic acid, C_8H_7COOH. Exposure of the acid to thionyl chloride ($SOCl_2$) produced the acid chloride, C_8H_7COCl, which was further reacted with NaN_3 to generate the acyl azide, $C_8H_7CON_3$. The azide was heated in a benzene solution to drive the Curtius rearrangement and formation of C_8H_7NCO.

Scheme 1. Synthesis of [8]Annulenyl Isocyanate (1) Starting from Cyclooctatetraene (COT)



The reduction of C_8H_7NCO under vacuum conditions in hexamethylphosphoramide (HMPA) at 293 K with sodium metal,[31] or in THF (with 1 equiv of 18-crown-6) with potassium metal at 180 K, gives rise to an EPR spectrum that upon computer simulation reveals that the anion radical of a substituted [8]annulene had been generated, Figure 1.[32,33] The two larger a_H's (4.13 G (2 Hs) and 4.37 G (2 Hs)) come from coupling to the four hydrogens on the even numbered carbons, while the smaller a_H (2.295 G (3 Hs)) is from the hydrogens on the odd numbered carbons. Interestingly, the magnitude of these a_H's would suggest that the substituent attached is a relatively weak electron-withdrawing group.[33] These EPR results are consistent with the reduced D_{8h} [8]annulene ring undergoing a Jahn–Teller distortion to a ring that has a planar D_{4h} geometry with alternating long and short bond lengths.[33b,34]

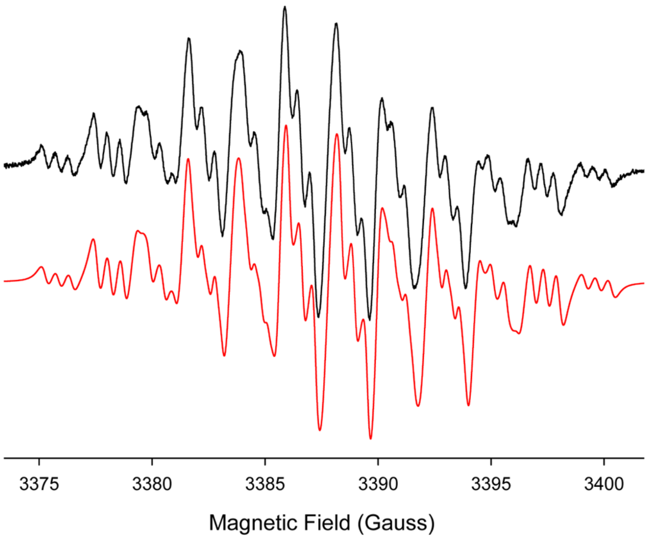


Figure 1. (Upper) X-band EPR spectrum recorded at 180 K after a THF solution containing [8]annulenyl isocyanate (C_8H_7NCO) with 1 equiv of 18-crown-6 was exposed to K metal under vacuum. Spectrum was obtained after solution was sufficiently reduced to generate the strongest signal possible. (Addition of more metal resulted in loss of signal intensity.) (Lower) Computer generated EPR spectrum using a_N of 0.58 G (1 N) and a_H's of 2.295 G (3 H's), 4.13 G (2 H's), and 4.37 G (2 H's). The peak-to-peak line width (Δw_{pp}) is 0.40 G.

On the basis of the EPR results obtained, our initial conclusion was that we had successfully generated the anion radical of C_8H_7NCO in solution for two important reasons: (1) The unpaired electron clearly resides within the annulene ring and exhibits coupling to only one nitrogen atom (a_N = 0.58 G) and (2) in previous studies with $PhNCO^{\bullet-}$, we found that the NCO

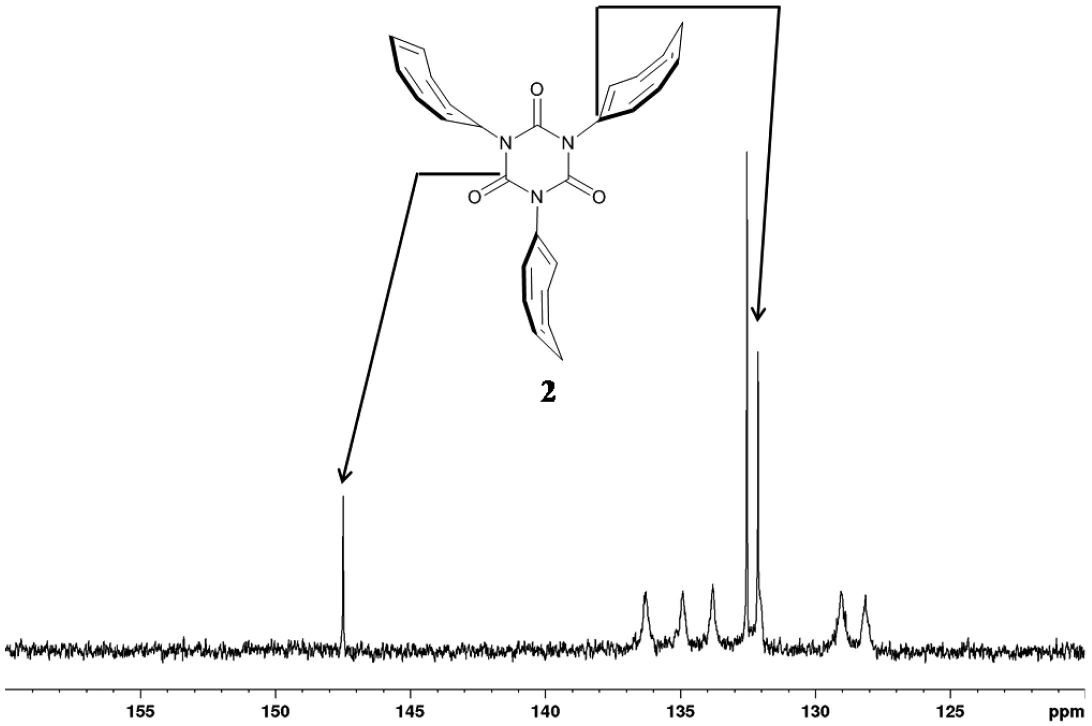


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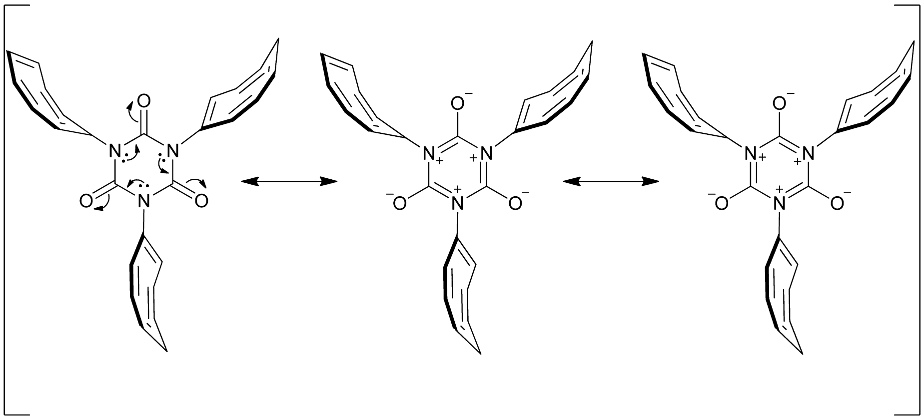
Figure 2. The 125 MHz $^{13}C\{^1H\}$ NMR spectrum of tris-[8]annulenyl isocyanurate (**2**) in $CDCl_3$. The isocyanurate was generated from the potassium metal reduction of C_8H_7NCO in THF along with 1 equiv of 18-crown-6. This spectrum was recorded after the THF solution was oxidized with I_2 and the yellow solid collected was purified. The broad peaks observed for some of the carbon resonances is a consequence of the COT ring inversion/bond shift process.

Scheme 2. Resonance Structures Depicting the Overlap of the Nitrogen Lone Pair Electrons with the π Molecular Orbitals of the Isocyanurate Ring in 2



group is in fact weakly electron withdrawing with respect to the phenyl ring.[21] However, additional experiments revealed that the EPR pattern shown in Figure 1 did not come from $\mathbf{1}^{\bullet-}$, but from a reduced form of tris-[8]annulenyl isocyanurate.

The low temperature potassium metal reduction of C_8H_7NCO in THF (with 18-crown-6) was repeated until the strongest EPR signal (the same as that shown in Figure 1) possible was obtained.[35] This THF solution was then oxidized with excess iodine to convert the reduced species in solution to their neutral state ($K^+R^{\bullet-} + 1/2\ I_2 \rightarrow R + KI$). The apparatus was opened and any remaining I_2 was quenched with $Na_2S_2O_3$. After further purification, the major product isolated was a yellow precipitate and the $^{13}C\{^1H\}$ NMR spectrum confirmed its identity to be tris-[8]annulenyl isocyanurate (**2**), Figure 2. The chemical shift at δ = 147.5 ppm is assigned to the three equivalent carbonyl carbons in the planar isocyanurate ring, and is proof of its formation upon reduction of C_8H_7NCO.[36] As further evidence that the EPR spectrum in Figure 1 comes from the reduction of **2**, this authentic isocyanurate was reduced with potassium in THF (as described above) and the EPR signal observed is the same as that shown in Figure 1, see Figure in Supporting Information. Unlike in the previously studied isocyanurate anion radicals, the unpaired electron is now localized within a COT moiety and not in the isocyanurate ring (reaction 2) due to the larger EA of the [8]annulenyl ring.[21,28,29]

These EPR results reveal that the electron-withdrawing effect upon the molecular orbitals of the COT ring(s) is in fact due to the isocyanurate ring and not to an NCO group. The electron-withdrawing nature is a consequence of the delocalization of the lone pair electrons on the three nitrogens into the π-system

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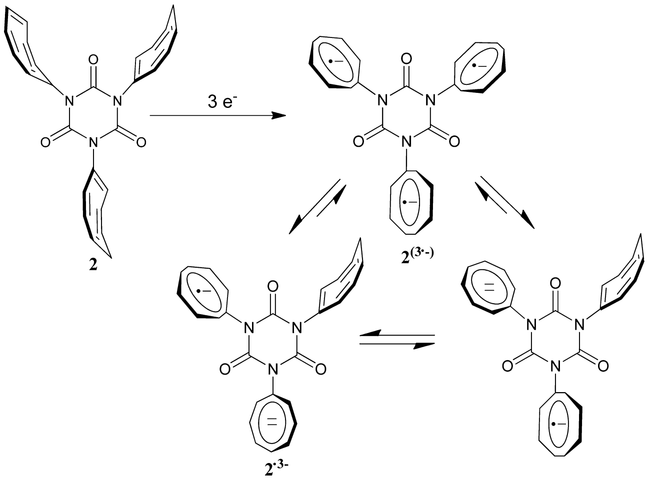
(amide bonds) of the heterocyclic ring resulting in partial positive charges on each of these nitrogens (Scheme 2 shows the resonance structures for **2**). Interestingly, the isocyanurate ring is often considered "aromatic" in a Hückel sense, because these six lone pair electrons contribute to its stability and D_{3h} planarity. The nitrogen lone pair electrons clearly do not donate much to the COT's π system; otherwise, the EPR data would resemble that from a COT anion radical with an electron donating group.[37]

Tris-[8]annulenyl isocyanurate should be capable of undergoing multielectron reductions (when exposed to ample alkali metal) where each of the three identical D_{2d} COT rings attached to the isocyanurate ring accepts an electron to form a trianion triradical of **2**, $\mathbf{2}^{3(\bullet-)}$, Scheme 3.[38] No electron−electron coupling would be expected in this system, because the COT D_{4h} structures are anticipated to be nearly perpendicular to the plane of the isocyanurate ring due to steric interference with the oxygen atoms. This arrangement will minimize any overlap of the π molecular orbitals between $\mathrm{COT}^{\bullet-}$ moieties and the isocyanurate ring. Furthermore, this system would not be capable of undergoing any typical intramolecular $\pi-\pi$ interactions between the planar $\mathrm{COT}^{\bullet-}$ rings due to their inability to stack properly.

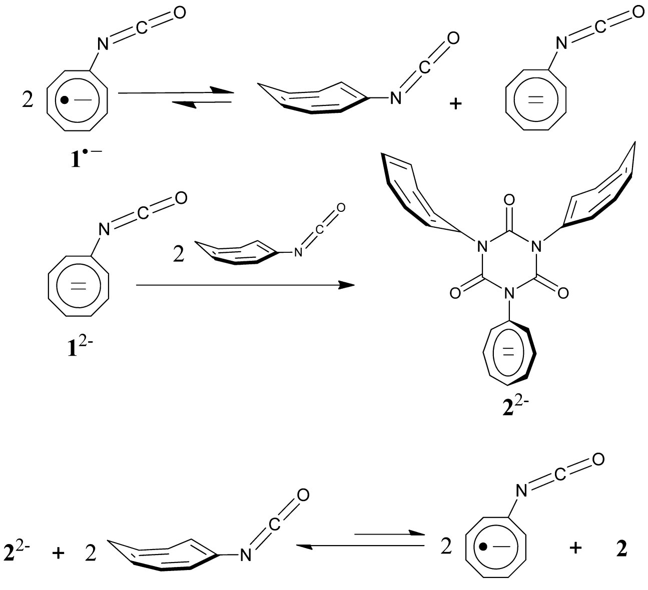
Scheme 3. Disproportionation of Tris-[8]annulenyl Isocyanurate Trianion Triradical



$\mathbf{2}^{3(\bullet-)}$ is expected to disproportionate just as other substituted [8]annulene anion radicals undergo effective disproportionation, Scheme 3.[33a,39] Therefore, the three electron reduction of **2** is also capable of generating a second spin isomer: a trianion monoradical ($\mathbf{2}^{\bullet 3-}$). Due to the equivalency of all three COT rings in **2**, both $\mathbf{2}^{3(\bullet-)}$ and $\mathbf{2}^{\bullet 3-}$ are expected to generate the same EPR pattern. The addition of more electrons to the THF solution containing both $\mathbf{2}^{3(\bullet-)}$ and $\mathbf{2}^{\bullet 3-}$ (e.g, the formation of the tetra-anion, etc.) will result in a decrease in the overall concentration of paramagnetic species in solution as more of the reduced COT rings accept a second electron. As mentioned above, the EPR spectrum shown in Figure 1 was recorded after sufficient electrons (e.g., K metal) were added to obtain the strongest EPR signal possible, and as expected, exposure of the solution to more metal results in a decrease in this signal. We therefore assert that a mixture of $\mathbf{2}^{3(\bullet-)}$ and $\mathbf{2}^{\bullet 3-}$, the dominant species in solution, gives rise to the EPR signal shown in Figure 1.

Many attempts to obtain an EPR spectrum of $C_8H_7NCO^{\bullet-}$ were performed using different conditions (e.g., different solvents, alkali metals, temperature conditions, etc.), but in all of these experiments, only the reduced form of **2** was observed. With our previous success in detecting the anion radical of PhNCO in solution,[21] it was initially unclear why we were unable to detect $C_8H_7NCO^{\bullet-}$. After further consideration, we propose that the presence of the C_8H_7NCO dianion ($\mathbf{1}^{2-}$), formed from the equilibrium disproportionation of $\mathbf{1}^{\bullet-}$ (Scheme 4), complicates our ability to detect any anion radical in solution.[33a,34b,39] (The equilibrium constant for disproportionation of C_8H_8 anion radical is ~10^9 in THF and 10^5 in HMPA.[40]) The large negative charge residing within $\mathbf{1}^{2-}$ would make this dianion a stronger anionic initiator (e.g., nucleophilic) relative to that of $\mathbf{1}^{\bullet-}$. Thus, $\mathbf{1}^{2-}$ will rapidly attack additional isocyanates in solution generating $\mathbf{2}^{2-}$, Scheme 4. Upon formation of $\mathbf{2}^{2-}$, electron transfer processes allows for regeneration of $\mathbf{1}^{\bullet-}$, and thus $\mathbf{1}^{2-}$, which further propagates the formation of **2**, Scheme 4. Room temperature NMR experiments performed support such a mechanism.

Scheme 4. Equilibrium Disproportionation of $C_8H_7NCO^{\bullet-}$ (Top Reaction) And the Production of Cyclotrimer ($\mathbf{2}^{2-}$) Initiated by $C_8H_7NCO^{2-}$[a]



[a]The bottom reaction describes the equilibrium electron transfer process to propagate the synthesis of **2**.

As further evidence that $\mathbf{1}^{2-}$ plays an important role in the formation of **2**, the potassium reduction of **1** was carried out at 293 K in THF-d_8 (needed for NMR lock) and was monitored using $^{13}C\{^1H\}$ NMR spectroscopy, Figure 3. (At room temperature, the concentration of $\mathbf{1}^{\bullet-}$ in THF is expected to be very small, Scheme 4 (top reaction).[40a]) Exposure of this solution to a small amount of potassium metal results in an immediate color change (dark green), and the NMR spectrum shows that **2** had begun to form, Figure 3B. As expected, the production of **2** continues to occur at the expense of **1** for a time, without the addition of more metal (data not shown). Further exposure to the metal surface completes the reaction with near quantitative conversion of **1** to **2**, Figure 3C. Once the production of trimer is complete, any additional exposure to metal will result in an increase in the number of COT dianion moieties in **2**.

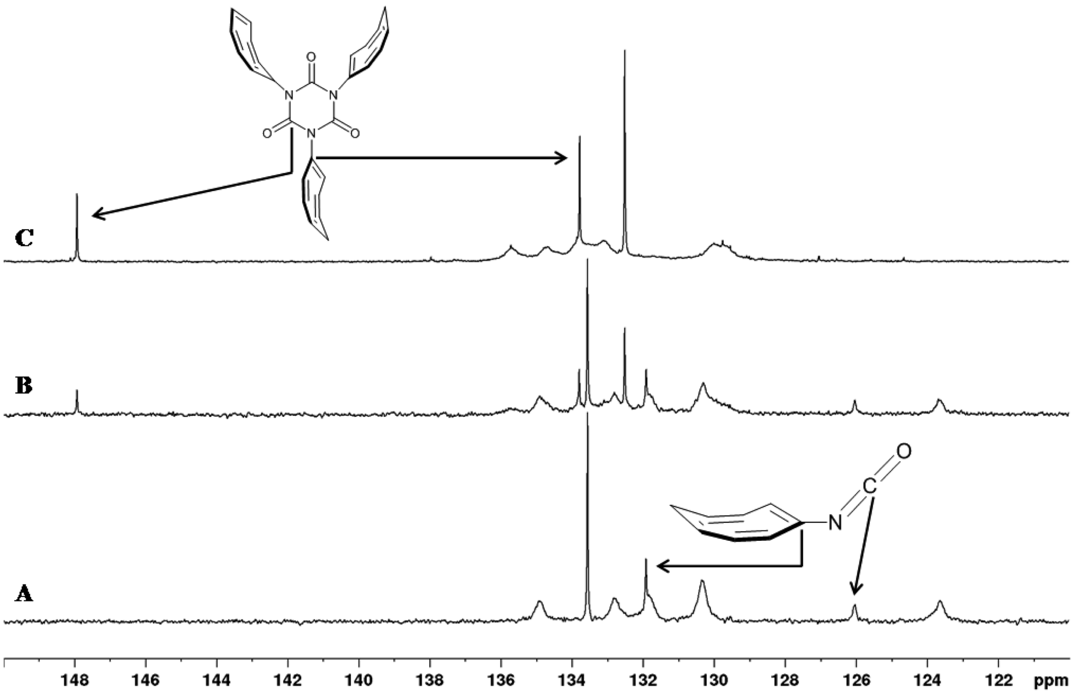


Figure 3. (A) The 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum of a THF-d_8 solution containing C_8H_7NCO at 293 K before exposure to potassium metal under vacuum. (B) NMR spectrum collected after the same THF-d_8 solution was exposed to a deficient amount of K metal at 293 K to begin conversion of isocyanate (**1**) to isocyanurate (**2**). (C) NMR spectrum revealing near quantitative conversion of **1** to **2** after further exposure of THF-d_8 solution to additional metal.

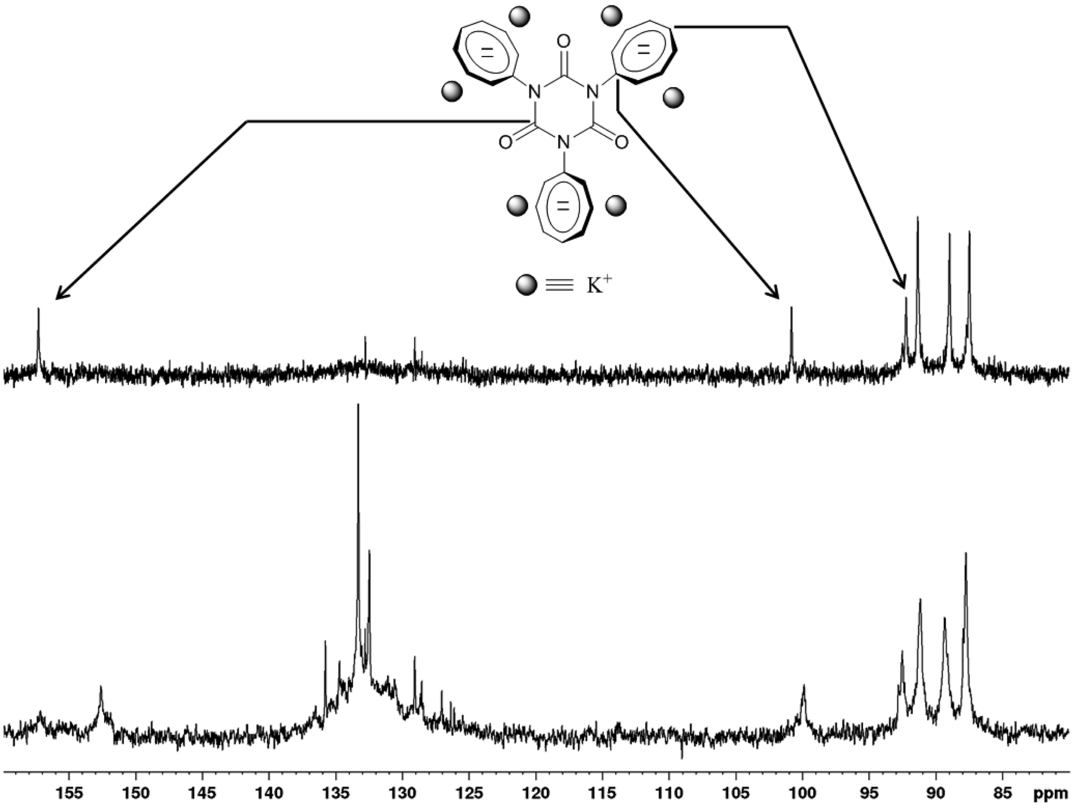


Figure 4. (Lower) The 125 MHz $^{13}C\{^{1}H\}$ NMR spectrum obtained after the THF-d_8 solution used to obtain **2** (see Figure 3) was exposed to additional potassium metal at 293 K. (Upper) NMR spectrum obtained after exhaustive reduction of this THF-d_8 solution with potassium metal. The potassium ions shown in the structure above are to indicate tight ion pairing to each of the COT^{2-} rings.

After the THF-d_8 solution (now containing **2**) was exposed to more metal, a new set of broad ^{13}C resonances centered near δ = 90 ppm are present, while those resonances for **2** have decreased considerably, Figure 4 (lower spectrum). These new peaks are

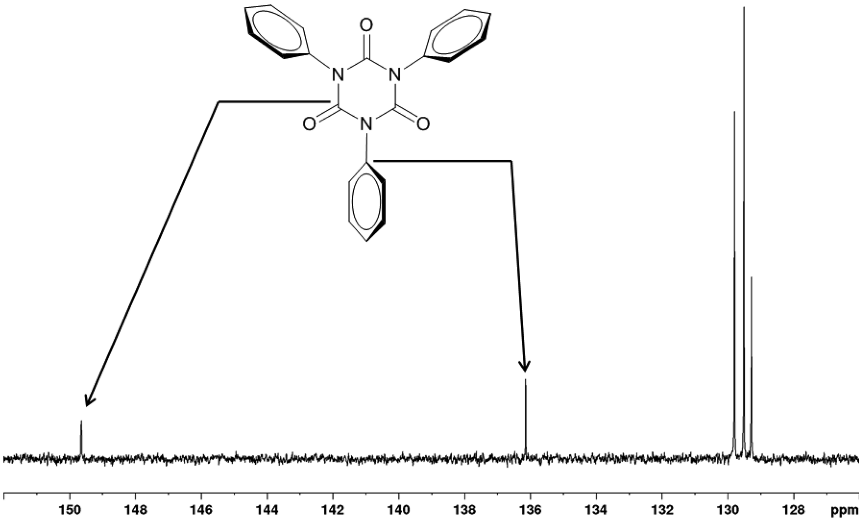
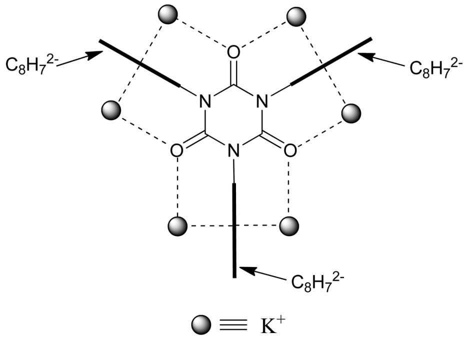


Figure 5. The 125 MHz ^{13}C{^{1}H} NMR spectrum of tris-phenyl isocyanurate in THF-d_8.

assigned to the aromatic D_{8h} COT^{2-} rings (10π e$^-$) formed as the neutral D_{2d} rings in **2** undergo a 2e$^-$ reduction. The upfield shift of these carbon resonances is a consequence of the shielding caused by these additional electrons in the π molecular orbitals of the ring. These chemical shifts match those of previously studied COT dianions with electron withdrawing substituents attached.[41] Clearly, some neutral D_{2d} COT moieties around the isocyanurate ring still remain since the characteristic resonances near δ = 133 ppm persist. Upon exhaustive reduction of **2** with potassium metal, we find a complete disappearance of any peaks from the neutral COT moieties; only the well-resolved carbon resonances from COT^{2-} rings are present in the NMR data, Figure 4 (upper). These results indicates that all three COT rings in **2** must have undergone the 2e$^-$ reduction resulting in the formation of the tris-[8]annulenyl isocyanurate *hexa-anion*, **2**$^{-6}$. Although much of this salt had precipitated out of solution as a dark green solid, the partial solubility of **2**$^{-6}$ was sufficient to obtain its NMR spectrum.[42]

A closer look at the ^{13}C NMR data also indicates that the isocyanurate carbons in **2** (Figure 3C) undergo a substantial downfield shift ($\Delta\delta_C \cong 9$ ppm) upon reduction to **2**$^{-6}$ (Figure 4 upper). This shift (δ_C = 148.0 for **2** to 157.3 ppm for **2**$^{-6}$) is somewhat unprecedented, especially since other isocyanurate compounds with aromatic substituents attached do not exhibit such a large deshielding of the carbonyl carbons.[36] For example, tris-phenyl isocyanurate is expected to have a structure similar to that of **2**$^{-6}$ where the most stable configuration of the phenyl rings is perpendicular to the isocyanurate.[21] Yet the ^{13}C NMR spectrum of this system has the chemical shift of the carbonyl carbons at δ_C = 149.6 ppm, Figure 5. Interestingly, comparing this resonance with the carbonyl resonance of **2** (Figure 3), a system that has nonaromatic (D_{2d}) COT rings attached, we find a difference of only $\Delta\delta_C$ = 1.6 ppm. Clearly, the diamagnetic ring current from the phenyl moieties in tris-phenyl isocyanurate cause a relatively small perturbation on the deshielding of the carbonyl carbons. A similar argument can be made for the D_{8h} COT^{-2} aromatic rings in **2**$^{-6}$, in that the ring current present does not fully explain the large downfield shift observed for the isocyanurate carbons.

A more plausible explanation for the observed deshielding comes from the close proximity of the K$^+$ ions to these carbonyls as a result of tight ion association with the COT^{2-} rings. In studies investigating the reduction of [8]annulene (C_8H_8) in THF with potassium metal, the dianion formed was found to be tightly ion paired with two K$^+$ ions.[43] The crystal structure of COT^{2-}/2K$^+$ has the planar COT dianion sandwiched between the metal cations where the K$^+$ ions are centered above and below the ring by approximately 2.3 Å.[44] Such a tight ion pairing arrangement likely exists for each of the three planar COT^{2-} rings in **2**$^{-6}$ (e.g., **2**$^{-6}$/6K$^+$, see Figure 4 and structure **2**$^{-6}$). A Coulombic attraction between these K$^+$ ions and the neighboring oxygen atoms would be expected in this tight ion pairing arrangement, which would enhance the polarity of these carbonyl bonds, structure **2**$^{-6}$ (dashed lines represent Coulombic attractions). The pull of electron charge density away from the carbon atoms in these bonds is manifested in the NMR data by the pronounced deshielding observed, Figure 4.



2^{-6}

■ CONCLUSION

The alkali metal reduction of [8]annulenyl isocyanate in aprotic solvents results in rapid cyclotrimerization to the tris-[8]-annulenyl isocyanurate where each of the three D_{2d} COT rings can accept a single electron, generating the trianion triradical in solution. The isocyanurate ring is found to act as an electron withdrawing substituent attached to these reduced COT rings. Upon further exposure to alkali metal, each of these D_{4h} planar COT$^{\bullet-}$ rings can be further reduced to the fully aromatic D_{8h} dianion generating the diamagnetic tris-[8]annulenyl isocyanurate hexa-anion, **2**$^{-6}$. The anion radical of [8]annulenyl isocyanate was not observed in these studies. This is a consequence of the favorable disproportionation of $C_8H_7NCO^{\bullet-}$ to form the dianion, $C_8H_7NCO^{2-}$, which is a powerful anionic initiator that readily propagates the formation of cyclotrimer. The presence of this highly reactive dianion will make it very difficult to observe the respective anion radical in solution.

The use of C_8H_7NCO to generate more complex molecular systems (e.g., poly-[8]annulenyl polyisocyanates or [8]annulene based protophanes) is of particular interest since the COT moiety undergoes significant (D_{2d} to D_{4h}) conformational change upon addition of a single electron. Such systems might exhibit unique electronic and optical properties, as has been observed with other polyisocyanates, resulting from possible intramolecular $\pi-\pi$ interactions between the planar $COT^{\bullet-}$ rings.

■ EXPERIMENTAL SECTION

Materials. Perdeuteriated tetrahydrofuran (THF-d_8) was purchased from Cambridge Isotope, Inc. and stored under vacuum over NaK.

Synthesis of [8]Annulenyl Isocyanate (C_8H_7NCO, 1). The synthesis of monobromo-cyclooctatetraene (COTBr) was carried out first based on Kreb's preparation.[30] The bromination of COT (5.0 g, 48 mmol) was performed in CH_2Cl_2 at −78 °C to give [4,2,0]-bicyclo-5,6-dibromo-1,3-octadiene. This solution was warmed to −20 °C before the dehydrohalogenation was carried out with a slight molar excess of solid potassium *tert*-butoxide. The COTBr was purified via vacuum distillation.

A molar excess of magnesium ribbon, polished with emery paper, was cut directly into a flask purged with argon gas. A THF solution containing COTBr was added slowly to the flask containing the Mg ribbon. The heterogeneous mixture was stirred at 0 °C over argon for approximately 1 h and then for an additional 4 h at room temperature until a dark blue-green colored solution was generated indicating formation of the Grignard, COTMgBr. This resulting solution was cooled to −78 °C followed by the addition of excess solid dry ice (CO_2), which generated the COT carboxylate. The reaction was quenched with water and acidified to pH = 2 with 1 M HCl. The resulting carboxylic acid, COTCOOH, was extracted from the aqueous solution using pentane. The $^{13}C\{^1H\}$ NMR spectrum confirmed the formation of the carboxylic acid, see Supporting Information. A mixture of the crude COTCOOH with a slight molar excess of $SOCl_2$ and 5 μL of DMF was dissolved in CH_2Cl_2. This solution was stirred for approximately 4 h at room temperature to ensure complete conversion to COTCOCl (confirmed by NMR). Once conversion was complete, the solvent was removed and the dark red colored liquid was dissolved in benzene.

An aqueous solution containing a 10-fold molar excess of NaN_3 was added to the benzene solution containing COTCOCl. This solution was stirred vigorously at room temperature to maximize the heterogeneous mixing of both layers and the formation of $COTCON_3$, which took about 24 h. After this time, the benzene layer (dried with anhydrous $MgSO_4$ and filtered) was refluxed for 1 h to drive the conversion of the acyl azide to the isocyanate via the Curtius rearrangement. Upon removal of the benzene, the crude isocyanate was purified via a reduced pressure distillation (1.5 Torr) where a bright yellow liquid was collected between 55 and 63 °C. NMR analysis (Figure 3A) and ESI−MS confirm formation of C_8H_7NCO with a 35% yield. See Supporting Information for ^{13}C NMR spectra of all compounds.

Reductions of [8]Annulenyl Isocyanate in HMPA and THF for EPR Experiments. The reductions were carried out by allowing HMPA solutions of C_8H_7NCO to come into contact with a sodium metal mirror at room temperature in vacuo as previously described.[21] The low temperature reductions (180 K) were carried out in a similar fashion with a THF solution containing a 1:1 mixture of C_8H_7NCO and 18-crown-6 being reduced with potassium metal. The reduction process in all of these experiments was continued until the strongest EPR signal-to-noise ratio was obtained. The EPR spectra were recorded with an X-band EPR spectrometer equipped with a variable temperature unit.

Purification of Tris-[8]annulenyl Isocyanurate. Once the reduction of C_8H_7NCO in THF was complete, a capillary containing iodine (I_2) was opened to oxidize the solution. The apparatus was opened to the atmosphere, and the THF solution was poured into an aqueous solution containing sodium thiosulfate to reduce the excess I_2. The organic material was extracted with ether, and this solution was dried with anhydrous $MgSO_4$ and filtered. The ether was removed, and the solid residue was purified via a silica gel column using a 5% MeOH/toluene mobile phase followed by a second column using a 1% MeOH/toluene mobile phase.

Reduction of [8]Annulenyl Isocyanate in THF-d_8 for NMR Experiments. C_8H_7NCO (26.0 mg, 0.180 mmol) was added directly to the bottom of the NMR tube in the apparatus shown in Figure 6. A small amount of potassium metal was placed into bulb A, which was then sealed at point B, and the entire apparatus was evacuated. The potassium metal was distilled into region C of the apparatus to form a pristine metal mirror, after which bulb A was sealed at point D.

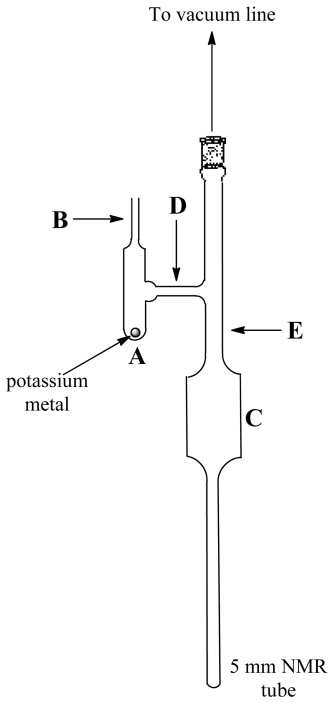


Figure 6. Glass apparatus used in the NMR experiments for the room temperature reduction of a THF-d_8 solution containing [8]annulenyl isocyanate.

Approximately 1 mL of THF-d_8 (dried over NaK) was distilled from the vacuum system directly into the NMR tube, and the evacuated apparatus was sealed from the vacuum line at point E. Prior to beginning the reduction with potassium metal, a $^{13}C\{^1H\}$ NMR spectrum of the isocyanate was obtained. Exposure to the potassium was done by simply inverting the apparatus so that the THF-d_8 solution came into contact with the metal. NMR data were collected periodically to monitor the reduction chemistry. All NMR spectra were recorded with either a 400 or 500 MHz spectrometer.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

EPR spectrum obtained from the reduction of authentic tris-[8]annulenyl isocyanurate, ESI-MS data for tris-[8]annulenyl isocyanurate and the spectroscopic data from the synthesis of C_8H_7NCO. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00859.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Wurtz, A. *Compt. Rend.* **1848**, *27*, 241−243.

(2) Ulrich, H. *Chemistry and Technology of Isocyanates*; John Wiley and Sons: New York, 1996.

(3) Delebecq, E.; Pascault, J.; Boutevin, B.; Ganachaud, F. *Chem. Rev.* **2013**, *113*, 80−118.

(4) (a) Raffel, B.; Loevenich, C. J. *J. Cell. Plast.* **2006**, *42*, 17−47. (b) Loevenich, C. J.; Raffel, B. *J. Cell. Plast.* **2006**, *42*, 289−305. (c) Wirpsza, Z. *Polyurethanes: Chemistry, Technology and Applications*; Ellis Horwood; London, 1993.

(5) Zitinkina, A. K.; Sibanova, N. A.; Tarakonov, O. G. *Russ. Chem. Rev.* **1985**, *54*, 1866−1898.

(6) Huard, K.; Bagley, S. W.; Menhaji-Klotz, E.; Preville, C.; Southers, J. A.; Smith, A. C.; Edmonds, D. J.; Lucas, J. C.; Dunn, M. F.; Allanson, N. M.; Blaney, E. L.; Garcia-Irizarry, C. N.; Kohrt, J. T.; Griffith, D. A.; Dow, R. L. *J. Org. Chem.* **2012**, *77*, 10050−10057.

(7) Rigby, J. H.; Brouet, J.; Burke, P. J.; Rohach, S.; Sidique, S.; Heeg, M. J. *Org. Lett.* **2006**, *8*, 3121−3123.

(8) Roberson, C. W.; Woerpel, K. A. *J. Am. Chem. Soc.* **2002**, *124*, 11342−11348.

(9) Barrett, A. G. M.; Betts, M. J.; Fenwick, A. *J. Org. Chem.* **1985**, *50*, 169−175.

(10) Rigby, J. H.; Shyama, S. *Org. Lett.* **2007**, *9*, 1219−1221.

(11) Lei, A.; Lu, X. *Org. Lett.* **2000**, *2*, 2357−2360.

(12) Brandi, A.; Cicchi, S.; Cordero, F. M. *Chem. Rev.* **2008**, *108*, 3988−4035.

(13) Zeidan, T. A.; Wang, Q.; Fiebig, T.; Lewis, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 9848−9849.

(14) Lewis, F. D.; Delos Santos, G. B.; Liu, W. *J. Org. Chem.* **2005**, *70*, 2974−2979.

(15) Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Cook, R.; Lifson, S. *Science* **1995**, *268*, 1860−1866.

(16) Green, M. M.; Park, J.-W.; Sato, T.; Teramoto, A.; Lifson, S.; Selinger, R. L. B.; Selinger, J. V. *Angew. Chem., Int. Ed.* **1999**, *38*, 3138−3154.

(17) Hino, K.; Maeda, K.; Okamoto, Y. *J. Phys. Org. Chem.* **2000**, *13*, 361−367.

(18) Shah, P. N.; Min, J.; Chae, C.; Nishikawa, N.; Suemasa, D.; Kakuchi, T.; Satoh, T.; Lee, J. *Macromolecules* **2012**, *45*, 8961−8969.

(19) Zhao, W.; Kloczkowski, A.; Mark, J. E.; Erman, B.; Bahar, I. *Macromolecules* **1996**, *29*, 2796−2804.

(20) Pijper, D.; Jongejan, M. G. M.; Meetsma, A.; Feringa, B. L. *J. Am. Chem. Soc.* **2008**, *130*, 4541−4552.

(21) Servos, M. A.; Smart, N. C.; Kassabaum, M. E.; Scholtens, C. A.; Peters, S. J. *J. Org. Chem.* **2013**, *78*, 3908−3917.

(22) Levin, G.; Jagur-Grodzinski, J.; Szwarc, M. *J. Am. Chem. Soc.* **1970**, *92*, 2268−2275.

(23) Ayscough, P. B.; Wilson, R. *Proc. Chem. Soc.* **1962**, 229−230.

(24) Canters, G. W.; De Boer, E. *Mol. Phys.* **1973**, *26*, 1185−1198.

(25) Peters, S. J.; Turk, M. R.; Kiesewetter, M. K.; Reiter, R. C.; Stevenson, C. D. *J. Am. Chem. Soc.* **2003**, *125*, 11212−11213.

(26) Tight ion pairing has been shown to play an important role in the reactivity of ketyl anion radicals as well. See for example: (a) Evans, A. G.; Evans, J. C.; Hodden, E. H. *J. Chem. Soc. B* **1969**, 546−547. (b) Chen, K. S.; Mao, S. W.; Nakamura, K.; Hirota, N. *J. Am. Chem. Soc.* **1971**, *93*, 6004−6013. (c) Staples, T. L.; Szwarc, M. *J. Am. Chem. Soc.* **1970**, *92*, 5022−5027. (d) Candida, M.; Shohoji, B. L. *Tetrahedron Lett.* **1995**, *36*, 6167−6170. (e) Scholz, M.; Gescheidt, G.; Daub, J. *J. Chem. Soc. Chem. Commun.* **1995**, 803−804. (f) Kamaura, M.; Hanamoto, T.; Kuwatani, Y.; Inanaga, J. *J. Am. Chem. Soc.* **1999**, *121*, 6320−6321.

(27) Symons, M. C.; Trousson, P. M. *Radiat. Phys. Chem.* **1984**, *23*, 127−135.

(28) Peters, S. J.; Klen, J. R.; Smart, N. S. *Org. Lett.* **2008**, *10*, 4521−4524.

(29) (a) Wenthold, P. G.; Hrovat, D. A.; Borden, W. T.; Lineberger, W. C. *Science* **1996**, *272*, 1456−1459. (b) Wentworth, W. E.; Ristau, W. *J. Phys. Chem.* **1969**, *73*, 2126−2133.

(30) (a) Krebs, A. *Angew. Chem.* **1965**, *77*, 966. (b) Krebs, A.; Byrd, D. *Liebigs Ann. Chem.* **1967**, *707*, 66−74.

(31) These experimental conditions are identical to those used to generate and observe via EPR the anion radical of PhNCO. See ref 21.

(32) The purpose of the 18-crown-6 ether was to generate solvated electrons in THF.

(33) For examples of substituted COT anion radicals, see: (a) Stevenson, C. D.; Concepcion, J. G.; Echegoyen, L. *J. Am. Chem. Soc.* **1974**, *96*, 5452−5455. (b) Hammons, J. H.; Bernsteln, M.; Myers, R. J. *J. Phys. Chem.* **1979**, *83*, 2034−2040.

(34) Examples of EPR data exhibiting the J−T distortion of substituted COT anion radicals. See: (a) Horvat, D. A.; Hammons, J. H.; Stevenson, C. D.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 9523−9526. (b) Stevenson, C. D.; Kiesewetter, M. K.; Peters, S. J. *J. Phys. Chem. A* **2004**, *108*, 2278−2283.

(35) Exposure to additional metal results in a diminishment and broadening of the EPR signal due to the formation of substituted COT dianion.

(36) The ^{13}C chemical shift at $d \sim 149$ ppm for the carbonyls is typical for all substituted isocyanurates. See: (a) Duff, D. W.; Maciel, G. E. *Macromolecules* **1990**, *23*, 3069−3079. (b) Lunazzi, L.; Mancinelli, M.; Mazzanti, A. *J. Org. Chem.* **2012**, *77*, 3373−3380.

(37) Stevenson, C. D.; Davis, J. P.; Reiter, R. C. *J. Phys. Chem. A* **1999**, *103*, 5343−5347.

(38) Multi-electron reduction of molecular systems with multiple COT moieties has been observed. See: Stevenson, C. D.; Reiter, R. C.; Szczepura, L. F.; Peters, S. J. *J. Am. Chem. Soc.* **2005**, *127*, 421−427.

(39) Stevenson, C. D.; Ocasio, I. *J. Am. Chem. Soc.* **1976**, *98*, 890−893.

(40) (a) Strauss, H. L.; Katz, T. J.; Fraenkel, G. K. *J. Am. Chem. Soc.* **1963**, *85*, 2360−2364. (b) Stevenson, C. D.; Consepcion, J. G. *J. Phys. Chem.* **1972**, *76*, 2176−2178.

(41) Stevenson, C. D.; Burton, R. D.; Reiter, R. C. *J. Am. Chem. Soc.* **1992**, *114*, 399−403.

(42) The solubility of $K_2(C_8H_8)$ in THF has been investigated. See: Stevenson, C. D.; Ocasio, I. *J. Phys. Chem.* **1975**, *79*, 1387−1390.

(43) Cox, R. H.; Harrison, L. W.; Austin, W. K. *J. Phys. Chem.* **1973**, *77*, 200−204.

(44) Noordik, J. H.; Van Den Hark, T. E. M.; Mooij, J. J.; Klaassen, A. A. *Acta Crystallogr.* **1974**, *B30*, 833−835.