Does the Aromatic Dianion of 1,2-Di-[13]C-[8]annulene Automerize As Does 1,2-Di-^{13}C-benzene?

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The solid dianion salt of 1,2-di-^{13}C-cyclooctatetraene was synthesized in order to measure the first [13]C−^{13}C NMR coupling in an aromatic annulene other than benzene and to find out if this dianion will undergo high-temperature automerizations analogous to those previously observed in the benzene system. The solid potassium salt was heated to over 600 °C for 2 h, and although decomposition with H_2 and CH_4 evolution takes place, there is no observable scrambling of the [13]C's. The positions of the [13]C's were monitored via NMR, which necessitated a rather complete understanding of the NMR couplings for the cyclooctatetraene dianion system. Interestingly, the $^1J_{CH}$ and $^1J_{CC}$ couplings for the aromatic COT^{2-} system of 145.9 and 55.8 Hz are all quite comparable to those recently reported for the 1,2-di-^{13}C-benzene system (158.6 and 55.8 Hz, respectively).

Introduction

There has been considerable interest in thermal automerizations[1] of hydrocarbons, heterocycles, and organometallic compounds. Perhaps the classic example of an automerization is the degenerate Cope rearrangement (e.g., of bullvalene), which allows every carbon atom to eventually occupy every position of the molecule.[2,3] Even though aromatic compounds are some of the most kinetically and thermodynamically stable organic compounds and can generally be heated to over 1000 °C without observable decomposition, they are not immune to automerization.

Scott and co-workers have studied the automerization of many polyaromatic systems[4] including naphthalene,[4a,f,h] azulene,[5] pyrene,[4d] and benz[*a*]anthracene.[4e] Benzyne has also been shown to automerize in the gas phase.[6] In 1987, Scott used 1,2-di-^{13}C-benzene to show that even benzene will automerize at 1100 °C in a flow tube with nitrogen as the carrier gas (reaction 1).[7]

The mechanism of these aromatic automerizations was unclear until recently but was thought to involve either
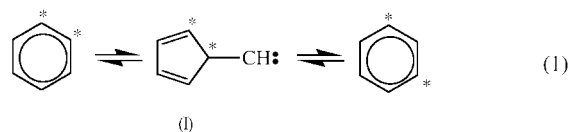
a carbene (shown in reaction 1) or a benzvalene (II).[7] At 1000 °C, the automerization of naphthalene was also thought to go through an analogous valene or carbene.[4f,h] Scott and co-workers preferred the benzvalene (II) intermediate over the cyclopentadienyl carbene intermediate for reaction 1.[4f,7]
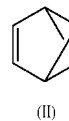
Recent experiments by Hopf et al.[8] show that benzene will automerize at temperatures as low as 800 °C when hydrogen serves as the carrier gas. Their work strongly suggests that the mechanism actually involves a radical-driven process where III as opposed to I or II is involved in the automerization mechanism.[8] The extreme interest in the automerization of aromatic molecules,[1–9] coupled with the fact that only one aromatic annulene had been studied, motivated us to investigate the possibility that the aromatic annulene dianions also might automerize at elevated temperatures.
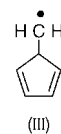
The first annulene after benzene is, of course, cyclooctatetraene (COT). The behavior of neutral COT, a 4*n* π-electron system, dramatically contrasts with that of the

(1) Automerizations are isomerizations that are degenerate in the absence of a substituent or isotopic label. Balaban, A. T.; Farcasiu, D. J. *J. Am. Chem. Soc.* **1967**, *89*, 1958.

(2) Poupko, R.; Muller, B. K.; Krieger, I. C.; Zimmermann, H.; Luz, Z. *J. Am. Chem. Soc.* **1996**, *118*, 8015. (b) Poupko, R.; Zimmermann, H.; Muller, B. K.; Luz, Z. *J. Am. Chem. Soc.* **1996**, *118*, 7995.

(3) (a) Doering, W. von E.; Roth, W. R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 115. (b) Schröder, G. *Chem. Ber.* **1964**, *97*, 3140. (c) Merenyi, R.; Oth, J. F. M.; Schröder, G. *Chem. Ber.* **1964**, *97*, 3150. (d) Seburg, R. A.; Patterson, E. V.; Stanton, J. F.; McMahon, R. J. *J. Am. Chem. Soc.* **1997**, *119*, 5847.

(4) Lawrence Scott has published a 15 paper series titled *Thermal Rearrangements of Aromatic Compounds*. The papers addressing the automerization of aromatic compounds are listed below and in refs 5 and 7. (a) Scott, L. T.; Agopian, G. K. *J. Am. Chem. Soc.* **1977**, *99*, 4506. (b) Scott, L. T.; Highsmith, J. R. *Tetrahedron Lett.* **1980**, *21*, 4703. (c) Scott, L. T. *Acc. Chem. Res.* **1982**, *15*, 52. (d) Scott, L. T.; Kirms, M. A.; Berg, A.; Hansen, P. E. *Tetrahedron Lett.* **1982**, *23*, 1859. (e) Scott, L. T.; Tsang, T.-H.; Levy, L. A. *Tetrahedron Lett.* **1984**, *25*, 1661. (f) Scott, L. T.; Roelofs, N. H. *J. Am. Chem. Soc.* **1987**, *109*, 5461. (g) Scott, L. T.; Roelofs, N. H. *Tetrahedron Lett.* **1988**, *29*, 6857. (h) Scott, L. T.; Hashemi, M. M.; Schultz, T. H.; Wallace, M. B. *J. Am. Chem. Soc.* **1991**, *113*, 9692.

(5) (a) Scott, L. T.; Kirms, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 5875. (b) Becker, J.; Wentrup, C.; Katz, E.; Zeller, K.-P. *J. Am. Chem. Soc.* **1980**, *102*, 5110.

(6) Barry, M.; Brown, R. F. C.; Eastwood, F. W.; Gunawardana, D. A.; Vogel, C. *Aust. J. Chem.* **1984**, *37*, 1643.

(7) Scott, L. T.; Roelofs, N. H.; Tsang, T. H. *J. Am. Chem. Soc.* **1987**, *109*, 5456.

(8) Zimmermann, G.; Nuchter, M.; Hopf, H.; Ibrom, K.; Ernst, L. *Liebigs Ann.* **1996**, 1407.

(9) Zeller, K.-P. *Angew. Chem.* **1982**, *94*, 448. (b) Zeller, K.-P. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 440.

benzenoid systems in that COT readily polymerizes at room temperature. Even gentle heating, 100 °C, results in the formation of dimers.[10] Higher temperature pyrolysis of COT, 400–600 °C, results in the automerization of the molecule.[10a,11a–c] In fact, Paquette and co-workers[11c] have found that "cyclooctatetraenes, as a class of compounds, are capable of thermally induced nondestructive skeletal rearrangement and that these isomerizations occur chiefly by intramolecular Diels–Alder and [1,5]-sigmatropic shift mechanisms".

The addition of two electrons, making a $(4n + 2)$ π-electron annulene, increases the stability of the molecule. In fact, the solid COT dianion salts are aromatic and have a fully planar geometry with full equilibration of the C–C distances (1.41 Å).[11d,e] Further, the solid COT dianion salts resist thermal decomposition beyond the temperature where Pyrex glass begins to soften, ca. 400 °C.[12] Despite the thermodynamic stability of K^+_2-$COT^{2-}_{(solid)}$, the COT dianion does not exist in the gas phase due to the large electron–electron repulsion energy, 444 kJ/mol.[13] Its large crystal lattice energy (1713.9 kJ/mol for the potassium salt)[14] and its aromatic character outweigh the electron–electron repulsion energy, rendering the solid salt of the cyclooctatetraene dianion thermodynamically stable.

At temperatures approaching 600 °C, the aromatic $K^+_2COT^{2-}_{(solid)}$ salt begins to decompose with the consequent liberation of both hydrogen and methane.[12] To account for the formation of a carbon bonded to four hydrogens from the dianion, where all of the carbons are bound to only one hydrogen, a carbene intermediate that is analogous to that considered in the benzene automerization (I)[7] was proposed (IV).[12] An intermediate like this could accommodate automerization as shown in reaction 2 as well as decomposition only if the first step were reversible. However, due to the extreme reactivity of carbenes, this seems unlikely.


$$(2)$$

(IV)
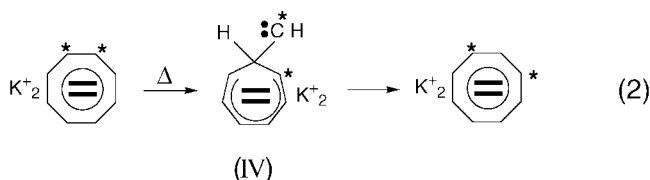
Scott and co-workers[7] elegantly observed the benzene automerization by heating 1,2-di-¹³C-benzene and then synthesizing the dinitrobenzenes from the products. The relationships between the ¹³C's and the substituents proved the point. The facts that the COT dianion has

eight carbons and does not undergo substitution render an analogous approach unwieldy. Fortunately, however, NMR-coupling information can be utilized to determine the connectivity relationship between two ¹³C's in the di-¹³C-COT dianion. This, however, would require a spin analysis of the ¹H and ¹³C NMR of 1,2-di-¹³C-COT²⁻. Given that this type of analysis has yet to be accomplished for any annulene dianion, this information would also be of value. The isotropic part of the spin–spin coupling tensors contains information on the electronic structure and is consequently of fundamental significance.

Results and Discussion

Heating a 30:1 mixture of acetylene (¹³C in natural abundance) and di-¹³C-acetylene in tetrahydrofuran (THF) under the conditions of the Reppe reaction in a sealed tube to 90 °C produced a mixture of COT, mono-¹³C-COT, and 1,2-di-¹³C-COT in a ratio of 100:8.8:15 (see the Experimental Section). The amount of tri-¹³C-labeled material is very small and henceforth will be ignored. The reduction of this mixture of isotopic isomers of COT in THF-d_8 yielded the dark red solution of the dianion (COT²⁻,K²⁺). The two ¹³C's in 1,2-di-¹³C-COT²⁻ are in magnetic environments that are different from those for the (1,3), (1,4), or (1,5)-di-¹³C-COT dianions in that the two ¹³C's in 1,2-di-¹³C-COT²⁻ each have one ¹³C neighbor and one ¹²C neighbor. In all of the other isotopomers of di-¹³C-COT²⁻, each ¹³C has two ¹²C neighbors. Thus, the 1,2-di-¹³C-COT dianion should yield an NMR pattern very different from those of the other isotopomers. Further, the 1,2-di-¹³C-COT dianion resonance should occur at a slightly higher field than those of the other isotopomer dianions. It has been shown that the difference between the resonances of aromatic compounds linked ¹²C–¹³C–¹³C–¹²C and a ¹²C–¹³C–¹²C is about 20 ppb.[7] The proton-decoupled ¹³C NMR spectra of our samples agree with this and clearly show that the resonance frequencies for the ¹³C's with an adjacent ¹³C are shifted by 19 ppb from those attached to only ¹²C's, Figure 1.

The proton-coupled (using gated decoupling) ¹³C NMR spectrum of the potassium dianion salt of the mixture of cyclooctatetraene isotopic isomers (structures V and VI)

V   VI
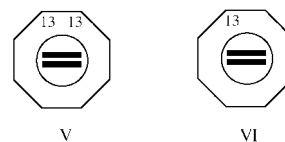
exhibits the strong second-order effects expected for the ¹³C–¹³C and ¹³C–¹H couplings in this system (Figure 2). Since the solution contained a mixture of mono- and dilabeled cyclooctatetraenes, a sample containing the natural abundance of ¹³C-COT (VI) was reduced with potassium and the proton-coupled spectrum recorded. The splitting of the signal into two multiplets is due to the large one-bond ¹H–¹³C coupling constant or possibly some sum involving this coupling constant. This NMR spectrum was simulated using a line width of 2.5 Hz and the coupling constants shown in Table 1. It should be noted here that other combinations of coupling constants would give a similar spectrum.

The completely coupled NMR spectrum of 1,2-di-¹³C-COT dianion (Figure 3) not only contains the ¹H–¹³C

(10) (a) Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Ann.* **1948**, *506*, 1. (b) Lord, R. C.; Walker, R. W. *J. Am. Chem. Soc.* **1954**, *76*, 2518. (c) Jones, W. O. *J. Chem. Soc.* **1953**, 2036. (d) Jones, W. O. *Chem. Ind.* **1955**, 16. (e) Schroder, G. *Chem. Ber.* **1964**, *97*, 3131. (f) Schroder, G.; Kirsch, G.; Oth, J. F. M. *Chem. Ber.* **1974**, *107*, 460.

(11) (a) Paquette, L. A.; Meisinger, R. H.; Wingard, R. E., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 9224. (b) Paquette, L. A.; Oku, M. *J. Am. Chem. Soc.* **1974**, *96*, 1219. (c) Paquette, L. A.; Oku, M.; Heyd, W. E.; Meisinger, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 5815. (d) Katz, T. J. *J. Am. Chem. Soc.* **1960**, *82*, 3784, 3785. (e) Noordlik, J. H.; van der Hark, T. E. M.; Mooij, J. J.; Klaassen, A. K. K. *Acta Crystallogr. Sect. B* **1974**, *30*, 833.

(12) Stevenson, C. D.; Fico, R. M., Jr. *J. Org. Chem.* **1995**, *60*, 5452.

(13) Dewar, M. J. S.; Harget, A.; Haselbach, E. *J. Am. Chem. Soc.* **1969**, *91*, 7521.

(14) (a) Stevenson, C. D.; Zigler, S. S. *J. Am. Chem. Soc.* **1981**, *103*, 2513. (b) Stevenson, C. D.; Zigler, S. S.; Reiter, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 6057. (c) The solid dianion salt is just $K^+_2COT^{2-}$ and does not have solvent (THF) incorporated in it; see: Concepcion, R.; Reiter, R. C.; Stevenson, C. D. *J. Am. Chem. Soc.* **1983**, *105*, 1778.
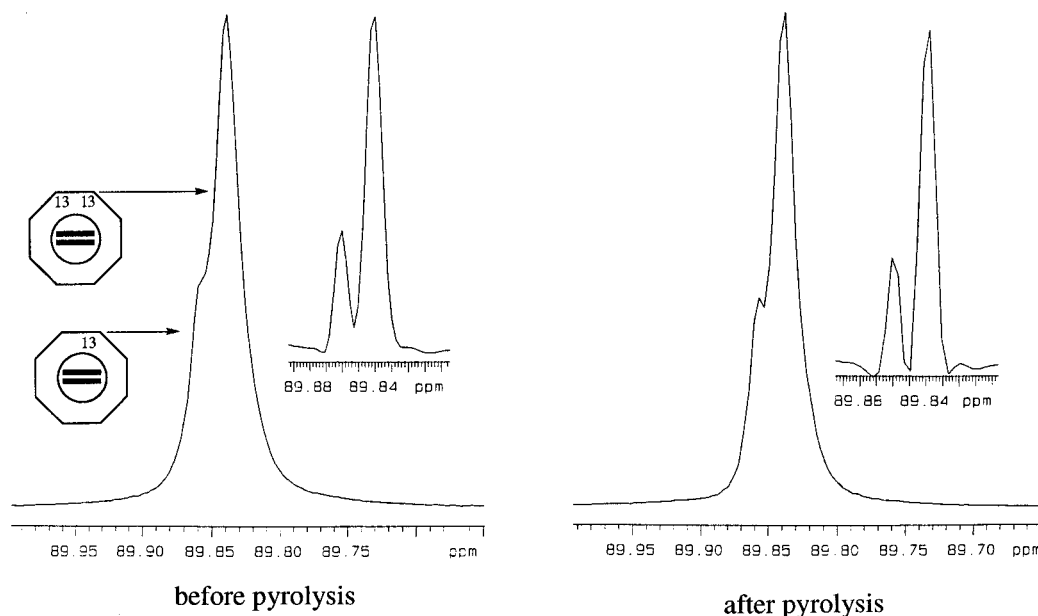
Figure 1. (Left) proton-decoupled 75 MHz ^{13}C NMR spectrum of the potassium salt of the 1,2-^{13}C-COT dianion. The downfield peak is due to mono-^{13}C-COT^{2-}, and the upfield peak 19 ppb upfield is due to the di-^{13}C-COT^{2-}. The relative intensity of the two peaks agrees with the predicted 8.8:15 ratio. The inset shows the spectrum processed using a resolution enhancement function. (Right) recording of the same sample but after the solid dianion was heated to 370 °C for 2 h. Note that the ratio of ^{12}C$-^{13}$C$-^{13}$C$-^{12}$C to ^{12}C$-^{13}$C$-^{12}$C linkages are the same.
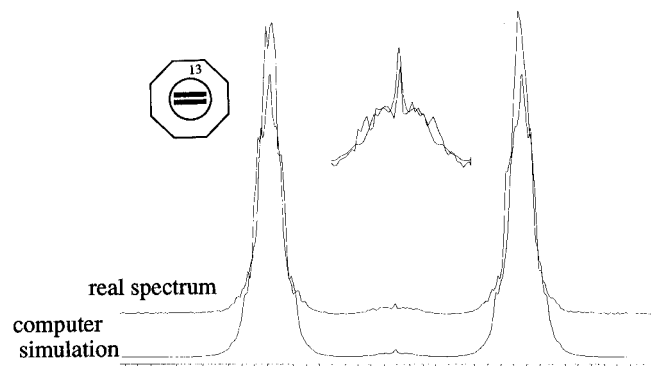

Figure 2. Completely coupled 75 MHz ^{13}C NMR spectrum of the dipotassium cyclooctatetraene dianion in THF-d_8 at 25 °C and the computer simulation obtained utilizing the coupling constants reported in Table 1 and a line width of 2.5 Hz. The inset is a vertically expanded view of the center portion of the spectrum.

Table 1. Coupling Constants (Hz) Used for the ^{13}C NMR Simulations of the ^{13}C$_1$-Cyclooctatetraene Dianion and the ^{13}C$_2$-Cyclooctatetraene Dianion along with the Known[15] Coupling Constants for Benzene

coupling	1,2-di-^{13}C$-$COT^{2-}	per-^{13}C-benzene[15b]
$^1J_{C-H}$	145.9	158.5
$^2J_{C-H}$	−1.25	1.0
$^3J_{C-H}$	10.95	7.5
$^4J_{C-H}$	−4.22	−1.28
$^5J_{C-H}$	9.45	
$^1J_{C-C}$	55.8	55.8
$^3J_{H-H}$	9.8	7.5
$^4J_{H-H}$	1.10	1.4
$^5J_{H-H}$	−0.31	0.65

splittings but also has a large ^{13}C$-^{13}$C splitting, which turns out to be close to that reported for the benzene system[15] (Table 1).

The NMR simulations of the mono-^{13}C-COT^{2-} and di-^{13}C-COT^{2-} spectra were combined using a scaling of
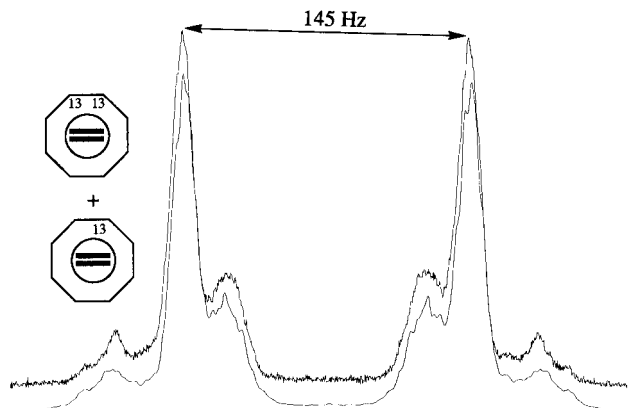

Figure 3. Completely coupled 75 MHz ^{13}C NMR spectrum of the 8.8:15 mixture of mono-^{13}C-cyclooctatetraene dianion and 1,2-di-^{13}C-cyclooctatetraene dianion in THF-d_8 at 25 °C and the computer simulation (below) obtained utilizing the coupling constants reported in Table 1 (line width = 2.7 Hz).

8.8:15 to yield the computer simulation of the ^{13}C NMR spectrum of the mixture of ^{13}C-labeled dianions, Figure 3. The splitting between the two large complex outside multiplets is due to the ^{13}C$-^{13}$C coupling $^1J_{^{13}C-^{13}C} = 55.8$ Hz. The coupling constants, $^2J_{^{13}C-^{13}C}$, $^3J_{^{13}C-^{13}C}$, and $^4J_{^{13}C-^{13}C}$, would be much smaller than $^1J_{^{13}C-^{13}C}$. Hence, any scrambling of the ^{13}C's (automerization) would dramatically alter the morphology of the spectrum of V.

With this understanding of the ^{13}C NMR spectrum of our mixture of isotopic isomers of the COT dianion, we were ready to carry out the thermolysis studies. After the NMR spectra were recorded, the solvent (THF-d_8) was removed under vacuum conditions. The samples of the solid dianion salts were then heated from 300 to 1000

(15) (a) Kaski, J., Vaara, J.; Jokisaari, J. *J. Am. Chem. Soc.* **1996**, *118*, 8879. (b) Diehl, P.; Bosiger, H.; Zimmermann, H. *J. Magn. Reson.* **1979**, *33*, 113−26.
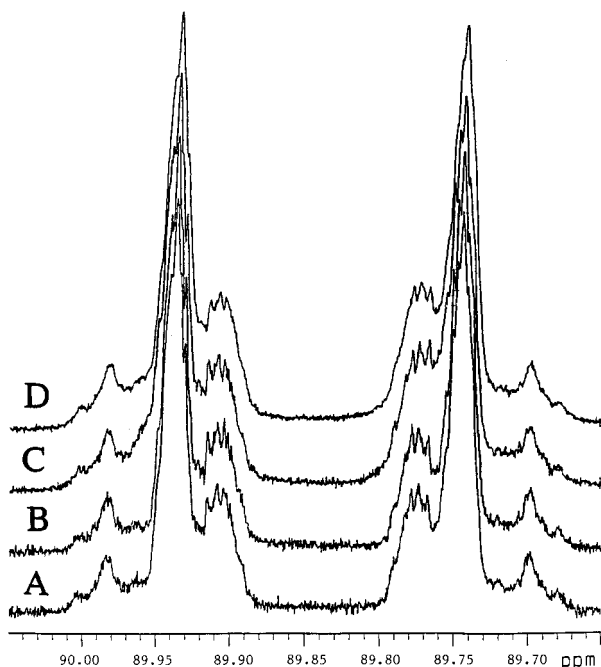
Figure 4. Proton-coupled 75 MHz ^{13}C NMR spectra of an 8.8:15 mixture of mono-^{13}C-cyclooctatetraene dianion and 1,2-di-^{13}C-cyclooctatetraene dianion. A. Prior to pyrolysis. B. After pyrolysis of the solid dianion salts at 300 °C for 5 min. C. After pyrolysis of the solid dianion salts at 370 °C for 5 min. D. After pyrolysis of the solid dianion salts at 370 °C for 2 h.
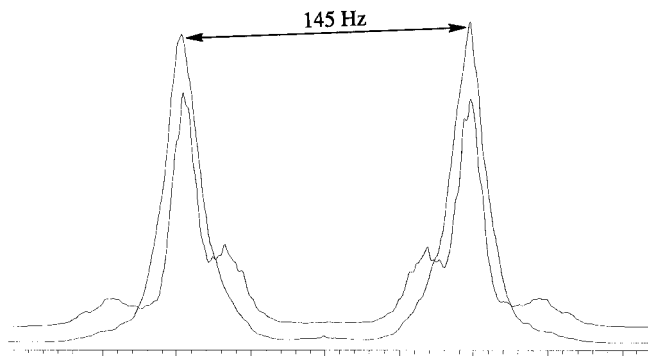

Figure 5. Simulated ^{13}C NMR spectra of the sample described in Figures 3 and 4 with (lower) and without (upper) automerization. It was assumed the automerized sample had undergone complete scrambling of the [13]C's. Note the loss of the large $^1J_{^{13}C-^{13}C}$ in the hypothetically automerized sample.

°C for periods of 5 min to 2 h. At the higher temperatures (>600 °C), there was some decomposition of the dianion to form methane, hydrogen, and polymer as previously described.[12] The readdition of THF-d_8, while high vacuum conditions were maintained, resulted in the dissolution of the undecomposed dianions, which could then be resubmitted to NMR analysis, Figure 4.

Surprisingly, all of the post-thermolysis samples yielded spectra nearly identical to those obtained prior to thermolysis, Figure 4, and spectra similar to those expected after automerization (Figure 5) were not observed. Hence, none of the samples exhibited any indication of automerization. An overlay of the NMR spectra shows that there is no apparent change in the chemical shifts, the line widths, or the relative line intensities in the spectra before and after heating.

These results are quite consistent with the conclusions

of Hopf et al.[8] An intermediate analogous to II would be very unlikely as it would involve the very unstable antiaromatic cycloheptatrienyl anion depicted in structure VII. Hence, we predict that all of the dianions of $4n\pi$-electron annulenes, in general, will resist automerization, as antiaromatic anionic intermediates would be mechanistically required.

(VII)
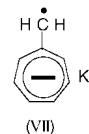
Conclusions

High-temperature pyrolysis of the aromatic cyclooctatetraene dianion does not automerize the planar COT ring system. However, neutral aromatic systems have been shown to do just the opposite and readily automerize in the gas phase.[4,5,7] Unlike the neutral aromatics, the cyclooctatetraene dianion is not stable in the gas phase due to large electron−electron repulsions.[9] While the thermal automerizations of the aromatics and the pyrolysis of the cyclooctatetraene dianion are both thought to go through similar carbene intermediates, the cyclooctatetraene dianion does not automerize. Hence, when the solid potassium salt of the dianion was heated, no apparent change in the gated decoupled ^{13}C NMR spectrum was observed. This is due to the fact that the solid salt is stabilized by a large crystal lattice energy.[10] When sufficient energy is applied to the system to overcome this lattice energy, the ring contracts, producing a carbene intermediate. The smaller ring thus has a larger electron−electron repulsion energy, and the electrons are transferred back to the metal cation. Thus, unlike the neutral aromatics, there is no aromatic conformer to return to. So, when sufficient energy is applied to the system to overcome this lattice energy and permit automerization the resulting dianion thermally decomposes. Finally, it is interesting to note that the J_{CH} and J_{CC} couplings recently reported for benzene[15a] are all quite comparable to those for the aromatic COT^{2-} system, Table 1.

Experimental Section

Synthesis. Cyclooctatetraene was purchased from Aldrich Chemical Co., Inc., and vacuum distilled prior to use. 1,2-Di-^{13}C-cyclooctatetraene was synthesized via the Reppe[10,16] synthesis by condensation of a mixture of 4.46 mmol of per-^{13}C-acetylene (Cambridge Isotope Laboratories) and 134 mmol of acetylene into a thick-walled glass tube that was charged with 92.1 mg of Ni(acac)$_2$ and 3 mL of THF. The apparatus was sealed from the vacuum line and placed into a 76 mL steel bomb. The bomb was then placed in a 90 °C oil bath for 9 h following our previously published protocol.[16] Since the desired reaction is $^{13}C_2H_2 + 3^{12}C_2H_2 \rightarrow$ 1,2-di-[13]COT and no tetralabeled cyclooctatetraenes were desired, the ratio of $^{13}C_2H_2$ to $^{12}C_2H_2$ was kept low. The experimental and statistical product ratio of $^{12}C_8$:$^{13}C_1$:$^{13}C_2$ cyclooctatetraenes is 100:8.8:13.3. The 8.8% mono-^{13}C-COT is due to the natural abundance

(16) Perdeuterated, per-^{13}C, and perdeuterated-per-[13]C-[8]annulenes have been synthesized in the laboratory using appropriately labeled acetylenes (MSD Isotopes) see: (a) Lippincott, E. R.; Lord, R. C.; McDonald, R. C. *J. Am. Chem. Soc.* **1951**, *73*, 3370. (b) Stevenson, C. D.; Peters, S. J.; Reidy, K. A.; Reiter, R. C. *J. Org. Chem.* **1992**, *57*, 1877. (c) Stevenson, C. D.; Burton, R. D.; Reiter, R. C. *J. Am. Chem. Soc.* **1992**, *114*, 4514. (d) The 1,2-[13]C−COT system was synthesized in an analogous manner.
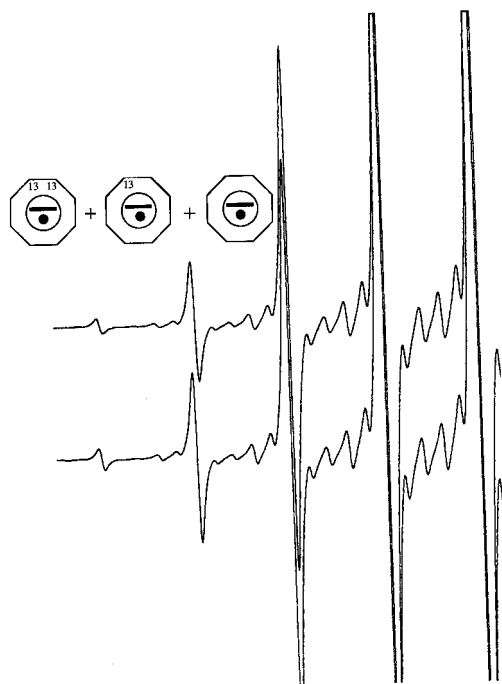
Figure 6. Low-field half of the EPR spectrum of the anion radicals resulting from the sodium reduction of our mixture of isotopically substituted cyclooctatetraenes in HMPA (upper). This spectrum is best simulated (lower) using a ratio of 100:8.8:15 for COT$^{\cdot-}$:mono-^{13}C—COT$^{\cdot-}$:1,2-di-^{13}C—COT$^{\cdot-}$. The proton-coupling constant is 3.196 G, the carbon-coupling constant is 1.25 G, and the line width is 0.2 G. The spectrum was recorded with a modulation amplitude of 0.05 G, and the larger lines due to COT$^{\cdot-}$ are off scale.

of carbon-13. The final product was purified using a GOW-MAC prep-GC series 580 on an 8 ft × 1/4 in. 20% DC-710 on a Chromo-P 80/100 mesh column at 150 °C.

Reductions. Samples of the dianions of the resulting cyclooctatetraenes were generated via exhaustive reduction in an evacuated apparatus on a freshly distilled potassium metal mirror under high vacuum in THF-d_8 that had been dried over NaK$_2$. EPR spectra recorded from the anion radicals prior to complete reduction exhibited all three anion radicals. The anion radical of 1,2-di-^{13}C-cyclooctatetraene can be clearly seen when our mixture is reduced in hexamethylphosphoramide (HMPA) with sodium metal, and the resulting EPR spectrum is best simulated using a ratio of 100:8.8:15 for COT$^{\cdot-}$:mono-
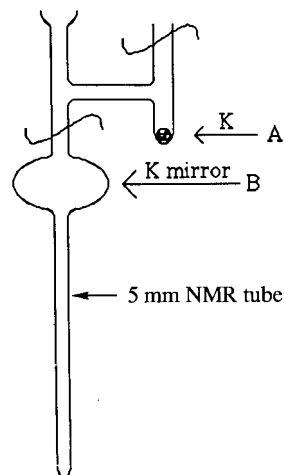

Figure 7. Apparatus used to generate the cyclooctatetraene dianions. The potassium mirror was generated via distillation of a piece of potassium metal from bulb A into bulb B with the entire apparatus under high vacuum.

^{13}C-COT$^{\cdot-}$:1,2-di-^{13}C-COT$^{\cdot-}$ respectively, Figure 6. The EPR spectra were recorded on an IBM (Bruker) ER-200D spectrometer and simulated using EWSIM, by Scientific Software Services, Bloomington, IL, 1992. Proton-decoupled and gated-decoupled (NOE but no decoupling) spectra were recorded at room temperature. NMR simulations were generated using version 4.0.1 of gNMR by Cherwell.

Pyrolysis of the 1,2-Di-^{13}C-cyclooctatetraene Dianion. The dianion solutions were generated via exhaustive reduction of the THF-d_8 solutions on the freshly distilled potassium metal mirror in bulb B of the apparatus shown in Figure 7. After the NMR spectra of the dianion solutions were recorded, the THF-d_8 was removed by cooling of bulb B to liquid nitrogen temperature. The remaining solid salt in the NMR tube was then placed in a sand bath oven where the temperature was monitored with a nickel—chromium vs nickel—aluminum thermocouple by Omega (−200—1250 °C). The dianion solutions were regenerated after both sides of the apparatus returned to room temperature.