$CH_2—CF_2$), 4.40 (t, 2 H, COO—CH_2), 3.28 (s, 2 H, CH_2—CO), 6.0 (m, 2 H, CH_2=C); IR (KBr) 1745, 1700 (CO), 1645 (C=C), 1230, 1160 (CF) cm^{-1}. Anal. Calcd for $C_{17}H_9O_4F_{21}$: C, 30.20; H, 1.34. Found: C, 30.41; H, 1.47.

Bis(1*H*,1*H*-perfluorooctyl)itaconamide, 5. The synthesis of **5** is described elsewhere.[23]

***N*,*N*-Bis(((2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-eicosafluoroundecyl)muconyl)ethyl)taurine, 6.** 1*H*,1*H*,11*H*-Eicosafluoroundecanol (10.64 g, 0.02 mol) was added slowly to a refluxing solution of 3.58 g (0.02 mol) of *trans*,*trans*-muconyl chloride[24] in dry chloroform (200 mL). After 3 h the chloroform was evaporated and the residue was distilled in vacuo. The resulting monoester monoacid chloride has a boiling point of 110 °C (0.03 torr): yield 9.85 g (73); mp 76–78 °C. **6** was obtained by refluxing 3.37 g (5 mmol) of the above hexadienoic acid mono 1*H*,1*H*,11*H*-eicosafluoroundecanoyl ester monoacid chloride with 0.53 g (2.5 mmol) of *N*,*N*-bis(2-hydroxyethyl)-2-aminoethanesulfonic acid in dry chloroform (600 mL) for 3 days. Purification of the crude product was achieved by repeated recrystallization from chloroform: yield 2.5 g (67%); mp 108 °C; ^1H NMR ($CDCl_3$) δ 2.7–3.6 (m, 8 H, $(CH_2)_2NCH_2CH_2SO_3$), 4.2 (br t, 4 H, $COOCH_2$), 4.64 (t, 4 H, $J = 15$ Hz, $CF_2—CH_2$), 6.03 (t, 2 H, $J = 50$ Hz, t, H—CF_2), 6.11–6.41 (m, 2 H, CH—COO), 7.20–7.48 (m, 2 H, CH—C—COO); IR (KBr) 1736 (CO), 1619, 1594 (C=C), 1203 (CF) cm^{-1}. Anal. Calcd for $C_{40}H_{27}O_{11}NSF_{40}$: C, 32.25; H, 1.81; N, 0.94, Found: C, 31.97; H, 1.63; N, 0.77.

Synthesis of the Comparable Hydrocarbon Compounds. For the synthesis of **7**, 13.4 g (65 mmol) of dicyclohexylcarbodiimide dissolved in dry chloroform (150 mL) was added to a solution of 14.2 g (50 mmol) of steric acid, 3 g (25 mmol) of bis(2-hydroxyethyl)methylamine, and 100 g of (dimethylamino)pyridine in dry chloroform (200 mL) at 0 °C. After the solution was stirred for 12 h at room temperature the urea was separated by filtration. The solution was washed 3 times with saturated sodium bicarbonate and with water. The crude reaction product was purified by liquid chromatography on silica gel by using methylene chloride as eluent and then recrystallized from ether: yield 10.6 g (65%); mp 49 °C; ^1H NMR ($CDCl_3$) δ 0.89 (t, 6 H, C–CH_3), 1.25 (br s, 60 H, $(CH_2)_{15}$), 2.25 (t, 4 H, CH_2–COO), 2.40 (s, 3 H, N–CH_3), 2.72 (t, 4 H, CH_2–N), 4.18 (t, 4 H, COO–CH_2); IR (KBr) 1735 (CO) cm^{-1}. Anal. Calcd for $C_{41}H_{81}NO_4$: C, 75.52; H 12.52; N, 2.15, Found: C, 75.23; H, 12.22, N, 1.96.

9 was synthesized as described by Fendler et al.[25] The same procedure was used to synthesized **8**. **10** was synthesized by the method described for **4**: yield 83%; mp 79–80 °C; ^1H NMR (CD_3OD) δ 0.89 (t, 3 H, CH_3), 1.28 (br, 24 H, $(CH_2)_{12}$), 3.27 (s, 2 H, CH_2—COO), 4.14 (t, 2 H, COO—CH_2), 6.01 (m, 2 H, CH_2=C); IR (KBr) 1730, 1692 (CO), 1640 (C=C) cm^{-1}. Anal. Calcd for $C_{19}H_{34}O_4$: C, 69.94; H, 10.43. Found: C, 69.61; H, 10.71.

Registry No. 1, 92844-67-2; **2**, 92844-68-3; **3**, 92844-69-4; **4**, 92844-70-7; **5**, 29883-10-1; **6**, 92844-71-8; **7**, 13998-76-0; **8**, 92844-72-9; **9**, 84454-87-5; **10**, 25328-98-7; $(HOCH_2CH_2)_2NMe$, 105-59-9; $CF_3(CF_2)_7CH_2C(O)Cl$, 64018-23-1; $H(CF_2)_{10}CH_2OH$, 307-70-0; $H(CF)_{10}CH_2OC(O)CH=CHCH=CHC(O)Cl$, 92844-73-0; $(HOCH_2CH_2)_2N(CH_2)_2SO_3H$, 10191-18-1; $CF_3(CF_2)_9(CH_2)_2OH$, 865-86-1; $CH_3(CH_2)_{13}OH$, 112-72-1; stearic acid, 57-11-4; *trans*,*trans*-muconyl chloride, 58823-55-5; itaconic anhydride, 2170-03-8.

Spin Distributions in Bridged Bis(cyclooctatetraene) Anion Radicals. Dicyclooctatetraenylmethane and Dicyclooctatetraenyldimethylsilane

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Abstract: The title compounds as well as some of their alkyl-deuterated derivatives and 1,2-dicyclooctatetraenylethane were synthesized and reduced with alkali metals in hexamethylphosphoramide (HMPA). The anion radical of COT–$(CH_2)_2$–COT has the spin density localized in one of the two COT rings as evidenced by the coupling constants observed: $a_{2H} = 2.55$ G, $a_{4H} = 2.00$ G, and $a_{3H} = 4.37$ G. These values are very similar to those measured for *n*-butylcyclooctatetraene. The anion radical of COT–CH_2–COT exhibits a totally different ESR spectrum where the spin density is clearly delocalized over the two COT moieties, with coupling constants $a_{4H} = 4.03$ G, $a_{2H} = 3.30$ G, and $a_{8H} = 0.73$ G. No hyperfine interaction was observed to occur with the bridging methylene, since the ESR spectrum of $(COT–CD_2–COT)^{-\cdot}$ was identical with that of the undeuterated compound. Comparison of the ESR spectrum of $(COT–CH_2–COT)^{-\cdot}$ with that previously reported for $(COT–COT)^{-\cdot}$ shows that the molecular orbital symmetry is similar, but the energy ordering of the two HOMO's is reversed. Conjugation between the two COT rings via an interannular interaction results in spin delocalization over the entire molecule while the methylene splitting is not observable. This conjugation is not possible for $(COT–Si(CH_3)_2–COT)^{-\cdot}$ where the spin is clearly localized in only one ring: $a_{4H} = 5.13$ G and $a_{3H} = 1.25$ G. These values have been used to determine the orbital degeneracy splitting of the COT by the $–Si(CH_3)_2–COT$ substituent ($\epsilon = -0.82$ kcal/mol). This value is the highest ever reported for any substituent on a COT system.

Electrochemical and chemical reduction of cyclooctatetraene (COT) and substituted COT's have been widely investigated for many years.[1-3] The anion radical of COT has been shown to undergo electron exchange only with the dianion, since exchange between the anion radical and the neutral molecule is slow due to the required flattening of the ring upon one electron reduction.[4] This is the same reason why electrochemical reduction shows an electrochemically irreversible first wave for the formation of the anion radical followed by a reversible one leading to the formation of the aromatic (in the Hückel sense) dianion.[5] That the anion radical and dianion of COT can be formed at all is itself a re-

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[†] University of Miami.

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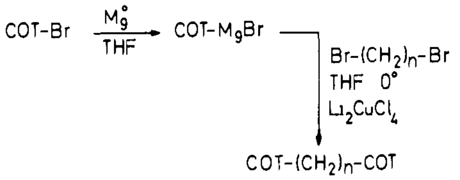
Scheme I

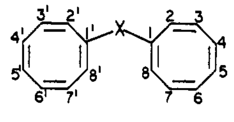


markable observation in view of the strain energy required to flatten an eight-membered ring and the electron–electron repulsion energy present in the dianion.

Electron transfer between aromatic anion radicals connected by an alkyl bridge has been studied by Szwarc and Shimada for the case where the aromatic moiety is naphthalene and the alkyl bridge is a polymethylene chain ranging in size from 3 to 20.[6] Intramolecular electron transfer rates were measured in these studies and found to be a pronounced function of the size of the bridging chain. When the number of bridging methylenes (*n*) was 3 and 4, the ESR signal observed after reduction corresponded to that of the "hypothetical" dimer (naphthalene–$(CH_2)_n)_2^{-\cdot}$. This indicates that electron transfer between the two naphthalene moieties is fast on the ESR time scale so that the unpaired electron is, in fact, completely delocalized over the entire molecule.

No equivalent studies have been reported where the alkyl-bridged moieties are COT. The only analogue known is the bis(cyclooctatetraenyl) (BCOT) anion radical, which exhibits complete spin delocalization over the molecule.[7]

We report here the synthesis of three new compounds (and some deuterated analogues), which have two COT moieties connected by an alkyl chain or by a dimethyl silane linkage, **1–3**, as well as the alkali metal reduction and ESR spectra of these systems.

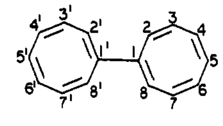


X = $-CH_2-$: **1**

= $-CD_2-$: **1a**

= $-(CH_2)_2-$: **2**

= $-Si(CH_3)_2-$: **3**



4

Experimental Section

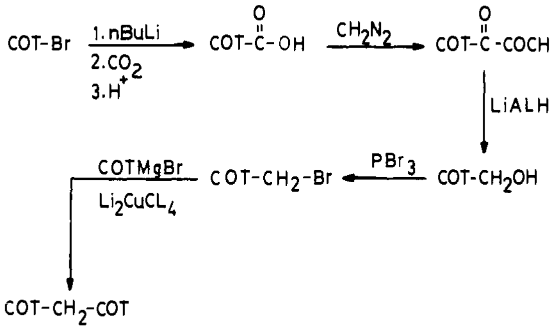
General. ESR spectra were recorded by using the X-band of a Varian E-9 or IBM ER-200D SRC spectrometer operating at room temperature (24 °C), unless otherwise specified in the text. Samples were prepared under vacuum (10^{-3} mm) by reaction of a 10^{-3} M solution of the compound in dry HMPA, as described in detail elsewhere.[8] Compound **3** reacts with Na or K in HMPA at room temperature to yield nonparamagnetic, decomposed solutions. For this reason **3** was reduced with Na in liquid NH_3 while maintaining the temperature at −78 °C.

NMR spectra were recorded on a JEOL FX-90Q or Varian FT-80A spectrometer. Chemical shifts were referenced to internal Me_4Si.

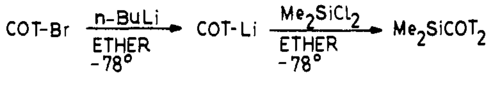
Synthesis. Compounds **1**, **1a**, and **2** were prepared by following the sequence presented in Scheme I.

Preparation of Bromocyclooctatetraene ((COT)Br). Bromocyclooctatetraene ((COT)Br) was prepared from COT (Aldrich) and bromine by following literature procedures[9] in 75% yield. This procedure consists of low-temperature bromination in CH_2Cl_2 followed by dehydrohalogenation with potassium *tert*-butoxide in the same reaction flask. Although the procedure is somewhat lengthy (ca. 18 h), it is much more convenient and efficient than the older method where the $(COT)Br_2$ had to be isolated and dehydrohalogenated with phenyllithium.[10]

Scheme II



Scheme III



(COT)MgBr was prepared from (COT)Br and Mg turnings in dry THF.[11] (COT)Br (6.0 g, 37.8 mM) dissolved in 120 mL of dry THF was slowly added (1 h) to 1.6 g of magnesium turnings in 120 mL of dry THF. Initial addition was carried out at room temperature, but as soon as there was evidence that the reaction had started the mixture was cooled in an ice bath. After addition was complete, the mixture was stirred for an additional 2 h at 0 °C and for an additional 2 h at room temperature. A 0.2-mL aliquot was titrated and the reaction was shown to have proceeded to 94% completion. The dark blue-green solution so formed was transferred with a syringe to a clean, three-necked, round-bottomed flask which was kept under a dry nitrogen atmosphere and immersed in an ice bath.

Preparation of 1. While the (COT)MgBr solution was vigorously stirred, a solution containing 1.43 g of dibromomethane (6.6 mM), 2.5 mL of 0.1 M Li_2CuCl_4,[12] and 50 mL of dry THF was added dropwise. After the addition was completed (20 min), the reaction mixture was stirred at 0 °C for 5 h and then at room temperature for 64 h. Saturated ammonium chloride (60 mL) was then added while the reaction mixture was cooled to 0 °C. The organic layer was separated, washed with saturated sodium bicarbonate solution (2 × 60 mL), dried over magnesium sulfate, filtered, and concentrated to yield the crude product. The major impurities found were bis(cyclooctatetraene) (BCOT) and (bromomethyl) cyclooctatetraene. The compound was purified by low-pressure liquid chromatography using hexane as eluent on silica gel. BCOT and the compound were difficult to separate chromatographically, and several extractions with pentane prior to the last chromatography proved to be a useful way to remove most of the BCOT present. BCOT is more soluble than the desired compound in pentane. This procedure afforded 0.3 g of pure compound (14% yield) as a pale yellow, viscous oil: ^1H NMR ($CDCl_3$) 2.78 (s, 2 H), 5.77 ppm (br s, 14 H); ^{13}C NMR ($CDCl_3$) 46.27, 128.45, 131.81, 134.08, and 141.50 ppm. Mass spectral analysis showed the parent peak at *m/e* 220.45 (33.7%) and a base peak at *m/e* 115.25.

An authentic sample of $(COT)CH_2Br$ was prepared according to literature procedures[13–16] (Scheme II) in 14% overall yield. (COT)MgBr was coupled with it in the presence of Li_2CuCl_4[12] to yield a sample of **1** which was spectroscopically identical with that prepared from CH_2Br_2.

Preparation of 1a. This compound was prepared by following the same procedure described above for **1**, using CD_2Br_2 instead of CH_2Br_2. The isolated yield was 16%. ^1H NMR in $CDCl_3$ showed only one resonance at 5.77 ppm. ^{13}C NMR showed identical resonances with those

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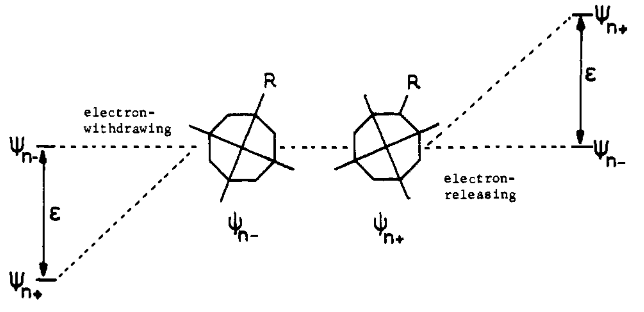
Scheme IV



of **1** in the aromatic region and a pentet centered at 46.27 ppm. Mass spectral analysis showed the parent peak at *m/e* 222.45 (23.2%) and base peak at *m/e* 149.20.

Preparation of 2. The procedure followed was essentially identical with that described for **1** and **1a** using 1,2-dibromoethane instead of the dibromomethane. The major side products found were BCOT and (2-bromoethyl)cyclooctatetraene. The latter was removed by vacuum distillation (55 °C (20 μm)). The pure compound was isolated as a yellow, viscous oil in 36% yield: ^{1}H NMR (CDCl$_3$) 2.16 (s, 4 H), 5.80 ppm (s with small shoulder at higher field, 14 H); ^{13}C NMR (CDCl$_3$) 36.89, 126.57, 131.78, 134.08, and 143.53 ppm. Mass spectral analysis showed the parent peak at *m/e* 234.20 (1.3%) and a base peak at *m/e* 117.0.

Preparation of 3. The synthesis of **3** was accomplished by the reaction of (COT)Br with *n*-BuLi followed by reaction with dichlorodimethylsilane as presented in Scheme III. (COT)Br (2.58 mL, 20 mM) was placed with 20 mL of anhydrous ethyl ether in a 100-mL, round-bottomed, three-necked flask. The flask was cooled in a dry ice-acetone bath and *n*-BuLi (20 mM) added slowly (30 min). The mixture was stirred at -78 °C for 1.5 h and then Me$_2$SiCl$_2$ (1.27 mL, 10 mM) in 120 mL of anhydrous ether added over a period of 30 min, with vigorous stirring. The reaction mixture was then allowed to warm slowly to room temperature during which time LiCl precipitated out of the solution. The mixture was filtered and distilled under reduced pressure to yield 60% of the pure compound (bp 95 °C (1 μm)). Mass spectral analysis showed the parent peak at *m/e* 264.25 (11%) and a base peak at 133.15. ^{1}H NMR (CDCl$_3$): 0.86 (s, 6.1 H), and 6.33-6.73 ppm (m, 14 H).

Results and Discussion

Sodium reduction of a 10^{-3} M solution of **2** in HMPA under vacuum results in the observation of an ESR spectrum which can be easily interpreted in terms of a coupling constant due to three equivalent hydrogens of 4.37 G, another hyperfine from two equivalent hydrogens of 2.55 G and a third coupling constant of 2.00 G due to four equivalent hydrogens. This spectrum is almost identical with that exhibited by the anion radical of *n*-BuCOT.[17] The quartet splitting arises from the hyperfine interaction with hydrogens 3, 5, and 7 (see general structures for numbering assignments), the pentet from hydrogens 2, 4, 6, and 8, and the triplet from the methylene hydrogens directly bonded to the COT ring. The spectral assignments clearly indicate that the spin density is localized in one of the two COT rings. This observation contrasts that of Szwarc et al. with naphthalene-(CH$_2$)$_{3,4}$-naphthalene, where the anion radical spectrum observed corresponded to spin delocalization over the entire molecule.[6] Individual peak-to-peak line widths (ΔH_{pp}) for the ESR spectrum of $\mathbf{2}^{-}\cdot$ were 0.3 G, larger than those measured for *n*-BuCOT, 0.15 G. This line-width difference is probably the result of intramolecular transfer between the two COT moieties, in what could be classified as a localized, rapidly equilibrating system.[18]

The splitting pattern observed for $\mathbf{2}^{-}\cdot$ (large quartet splitting and smaller pentet) is clearly the result of the substituent group acting as an electron donating moiety relative to COT[19,20] (see Scheme IV). In this scheme, Ψ_{n+} and Ψ_{n-} represent the degenerate HOMO's for unsubstituted, planar COT. Since Ψ_{n+} is destabilized by an electron-releasing substituent while Ψ_{n-} is essentially unperturbed, the unpaired electron resides primarily in Ψ_{n+}. This results in the observation of a large quartet splitting from hydrogens 3, 5, and 7, which are nonnodal positions in Ψ_{n+}. The orbital splitting parameter (ε) is defined as the energy difference between that of Ψ_{n+} and Ψ_{n-}, and thus is positive for electron-releasing substituents and negative for electron-withdrawing groups.[20] This energy difference of the degenerate nonbonding molecular orbitals of planar COT brought about as a result of the introduction of a substituent on the COT ring is easily determined from the experimental values of the coupling constants.[19] Measured in this way ε is 0.46 kcal/mole for (COT)CH$_2$CH$_2$-, almost identical with the value of an *n*-Bu substituent on COT. In conclusion, the spin is localized in one of the rings in $\mathbf{2}^{-}\cdot$ in contrast to the observations with the naphthalene substituted analogue.[6] This is not an unexpected result in view of the drastic geometrical changes associated with one electron reduction of COT.[4]

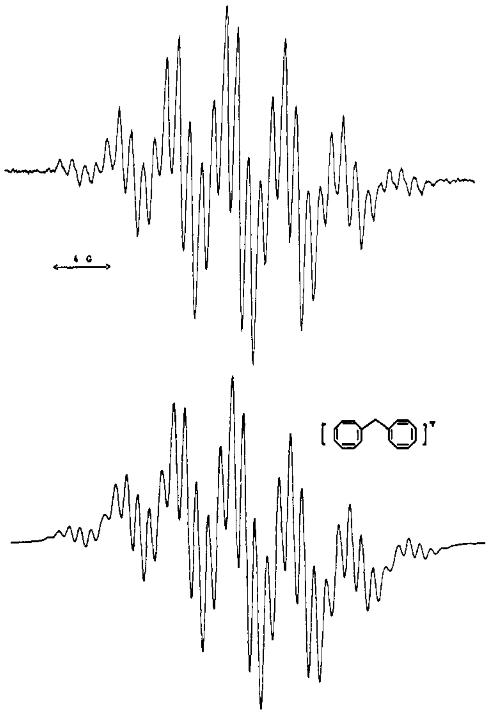


Figure 1. (a) Experimental ESR spectrum of $\mathbf{1}^{-}\cdot$, generated under vacuum by sodium reduction in HMPA at 25 °C. (b) Simulated spectrum using the coupling constants given in the text and in Table I.

Table I. Parameters for the Anion Radicals of **1-4**

compd	position	a_h, G	kcal mol^{-1}
1, 1a	5, 5′	3.30	
	7, 3, 7′, 3′	4.03	
	4, 6, 2, 8, 4′, 6′, 2′, 8′	0.73	
2	methylene	2.55	
	4, 6, 2, 8	2.00	0.46
	5, 7, 3	4.37	
3	4, 6, 2, 8	5.13	
	5, 7, 3	1.25	-0.82
4	5, 5′	0.56	
	7, 3, 7′, 3′	0.28	
	4, 6, 2, 8, 4′, 6′, 2′, 8′	2.38	

Alkali metal reduction of **1** under identical conditions with those used for the generation of $\mathbf{2}^{-}\cdot$ results in the observation of a very different ESR spectrum (Figure 1). This spectrum cannot be assigned on the basis of spin localization into only one of the COT rings. An even more puzzling result is that the ESR spectrum of $\mathbf{1a}^{-}\cdot$ is identical with that of $\mathbf{1}^{-}\cdot$. This is clear evidence that no hyperfine interactions from the methylene hydrogens are being observed in the ESR spectrum of $\mathbf{1}^{-}\cdot$. Since at least 33 spectral lines can be counted in Figure 1, it follows that the splittings must

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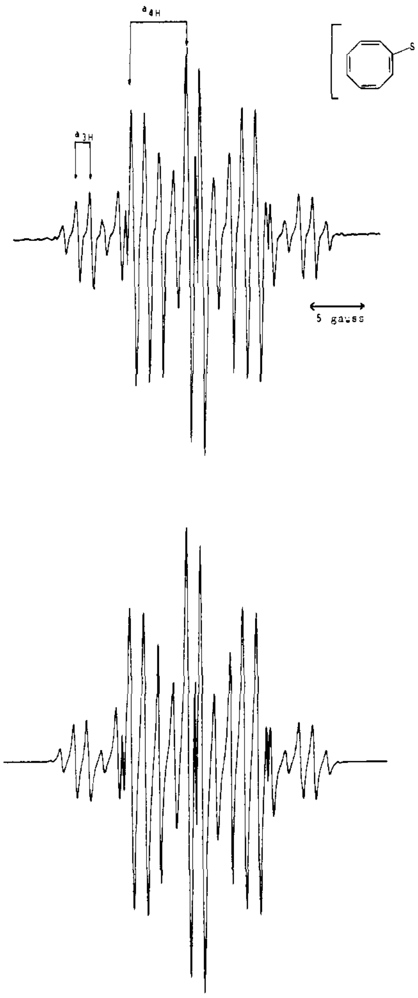

Figure 2. (a) Experimental ESR spectrum of $\mathbf{3}^{-\cdot}$, generated under vacuum by sodium reduction in liquid ammonia at −40 °C. (b) Simulated spectrum using the parameters given in the text and in Table I.

be arising from hyperfine interactions with hydrogen atoms on both COT rings. The simulation presented in the bottom of Figure 1 was obtained by using a coupling constant due to 4 equivalent hydrogens of 4.03 G, one of 3.30 G due to 2 equivalent hydrogens, and another splitting of 0.73 G due to 8 equivalent hydrogens, for a total of 14 hydrogens. All coupling constants for these systems are presented in Table I. Also given in Table I are the values taken from ref 7 for the anion radical of **4**. Note that $\mathbf{4}^{-\cdot}$ has eight hydrogens with a large coupling constant (2.38 G assigned to positions 2, 4, 6, 8 and 2′, 4′, 6′, and 8′) followed by two hydrogens with a coupling constant of 0.56 G (assigned to 5 and 5′) and the smallest coupling constant of 0.28 G corresponding to four hydrogens (assigned to 3, 7, 3′, and 7′). Although the orbital diagram presented in Scheme IV is an oversimplified approximation even for monosubstituted COT's, it can be used to provide useful qualitative insight into the results observed for $\mathbf{4}^{-\cdot}$ and $\mathbf{1}^{-\cdot}$.

If attention is focussed on one of the two rings of $\mathbf{4}^{-\cdot}$ and the other ring is simply regarded as a substituent group, the orbital splitting behavior expected would be the typical one observed for electron-withdrawing substituents on a COT. Therefore the unpaired electron would preferentially occupy a Ψ_{n-} type orbital and the ESR spectrum should contain a large pentet splitting and a smaller quartet one. This is, on a first approximation, what is observed in the ESR spectrum of $\mathbf{4}^{-\cdot}$ (looking at only one of the rings) where a large splitting (2.38 G) due to four equivalent hydrogens is observed. Due to the use of this approximate argument the remaining three hydrogens are not exactly equivalent as predicted, but they are nearly so (one hydrogen has a coupling of 0.56 G and the other two have a coupling constant of 0.28 G). Considering the crudeness of the argument the predictions are quite good. That each COT ring acts as an electron-withdrawing group relative to the other is experimentally known from the fact that the electron spin density is delocalized over the entire molecule in the anion radical.

Using a similar argument and assuming that the bridging methylene in $\mathbf{1}^{-\cdot}$ (or $\mathbf{1a}^{-\cdot}$) is electron releasing relative to both COT rings leads to the opposite prediction. That is, the substituent should destabilize Ψ_{n+} relative to Ψ_{n-} (considering the orbitals of each COT ring independently) and spin density should be localized primarily in a Ψ_{n+} orbital. This should result in the observation of a large splitting from three hydrogens (in each ring) and a smaller splitting from four equivalent hydrogens. These predictions are again borne out by experiment. Each ring in $\mathbf{1}^{-\cdot}$ exhibits a small splitting from four equivalent hydrogens of 0.73 G and, although not exactly equivalent, the remaining three hydrogens in each ring have much larger coupling constants (two hydrogens have 4.03 G and the other one has a splitting of 3.30 G). Based on these arguments the following assignments were made for $\mathbf{1}^{-\cdot}$: $a_{2,4,6,8} = 0.73$ G, $a_{3,7} = 4.03$ G, and $a_5 = 3.30$ G (similar assignments are made for the prime positions in the other ring). All assignments are given in Table I.

The reason why the methylene splitting is not observed in $\mathbf{1}^{-\cdot}$ is not difficult to explain. 1–1′ interannular interactions have been previously observed in diphenylmethane anion radicals.[18] It was found that substituent groups on the phenyl groups which increased the spin densities at C-1 and C-1′ enhanced the interannular interaction.[18] Under these circumstances the methylene splitting could be sufficiently small to be buried under the relatively large ΔH_{pp} observed (0.5 G).

Sodium reduction of **3** in liquid ammonia results in a solution exhibiting the spectrum shown in Figure 2. The spectrum is easily interpreted since it is almost free of overlapping lines. Coupling constants used to generate the simulated spectrum shown on the bottom of Figure 2 were $a_{4H} = 5.13$ G and $a_{3H} = 1.25$ G (see Table I). This pattern clearly indicates that the spin density is localized in a parimarily Ψ_{n-} type orbital of one of the COT rings, and that the $-Si(CH_3)_2-$COT group is thus acting as a strong electron-withdrawing substituent relative to COT.

In addition to the pentet and quartet splittings there are other lines, much sharper, which can be clearly seen in Figure 2. One of these appears exactly at the center of the spectrum. These lines correspond to the anion radical of COT, which is apparently formed as a decomposition product of $\mathbf{3}^{-\cdot}$. The COT signal was observed to increase in intensity as a function of time, at the expense of the signal of $\mathbf{3}^{-\cdot}$. The simulated spectrum shown in Figure 2b includes the simulated spectrum of COT$^{-\cdot}$ ($a_{8H} = 3.14$ G) which was added to that of $\mathbf{3}^{-\cdot}$ but only at 15% of its unit intensity. ^{29}Si satellites were not looked for in this work.

From the measured coupling constants of $\mathbf{3}^{-\cdot}$, ϵ was determined to be −0.82 kcal/mol, the highest value ever reported for a substituent on COT. This strong electron-withdrawing effect is partially responsible for the observation of spin localization in one of the rings. The strong stabilizing effect on Ψ_{n+} leaves the unpired spin density primarily in Ψ_{n-}, which has a node at C-1 and C-1′. This situation decreases the probability of interannular interactions. In addition, the longer Si–C bond distances also result in a decreased probability for this interaction to exist.

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