

pure by GLC (~5% of the saturated alcohol); ^1H NMR (60 MHz, CDCl_3) δ 5.3-5.8 (2 H, vinyl, m), 4.2 (2 H, OCH_2 , d, $J = 5$ Hz), 3.9 (4 H, $\text{O}(\text{CH}_2)_2\text{O}$, s), 2.1-2.4 (3 H, $\text{CH}_2\text{C}=\text{C}$, OH, m), 1.6-1.8 (4 H, 2CH_2 , m), 1.3 (3 H, CH_3 , s). Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{O}_3$: C, 64.49; H, 9.75. Found: C, 64.77; H, 10.13.

Preparation of (Z)-7-Oxo-2-octen-1-ol (6). Three drops of concentrated H_2SO_4 were added to an acetone solution (350 mL) of **4** (15.0 g, 81 mmol). After the mixture was stirred for 2 h at 23 °C, anhydrous K_2CO_3 (~2 g) was added and the stirring continued for a further 0.5 h. The reaction mixture was filtered and concentrated in vacuo. Vacuum distillation yielded **6**: 10.1 g (88%); bp 100-102 °C (0.2 mmHg) [lit.¹⁰ bp 120-125 °C (0.5 mmHg)]; 98% pure.

Preparation of (+)-(1R,7R)-7-(Hydroxymethyl)-5-methyl-6,8-dioxabicyclo[3.2.1]octane ((+)-7). A 0.1 M solution of titanium tetrakisopropoxide (510 mL, 51 mmol) in CH_2Cl_2 at -30 °C (dry ice/ CCl_4 bath) was treated with 11.3 g (55 mmol) of (-)-diethyl tartrate (Aldrich). After 10 min, alkene **6** (7.1 g, 50 mmol) was added followed by 27 mL (111 mmol) of a 4.1 M anhydrous solution of *tert*-butyl hydroperoxide in CH_2Cl_2 . The reaction mixture was kept at -25 °C for 4 days under argon. An aqueous tartaric acid solution (10%, 150 mL) was added and the reaction mixture allowed to warm slowly to 0 °C. After 3 h at 0 °C and 1 h at 23 °C the CH_2Cl_2 phase was separated from the clear aqueous phase that was further extracted with CH_2Cl_2 (3 \times 75 mL). The combined CH_2Cl_2 extracts were dried over anhydrous K_2CO_3 , filtered, and concentrated in vacuo to yield a mixture of (+)-**7** and diethyl tartrate. This mixture was taken up in ether (300 mL) and shaken for 5 min with a 1 N NaOH solution (150 mL) in order to remove the diethyl tartrate by hydrolysis. The aqueous layer was extracted with ether (2 \times 100 mL), and the combined ether extracts were dried over anhydrous MgSO_4 . Removal of the solvent in vacuo and vacuum distillation yielded (+)-**7**: 6.5 g (82%); bp 65-72 °C (0.1 mmHg). GLC analysis revealed (+)-**7** was 90% pure and contaminated with <5% unreacted **6**. An analytical sample, purified by column chromatography (silica gel; hexane/ethyl acetate, (5:1) gave a sample that was 95% pure by GLC: $[\alpha]_D^{27} +53.7 \pm 2.0^\circ$ (c 0.94, CHCl_3); mass spectrum, *m/e* (relative intensity) 125 (25), 112 (20), 98 (15), 83 (22), 69 (31), 67 (39), 59 (92), 54 (100), 43 (57); ^1H NMR (400 MHz, CDCl_3) δ 4.26 (1 H, C_1 , br s), 4.12 (1 H, C_7 , t, $J = 7$ Hz), 3.55 (2 H, CH_2O , overlapping dd, $J = 7$ Hz), 2.12 (1 H, OH, s), 1.45-2.00 (6 H, 3 CH_2 , m), 1.43 (3 H, CH_3 , s). Anal. Calcd for $\text{C}_8\text{H}_{14}\text{O}_3$: C, 60.74; H, 8.92. Found: C, 60.60; H, 8.99.

Preparation of (-)-7. Chiral isomer **7** was prepared in 73% yield by using the same procedure for epoxidation of **6** with the exception that (+)-diethyl tartrate was employed: $[\alpha]_D^{27} -58.0 \pm 2.0^\circ$ (c 1.0, CHCl_3). Anal. Calcd for $\text{C}_8\text{H}_{14}\text{O}_3$: C, 60.74; H, 8.92. Found: C, 60.71; H, 8.81.

Preparation of (1R,7S)-7-(Bromomethyl)-5-methyl-6,8-dioxabicyclo[3.2.1]octane ((+)-8). To a solution of (+)-**7** (6.5 g, 41 mmol) in 30 mL of dry HMPA was added 11.0 g (42 mmol) of triphenylphosphine followed by 14.0 g (42 mmol) of carbon tetrabromide. An immediate exothermic reaction occurred that temporarily produced a homogeneous solution. The reaction mixture cooled to room temperature over 0.5 h and solidified. The reaction mixture was then reheated to 100 °C for 0.5 h and after cooling was triturated with pentane (5 \times 100 mL). The combined pentane extracts were filtered, washed with water (100 mL) and brine (100 mL), dried over anhydrous MgSO_4 , filtered, and concentrated in vacuo. Vacuum distillation yielded 8.0 g (88%) of (+)-**8**: bp 82-85 °C (0.1 mmHg); $[\alpha]_D^{27} +0.9 \pm 0.5^\circ$ (c 1.3, CHCl_3); 99% pure by GLC; mass spectrum, *m/e* (relative intensity) 180/178 (7), 141 (95), 127 (21), 113 (17), 99 (73), 81 (48), 71 (10), 43 (100); ^1H NMR (400 MHz, CDCl_3) δ 4.44 (1 H, C_1 , br), 4.23 (1 H, C_7 , dd, $J = 10$, 5 Hz), 3.32 (1 H, CHBr , dd, $J = 10$, 5 Hz), 3.22 (1 H, CHBr , $J = 10$ Hz), 1.40-2.00 (6 H, 3 CH_2 , m), 1.42 (3 H, CH_3 , s). Anal. Calcd for $\text{C}_8\text{H}_{13}\text{O}_2\text{Br}$: C, 43.46; H, 5.93. Found: C, 43.70; H, 6.08.

Preparation of (-)-8. The same bromination procedure applied to (-)-**7** yielded (-)-**8**: 85% yield; 95% pure by GLC; $[\alpha]_D^{27} -0.6 \pm 0.5^\circ$ (c 1.4, CHCl_3). Anal. Calcd for $\text{C}_8\text{H}_{13}\text{O}_2\text{Br}$: C, 43.46; H, 5.93. Found: C, 43.65; H, 5.98.

Preparation of exo-(1R,7R)-7-Ethyl-5-methyl-6,8-dioxabicyclo[3.2.1]octane [(+)-9, (1R,7R)-exo-Brevicomine]. An ether solution of MeLi (1.6 M, 65 mL, 104 mmol) was added

dropwise to a slurry of CuI (9.5 g, 50 mmol) in 200 mL of dry ether under argon at 10 °C. The reaction mixture was stirred for 10 min, and then a solution of (+)-**8** (8.0 g, 36 mmol) in 50 mL of HMPA was added. The reaction mixture was allowed to warm to room temperature and stirred for 24 h at room temperature. The reaction mixture was poured into cold saturated NH_4Cl solution (350 mL). The ether layer was separated and the aqueous phase extracted with ether (2 \times 150 mL). The combined ether extracts were washed with water (100 mL) and brine (100 mL) and dried over anhydrous MgSO_4 . Filtration and removal of the solvent by distillation at atmospheric pressure yielded crude (+)-brevicomine that was purified by distillation to yield 3.5 g (62%) of (+)-**9**: bp 60-62 °C (15 mmHg) [lit.^{4f} bp 70 °C (20 mmHg)]; $[\alpha]_D^{27} +59.0 \pm 0.5^\circ$ (c 2.5, CHCl_3) (lit. $[\alpha]_D +84.1^\circ$,^{4a} +52°,^{4b} +70°,^{4d} +81.5°^{4e}). The ^1NMR and mass spectra were identical with those published.¹⁸ GLC of (+)-*exo*-brevicomine used for rotation revealed >99% chemical purity. Determination of optical purity by Professor F. V. Schurig by complexation chromatography revealed 95% ee. The results of the optical purity determinations are to be reported elsewhere.

Preparation of (1S,7S)-exo-Brevicomine ((-)-9). Reaction of lithium dimethylcuprate with (-)-**8** yielded (-)-**9**: 69% yield; $[\alpha]_D^{27} -60.6 \pm 0.5^\circ$ (c 2.3, CHCl_3) (lit. $[\alpha]_D -80.6^\circ$,^{4a} -67.5°,^{4h} -66°^{4d}).

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Registry No. 1, 57558-50-6; 2, 74066-96-9; 3, 26330-18-7; (Z)-4, 83732-30-3; (Z)-6, 51580-48-4; (+)-7, 83732-31-4; (-)-7, 83780-99-8; (+)-8, 83732-32-5; (-)-8, 83781-00-4; (+)-9, 20290-99-7; (-)-9, 64313-75-3; acetylene, 74-86-2; formaldehyde, 50-00-0.

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Anion and Trianion Radicals of Aryl-Substituted Cyclooctatetraenes

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The chemistry of cyclooctatetraene (COT) and its derivatives has been the subject of extensive research for many years.¹ In particular, electronic distributions in substituted COT's have been the subject of much study.^{2,3} Phenylcyclooctatetraene (PCOT) has been shown to reduce to an anion radical where significant spin density occurs in the phenyl group.⁴ Other substituted PCOT's were found to follow a reasonable Hammett correlation when the phenyl substituent parameters were compared with the measured orbital splitting (ϵ) as determined by ESR spectroscopy.⁵ When two ortho substituents were

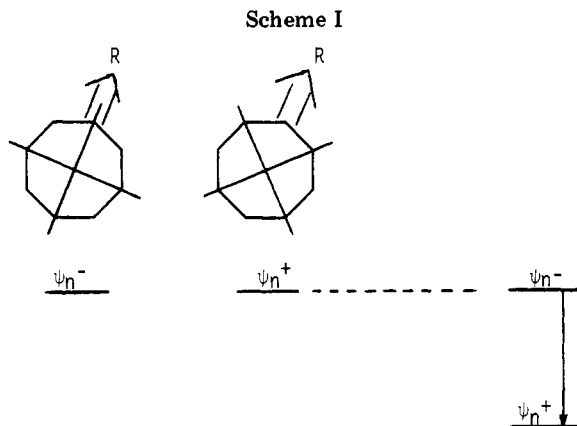
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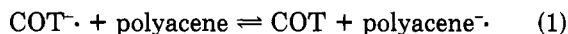
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incorporated into the phenyl moiety, the aromatic group was transformed from an electron-withdrawing group by resonance to an electron-donating substituent by induction due to steric interactions.⁵

The orbital splitting parameter (ϵ) is defined as the energy difference of the degenerate nonbonding π molecular orbitals of planar COT brought about as a result of the introduction of a substituent on the COT ring (see Scheme I).⁶ Since ϵ is defined as the energy difference between ψ_n^+ and ψ_n^- , it will have positive values for electron-releasing substituents⁶ and negative values for electron-withdrawing substituents. The situation depicted in Scheme I is that where the substituent, R, is electron withdrawing. In either situation (releasing or withdrawing) ψ_n^- remains essentially unperturbed while ψ_n^+ is destabilized by electron-releasing substituents and stabilized by electron-withdrawing groups. ϵ can be easily determined from the experimental values of the EPR coupling constants of the corresponding COT anion radicals as described elsewhere.⁴

We have measured the enthalpy changes associated with electron transfer between COT⁻ and neutral polyacenes in hexamethylphosphoramide (HMPA) and found that ΔH is very close to zero when the polyacene is tetracene (eq 1).⁷ The largest enthalpy change measured for the ex-



change reaction was that with naphthalene, as expected, which had a value of 16 kcal/mol. These results correlated well with the electron affinities of the polyacenes. It was of interest to measure the spin density distribution in molecules which contained both the polyacene and COT directly bonded. Furthermore, we were interested in the possibility of generating trianion radicals of these new molecules.

Experimental Section

Instrumentation. NMR spectra were obtained at 90 MHz (hydrogen) on a JEOL FX-90Q spectrometer. ESR spectra were recorded by using the X band of a Varian E-9 spectrometer equipped for variable temperature and having a dual cavity. Mass spectra were obtained with a Hewlett-Packard 5995-A system, using the direct ion probe option. The ionization potential was set at 70 eV, and the probe temperature was varied from 90 to 260 °C at a rate of 15 °C/min.

1-Cyclooctatetraenyl- (I) and 2-Cyclooctatetraenyl-naphthalene (II). The general procedure described in ref 8 was

followed but was slightly modified according to ref 9. Bromonaphthalene (8 g, 38.6 mmol), 1- or 2-substituted, in 75 mL of dry ether was added to 1 g of finely divided Li (145 mmol) in 50 mL of ether over a period of 0.5 h. The reaction mixture was then refluxed while being vigorously stirred for an additional hour. Quenching and titration of a 0.5-mL aliquot with standardized acid showed that the reaction was 80% complete. The solution was then removed from the excess Li by siphoning the mixture through a fritted glass filter into another round-bottomed flask kept under a nitrogen atmosphere. COT (2.0 g, 19.2 mmol) in 15 mL of dry ether was then added dropwise to the organolithium solution. The reaction mixture was then refluxed for 1 h. The reflux condenser was replaced by a distillation column and the solvent evaporated from the reaction mixture. The resulting sludge was heated for 3 h at 100 °C. The mixture was allowed to cool to room temperature, 50 mL of anhydrous ether added, and oxygen bubbled through. The mixture was then hydrolyzed with 20 mL of saturated ammonium chloride and extracted with three 10-mL portions of ether. The combined extracts were dried and rotoevaporated. The crude product was placed under high vacuum (2 μ m) at 40 °C to separate naphthalene by sublimation. Low-pressure liquid chromatography on silica gel with hexane as the eluent afforded 0.48 g of pure I (11% yield). Similarly, liquid chromatography afforded 0.32 g of pure II (7% yield). Both I and II are pale yellow viscous liquids. The major impurities found in the crude products were the naphthalene dimers. Mass spectral analysis of I and II showed parent and base peaks at m/e 230: ¹H NMR analysis (CDCl₃) of I δ 6.00 (br s, COT H's, relative intensity 7), 7.31–7.62 (m), 7.74–8.00 (m), 8.34–8.48 (m), relative intensity of all aromatic H's = 7; ¹H NMR (CDCl₃) of II δ 5.93 (br s), 6.15 (br s), 6.36 (br s), 7.23–7.90 (m), with COT vs. aromatic H's in a ratio of 1:1.

9-Cyclooctatetraenylanthracene (III). A 0.5-g sample of Mg (20.6 mmol) was placed in a three-necked, round-bottomed flask together with 10 mL of dry ether, all under a dry nitrogen atmosphere.¹⁰ 9-Bromoanthracene (1.8 g, 7.0 mmol) in 15 mL of dry ether was then added to the flask. The reaction mixture was refluxed overnight, before the ether was distilled out. After the ether was distilled, 50 mL of dry benzene (previously dried over P₂O₅) was added, and the resulting solution was stirred and refluxed overnight. Li₂CuCl₄¹¹ (1.0 mL of a 0.1 M solution in THF) was added and the reaction mixture stirred for an additional hour. COTBr (1.9 g) was then added and the mixture stirred overnight. The reaction mixture was hydrolyzed with a saturated ammonium chloride solution, extracted with hexane, and rotoevaporated. The crude product was purified by low-pressure liquid chromatography on silica gel with hexane as the eluent. A 0.21-g sample of the pure compound was isolated as a crystalline yellow solid: mp 136–137 °C; 10.5% yield based on 9-bromoanthracene. Mass spectral analysis showed the parent peak at m/e (relative intensity) 280 (45) and the base peak at m/e 202 (100): ¹H NMR (CDCl₃) δ 6.0 (br d, 7 H), 7.42 (m), 7.91 (m), 8.37 (m), relative intensity of the combined aromatic signals 9 H's.

1-Cyclooctatetraenyl-naphthalene-*d*₇ and 9-Cyclooctatetraenylanthracene-*d*₉. The perdeuterated aromatic analogues of I and III, I-*d*₇ and III-*d*₉, were prepared exactly as described in 1 and 2 above, respectively, starting with the correspondingly perdeuterated bromopolyacenes. (Perdeuteration refers exclusively to the aromatic moiety, not to the COT group.)

I-*d*₇ was obtained in 16% yield. Mass spectral analysis of I-*d*₇ showed a base peak at m/e 159 and the parent peak at m/e 237 (68%). ¹H NMR analysis (CDCl₃) of I-*d*₇ gave δ 6.00 (br s).

III-*d*₉ was obtained in 27% yield. Mass spectral analysis showed a base peak at m/e 211 and the parent peak at m/e 289 (64%). ¹H NMR analysis (CDCl₃) of III-*d*₉ gave δ 6.00 (br d).

ESR Sample Preparation. All ESR samples were prepared and sealed under high-vacuum conditions (10⁻⁴ mm) in an all-glass apparatus as described elsewhere.¹² The solvent, hexamethylphosphoramide (HMPA), was twice distilled from potassium

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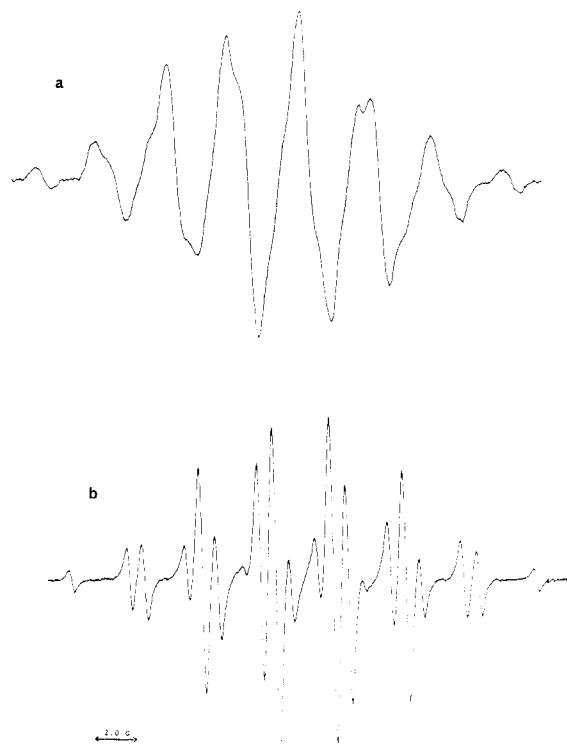


Figure 1. (a) ESR spectrum of I reduced with sodium in HMPA. (b) ESR spectrum of I- d_7 reduced under conditions identical to those in a. Note the resolution enhancement obtained upon deuteration.

under vacuum, the last distillation directly into the reaction flask. Reductions were accomplished by reacting the 5×10^{-3} M solution of the compound in HMPA with either a potassium or sodium mirror formed by vacuum sublimation of the purified metal.

Results and Discussion

The spectrum of I \cdot^- in HMPA is poorly resolved, but clearly consists of eight broad groups of lines (Figure 1a). We attribute the large line widths to unresolved hyperfine splittings which arise from small spin densities in the naphthyl group. A well-resolved spectrum was obtained from (I- d_7) \cdot^- (Figure 1b). This spectrum is easily interpreted in terms of a pentet splitting of 3.55 G corresponding to four equivalent hydrogens and a smaller quartet splitting of 2.80 G corresponding to three equivalent hydrogens. The pentet splitting arises from spin localization in the ψ_n^- orbital and the consequent coupling of the unpaired electron with the four equivalent, nonnodal hydrogens in ψ_n^- . As a consequence of thermal mixing there is some spin density in ψ_n^+ which gives rise to the quartet splitting when the unpaired electron couples with the three equivalent, nonnodal hydrogens in ψ_n^+ . Since the unpaired spin occupies a π molecular orbital which has a larger contribution from ψ_n^- than from ψ_n^+ (the lowest energy configuration has two paired spins in ψ_n^+ and one unpaired spin in ψ_n^-), the observed pentet has a larger coupling constant than the quartet. The larger the value of ϵ the larger the difference between these splittings. These arguments clearly show that the orbital energy diagram presented in the introduction corresponds to that observed for I \cdot^- and (I- d_7) \cdot^- , thus confirming that naphthyl is acting as an electron withdrawing group relative to COT. These hyperfine constants can be used to determine the orbital splitting energy,^{4,5} ϵ (Table I). The ϵ value calculated from the coupling constants for α -naphthyl is -0.14 kcal/mol, a more positive value than that previously calculated for phenyl, -0.26 kcal/mol.⁵ This is in direct contradiction to the expected result on the basis of gas-

Table I. Coupling Constants, ϵ , and Electron Affinity Values for the Anion Radicals of I-III

compd	substituent	a_H , G	ϵ , kcal/mol $^{-1}$	polyacene gas phase E_a , eV
I	H	3.12 (nonet)	0	
I	phenyl	3.68 (pentet), 2.38 (quartet)	-0.26	0.052
I	α -naphthyl	3.55 (pentet), 2.80 (quartet)	-0.14	0.152
II	α -naphthyl	4.1 (pentet), 2.2 (quartet)	-0.4	0.152
III	9-anthracenyl	3.50 (octet)	0.00	0.552

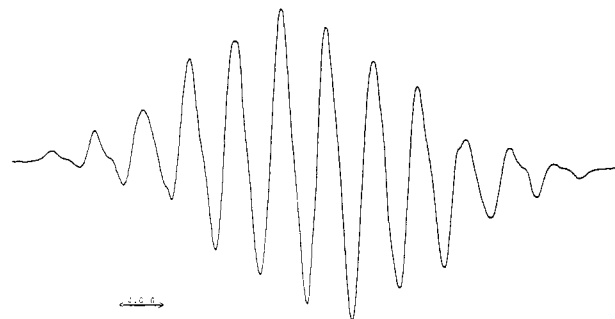
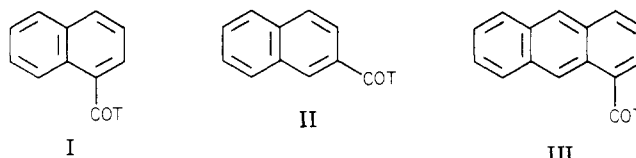


Figure 2. ESR spectrum of II \cdot^- generated by sodium reduction in hexamethylphosphoramide. Although resolution is relatively poor, the spectrum can be easily analyzed (see text).

phase electron-affinity values¹³ (Table I). Naphthyl should be more electron withdrawing than phenyl, yet the opposite result is observed. The reason for this behavior is the consequence of steric interaction between the COT hydrogens and the peri hydrogen on the 8-position of the naphthyl group. This interaction leads to substantial inhibition to conjugation. This interaction is similar to that observed for 2,4,6-trimethylphenylcyclooctatetraene.⁵



COT = cyclooctatetraenes

In order to check this explanation, II was prepared and reduced similarly. The ESR spectrum observed upon formation of the anion radical is shown in Figure 2. This spectrum can be interpreted in terms of a large pentet splitting of 4.1 G and a smaller quartet of 2.2 G. Note that the magnitude of the pentet is approximately twice that of the quartet, indicating that this group is clearly acting as a strong electron-withdrawing substituent ($\epsilon = -0.4$ kcal/mol, Table I). This value is more negative than that of either 1-naphthyl or phenyl, indicating more electron delocalization onto this group than the others. Since the steric interaction of II is similar to that of PCOT, the measured ϵ values should correlate well with the electron affinities of these groups. The values of Table I clearly show that this is the case.

Neither I nor II showed ESR spectral changes upon temperature variation of the samples, nor upon further alkali metal reduction. The signals only decreased in intensity as more alkali metal was reacted, presumably the result of dianion formation. No evidence for trianion radical formation was observed.

Alkali metal reduction of III in HMPA results in the observation of a well-resolved ESR spectrum (see Figure 3a). Surprisingly, this ESR spectrum is composed of eight

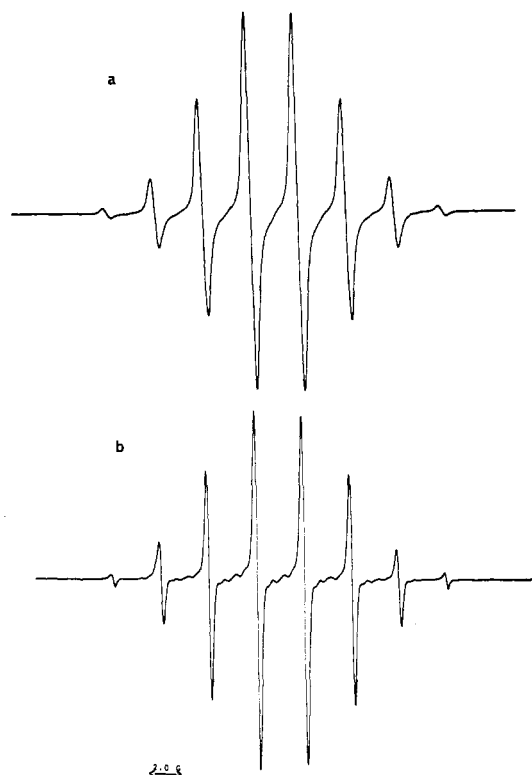


Figure 3. (a) ESR spectrum of III⁻ generated by sodium reduction in HMPA. Note that the spectral lines are well resolved as opposed to the spectra in Figures 1a and 2. (b) ESR spectrum of III-*d*₉⁻ generated by sodium reduction in HMPA. Although the line widths are somewhat smaller than those in 3a, the improvement is hardly comparable to that observed in Figure 1.

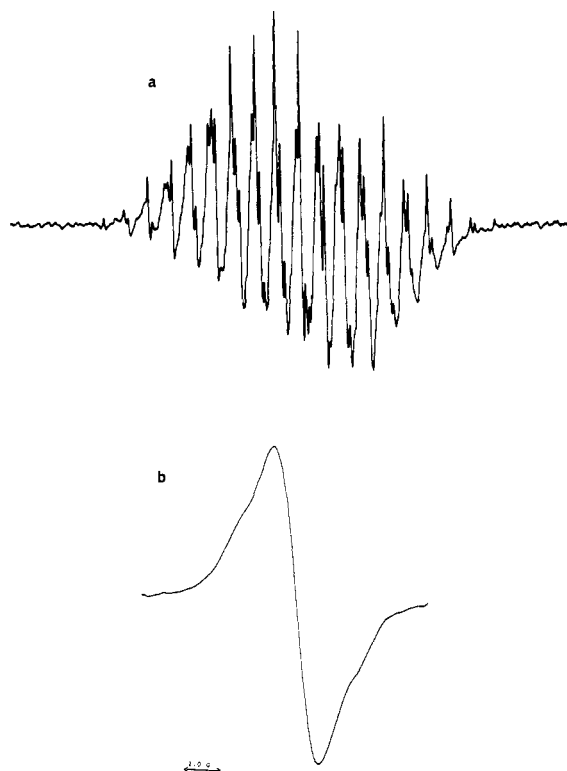


Figure 4. (a) ESR spectrum observed after further sodium reduction of the solution, giving rise to spectrum 3a. Although not fully interpreted, this spectrum has been assigned to III, with most of the spin density residing in the anthracenyl moiety. (b) ESR spectrum observed after further sodium reduction of the solution, giving rise to spectrum 3b. The observation of this broad line is consistent with spin localization in the deuterated anthracenyl moiety. This spectrum is assigned to (III-*d*₉)³⁻.

equally spaced lines of relatively small line width, indicative of an ϵ value very close to zero. No separate pentets or quartets were detected as in the previous cases. The spectrum is thus composed of one single splitting by seven equivalent hydrogens ($a = 3.50$ G), indicating equal spin populations in ψn^+ and ψn^- . The obvious explanation for this observation falls in line with the steric effect argument already presented. In III, two peri hydrogen interactions are present, thus twisting the substituent out of planarity with the COT, much more so than in I. In order to try to resolve splittings, III-*d*₉⁻ was generated and its ESR spectrum recorded (Figure 3b). The resulting octet pattern is much sharper than that of III⁻, with a peak to peak line width of 0.15 G, but no further splittings can be detected. Therefore, COT orbital splitting by anthracenyl has $\epsilon \approx 0$ ($\epsilon < 0.15$ G).

Interestingly, further alkali metal reduction of III and III-*d*₉ resulted in the observation of different ESR spectra (see Figures 4a and 4b, respectively). Spectrum a of Figure 4 contains many hyperfine coupling constants and, although not fully interpreted, suggests spin localization primarily in the polyacene moiety (162 theoretical spectral lines). This observation can be explained by invoking the formation of a trianion radical. Spectrum b of Figure 4 is consistent with the formation of a trianion radical of III-*d*₉, where most of the spin density resides on the aryl moiety. Unresolved splittings from the many deuterons result in a single, relatively broad signal.

Formation of these trianion radicals of III and III-*d*₉ is only possible if the dihedral angle between the two bonded moieties is very close to 90°. If this is the case, the unpaired electron density can reside in an orbital which is essentially orthogonal to the dianionic COT moiety.

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Registry No. I, 83463-20-1; I⁻, 83463-22-3; I-*d*₇, 83463-21-2; (I-*d*₇)⁻, 83463-23-4; II, 83463-24-5; II⁻, 83463-25-6; III, 83463-26-7; III⁻, 83463-28-9; III²⁻, 83463-19-8; III-*d*₉, 83463-27-8; (III-*d*₉)⁻, 83463-29-0; (III-*d*₉)²⁻, 83476-29-3; COT, 629-20-9; 1-bromonaphthalene, 90-11-9; 2-bromonaphthalene, 580-13-2; 9-bromoanthracene, 1564-64-3; naphthalene-*d*₈, 1146-65-2; anthracene-*d*₁₀, 1719-06-8.

Nitration of *s*-Triazolo[3,4-*a*]phthalazine

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During the course of preparation of several derivatives of *s*-triazolo[3,4-*a*]phthalazine (1), we had need of the 8-nitro

