

Electrochemical Evidence for Hypervalent (10-C-5) [1] Pentacoordinate Carbon

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ABSTRACT

The electrochemical oxidation of 1,8-bis(4-methylphenylthio)-9-(2,6-dimethoxyphenyl)-10-phenylanthracene (**2**) is discussed. It undergoes facile, reversible two-electron electrooxidation in two closely spaced one-electron steps at $E_1^{0'} = 0.98$ V and $E_2^{0'} = 1.02$ V (vs. SCE). This behavior is discussed in terms of relief of three-center antibonding interaction involving the 1-, 8-, and 9-substituents of **2** with two sulfurs and a carbon of the 2,6-dimethoxyphenyl group, which becomes a stabilized three-center bonding interaction in dication **1**. The central atom in the three-center bond is a hypervalent pentacoordinate carbon atom.

A related two-center antibonding interaction present in 1-(4-methylphenylthio)-9-(2,6-dimethoxyphenyl)-10-phenylanthracene (**5**) is relieved by facile one-electron oxidation ($E_p = 1.14$ V vs. SCE) forming **7**. Removal of a second electron ($E_p = 1.34$ V vs. SCE) from anthracene **5** results in an unstable dication, **8**.

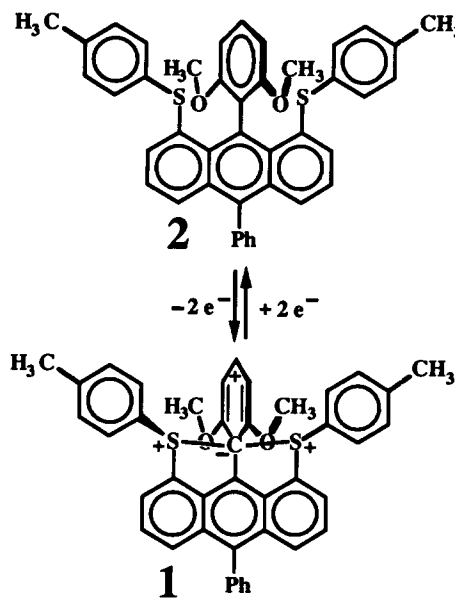
Other analogous anthracene derivatives lacking both thioaryl groups (**4**) or the 9-aryl group (**4**) prove much more difficult to oxidize, both showing one-electron reversible oxidation potentials of 1.27 V (vs. SCE) similar to 9-phenylanthracene (1.34 V vs. SCE) and 9,10-diphenylanthracene (1.22 V vs. SCE).

These results provide strong evidence for the postulated structure of dication **2** which incorporates

hypervalent pentacoordinate carbon, a 10-C-5 species [2,3].

INTRODUCTION

It has been postulated [2,3] that anthracene dication **1** has a structure with a hypervalent trigonal bipyramidal (TBP) carbon atom (a 10-C-5 species [1], i.e., one in which five ligands are bonded to carbon, formally using 10 electrons). The chemical properties and ^1H , ^{19}F , and ^{13}C NMR spectroscopic characteristics of **1** and derivatives of **1** provide evidence against other possible alternative structures for this dication and are consistent with structure **1**.



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The close juxtaposition of the three electron-rich substituents at the 1-, 8-, and 9-positions of anthracene **2** engenders repulsive interactions which can be described as resulting from interaction of filled molecular orbitals. The removal of two electrons from an orbital which is raised in energy by this interaction is postulated to give **1**, in which the interactions of the three substituents become an attractive one, bonding both sulfur atoms to the central carbon. An electrochemical study of this two-electron oxidation of **2** and of model compounds lacking one or two of these substituents at the 1-, 8-, and 9-positions was undertaken to explore the importance of this three-center interaction.

EXPERIMENTAL

Chemicals

Acetonitrile, benzonitrile, and sulfur dioxide were distilled twice from P₂O₅. Electrochemical grade tetra-*n*-butylammonium tetrafluoroborate (TBABF₄) obtained from Southwestern Analytical Chemicals was recrystallized three times from acetonitrile and dried in vacuum at 100°C. Potassium trifluoromethanesulfonate (TfOK) was precipitated by neutralization of an aqueous solution of the acid with KOH and then recrystallized three times from distilled water and dried in vacuum at 100°C.

Synthesis

Anthracenes **2** and **5** were prepared by treatment of SO₂ solutions of the corresponding dications with aqueous NaOH as previously described [2]. Microanalyses, performed by Mr. Joe Nemeth and associates, agreed within 0.4% with the theoretical values for the elements listed. Satisfactory analytical data ($\pm 0.4\%$ for C, H, halogen, etc.) were reported for all new compounds listed.

1,8-Bis(4-methylphenylthio)-10-phenyl-9-anthrone (6)

To 1.00 g (1.9 mmol) of 1,8-*bis*(4-methylphenylthio)-10-phenyl-10-hydroxy-9-anthrone [2] in a mixture of 1,4-dioxane (30 mL), acetic acid (30 mL), and 20% aqueous HCl (15 mL) was added 10 g of granular tin and the solution was boiled for 12 hours. Cooling provided crystalline **6** which was recrystallized from ethanol to give 0.91 g (1.8 mmol, 94%): mp 194–196°C; ¹H NMR (CDCl₃/TMS) δ 7.50 (d, 4H, SC₆H₄CH₃, meta- to S), 7.33–6.87 (m, 13H, ArH), 6.73 (d, 2H, 4- and 5-anthryl CH), 5.40 (s, 1H, 10-anthryl CH), 2.40 (s, 6H, CH₃). Anal. (C₃₄H₂₆S₂O) C, H, S.

1,8-Bis(4-methylphenylthio)-10-phenylanthracene (3)

Approximately 1 g of LiAlH₄ in 20 mL of tetrahydrofuran (THF) was added to 0.03 g (0.06 mmol) of solid **6**, and the resulting red solution was stirred for 12 hours at 25°C. The reaction was quenched with methanol, followed by H₂O. It was then washed with 10% HCl, and the solution was dried (MgSO₄). Solvent was removed in vacuum to give crude **3**. Recrystallization from THF gave 0.03 g (ca. 0.06 mmol, 100%) of **3**: mp 168–170°C; ¹H NMR (CDCl₃/TMS) δ 9.75 (s, 2H, 9-anthryl CH), 7.60–6.93 (m, 19H, ArH), 2.30 (s, 6H, CH₃); MS (10 eV) *m/e* (relative intensity) 498 (M⁺, 100), 376 (4, -SC₆H₅). Anal. (C₃₄H₂₆S₂) C, H, S.

9-(2,6-Dimethoxyphenyl)-10-phenylanthracene (4)

To 247 mg (0.86 mmol) of 10-phenyl-10-hydroxy-9-anthrone [2] in 25 mL of THF was added a solution of 2,6-dimethoxyphenyllithium [3] (6.4 mmol in 10 mL of THF), and the solution was stirred for 2 hours at 25°C. Water was added, and the organic layer was dried (MgSO₄). Solvent was removed in vacuum to give a solid. This solid was dissolved in a mixture of 1,4-dioxane (60 mL), 50% aqueous acetic acid (120 mL), and conc HCl (60 mL) with 6 g (51 mmol) of SnCl₂, and the solution was boiled 12 hours. The solution was poured into ice water, and this solution was extracted with CH₂Cl₂. The extract was washed with saturated NaHCO₃ solution and then with H₂O. Solvent was removed to give crude **4**. Recrystallization from CH₂Cl₂/hexane gave 215 mg (0.55 mmol, 64%) of **4**: mp 263–265°C; ¹H NMR (CDCl₃/TMS) δ 7.70–7.50 (m, 10H, ArH), 7.31–7.26 (m, 4H, 1-, 4-, 5-, and 8-anthryl CH), 6.80 (d, 2H, ArH, ortho- to OCH₃), 3.57 (s, 6H, OCH₃); MS (70 eV) *m/e* (relative intensity) 390 (M⁺, 100), 375 (6, -CH₃), 359 (8, -OCH₃), 313 (4, -C₆H₅), 253 (3, -C₈H₉O₂), 195 (3, M²). Anal. (C₂₈H₂₂O₂) C, H.

Electrochemistry

In experiments using SO₂, vacuum techniques [4] were used to purify and transfer the SO₂ to a standard two-compartment H-cell [5]. In one compartment was a 0.20 cm² (geometric area) Pt disk working electrode and an Ag wire quasi-reference electrode (QRE). A Pt helix was employed as the counter electrode in the other compartment. The SO₂ solutions were maintained at approximately –45°C by an acetonitrile/dry-ice slush. With acetonitrile or benzonitrile as solvent, a three compartment H-cell was used, with the working and counter electrodes in the end compartments and the tip of an aqueous saturated calomel electrode (SCE) making contact with the electrolyte in the middle compartment as a reference electrode.

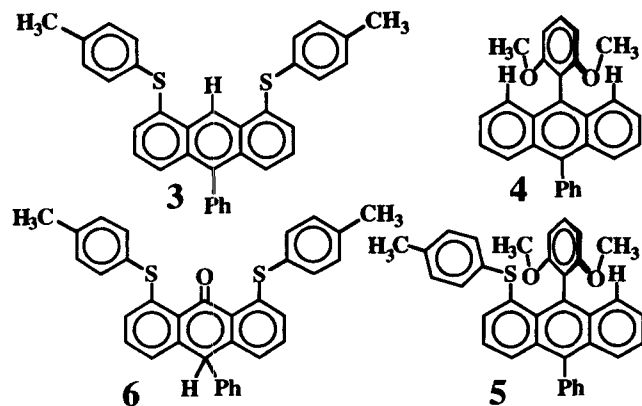
TABLE 1 Cyclic Voltammetric Peak Potentials^a

Compound	E_p (Anodic)/ E_p (Cathodic) ^b	
	First Peak	Second Peak
2	1.07/0.92	~1.7 ^{c,d}
3	1.27/1.20	~1.7 ^d
4	1.27/1.19	~1.7 ^d
5	1.14/1.02	1.34/1.18 ^e
9-PA ^f	1.34/1.22	~1.7 ^d
9,10-DPA ^f	1.22/1.16	~1.7 ^d

^aIn acetonitrile/0.05 TfOK at 25°C, $n = 100$ mV/s. ^bPotentials in V vs. SCE. ^cThird-electron oxidation. ^dIrreversible. ^eSecond oxidation product partially unstable. ^fData taken from Ref. [6]; in CH₂Cl₂ at $n = 100$ mV/s. 9-PA = 9-phenylanthracene; 9,10-DPA = 9,10-diphenylanthracene.

Preparation of these solutions and experimental measurements were conducted in a nitrogen atmosphere at room temperature.

Coulometry was done in acetonitrile at a 6.0 cm² Pt gauze working electrode with stirring. The electrode was maintained at a potential 100 mV more positive than the corresponding peak potential, as reported in Table 1, until the current decayed essentially to zero. The n -values were calculated from recorded current-time profiles by cut-and-weigh methods.



Compounds 2 and 5 differ from 3 and 4 in several important aspects of their electrooxidative behavior. One electron can be removed from either 2 or 5 much more easily than from compounds 3, 4, 9-PA, or 9,10-DPA (comparisons in Table 1). The second electrooxidation steps are even more facile, and there is increased stability of the nucleus [9,10]. From the results of Table 1 we may conclude that the substituents of 3 (relative to 9,10-DPA) or of 4 relative to 9-PA do not change the energy of electrooxidation appreciably. Removal of a second electron from any of these four compounds (3, 4, 9-PA, and 9,10-DPA) is much more difficult and results in irreversible loss of product to homogeneous chemical decay.

Electrochemical control was exercised by a

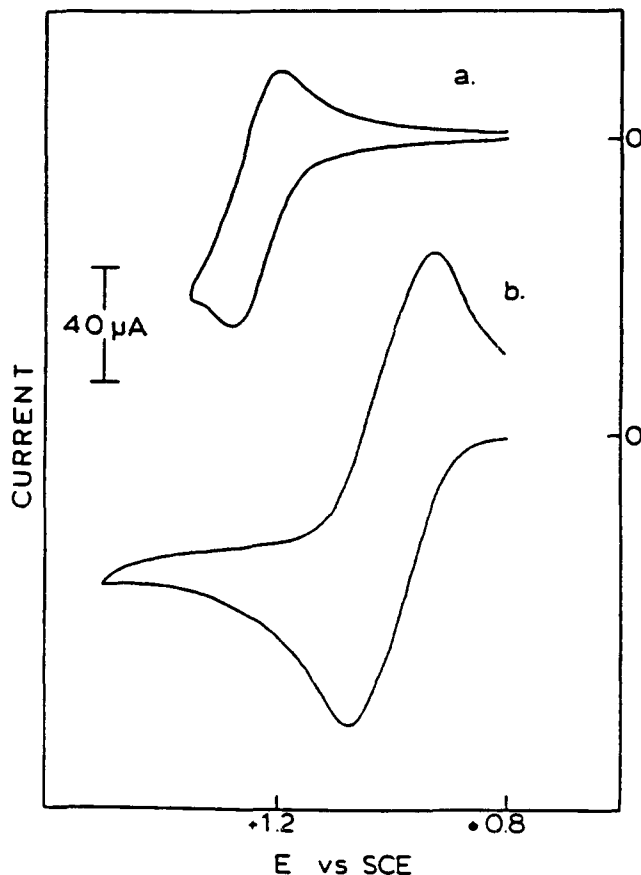


FIGURE 1 Cyclic voltammetry in acetonitrile/0.10 M TBABF₄. $n = 100$ mV/s; $T = 25^\circ\text{C}$; $A = 0.20$ cm². (a) 1.10 mM anthracene 3; (b) 0.89 mM anthracene 2. Oxidation currents are down; reductive currents are up.

Princeton Applied Research Model 173 potentiostat with a Model 176 current-to-voltage converter. A custom-built waveform generator fed the potentiostat, and voltammograms were recorded on a Houston Instruments Model 2000 X-Y recorder. Positive feedback compensation of IR losses at 80% of the oscillation level was employed in voltammetry.

RESULTS

Compounds 2, 4, and 5 were synthesized by reactions described earlier [2] or by very close analogs of such reactions. Compound 3 was prepared by reduction of anthrone 6 with lithium aluminum hydride.

Table 1 and Figures 1 and 2 display the basic voltammetric characteristics of compounds 2, 3, 4, and 5 in acetonitrile with either 0.05 M TfOK or 0.1 M TBABF₄ as supporting electrolyte. No noticeable changes in the voltammetry were observed with the different supporting electrolytes or with alteration in scan rates. The results in ben-

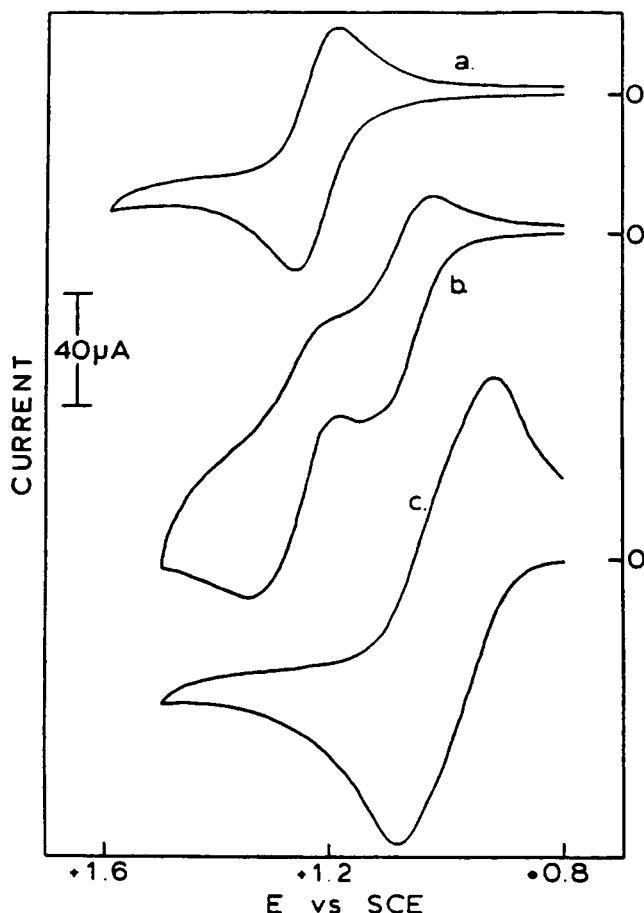


FIGURE 2 Cyclic voltammetry in acetonitrile/0.10 M TBABF₄. $n = 100$ mV/s; $T = 25^\circ\text{C}$; $A = 0.20$ cm². (a) 0.95 mM anthracene 4; (b) 0.90 mM anthracene 5; (c) 0.89 mM anthracene 2.

zonitrile were identical. In sulfur dioxide at ca. -45°C , the anodic peak potentials measured relative to a silver quasi-reference electrode show the same relative positions within 10 mV but are shifted negatively by a fixed amount. This shift can be ascribed to the difference in reference electrode potentials.

These data, together with the coulometric n -values reported in Table 2, show some striking

TABLE 2 Coulometric Results^a

Compound	Electrolysis Potential ^b	n^c
2	1.17	1.86
3	1.37	0.86
4	1.37	0.83
5	1.24, 1.44	0.87, 1.85

^aIn acetonitrile/0.1 M TBABF₄ at 25°C . ^bIn V vs. SCE. ^cThe deviation from integral values is believed to reflect losses from the working electrode compartment by diffusion and migration.

TABLE 3 Cyclic Voltammetric Data for 2^a

n (Vs ⁻¹)	i_{pa} (mA)	i_{pc}/i_{pa}	$i_{pa}/n^{1/2}$ (mA·s ^{1/2} ·V ^{1/2})	$E_{pa} - E_{pc}$ (mV)
10	700	0.99	220	157
5	520	1.00	230	135
2	350	0.99	250	110
1	255	0.98	255	110
0.5	188	0.99	265	95
0.2	122	0.98	270	93
0.1	84	0.99	265	85
0.05	62	0.93	275	83
0.02	40	0.93	285	93
0.01	32	0.92	315	85

^aAt 1.2 mM in acetonitrile/0.1 M TBABF₄ at 25°C . Scan from 0.5 V to 1.4 V vs. SCE and return. n = scan rate; i_{pa} = anodic peak current; i_{pc} = cathodic peak current; E_{pa} = anodic peak potential; E_{pc} = cathodic peak potential.

changes in behavior with structural modification around the anthracene nucleus. Compounds 3 and 4 follow the well-established pattern for electrochemical oxidation of anthracenes [6–9]. The first electron is removed reversibly at 1.2–1.3 V vs. SCE to produce the cation radical. Comparable data from the literature for 9-phenylanthracene (9-PA) and 9,10-diphenylanthracene (9,10-DPA) are included in Table 1 to illustrate the similarity between their electrochemical behavior and that of 3 and 4. Electron paramagnetic resonance (EPR) and electrochemical studies have shown that the unpaired spin and charge densities in the cation radicals of 9-PA and 9,10-DPA reside almost totally in the anthracene two-electron oxidation product. In compound 2, a near merger of the first and second oxidation potentials is observed, leading directly to a stable dicationic species. For compound 5, the second oxidation potential is reduced relative to the other anthracenes studied but is well separated from the first. Its two-electron oxidation product is, however, not stable on the voltammetric time-scale used here. This parallels previous observations on the chemical generation of these dications [2].

The scan rate dependence of voltammetric behavior for 2 is summarized in Table 3. The splitting $E_{pa} - E_{pc}$ increases with scan rate. This effect could reflect the influence of relatively slow charge transfer across the interface or the inclusion of resistance losses upon passage of current through the solution [11,12]. Since the splitting increases quite linearly with i_{pa} , as shown in Figure 3, it is likely that the phenomenon is totally resistive in origin. The slope of the plot is 110 W, which is a reasonable value for remaining uncompensated resistance. Moreover, a constant value for standard heterogeneous rate parameter k^0 cannot be extracted by the method of Nicholson [12] if the splitting is regarded as having kinetic origin. Thus, it seems likely that the electrode process is reversible in a

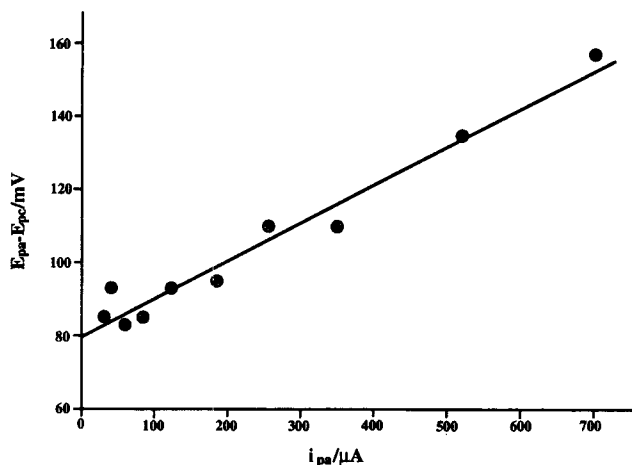
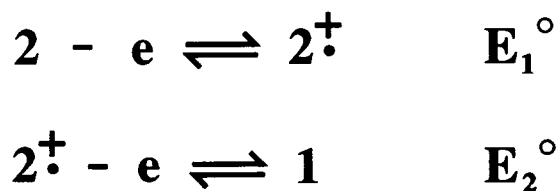


FIGURE 3 Peak splitting vs. anodic peak current for 1.2 mM anthracene **2** in acetonitrile/0.1 M TBABF₄ at 25°C. Data were obtained by recording voltammograms at various scan rates.

kinetic, as well as a chemical, sense. The intercept of Figure 3 is 79 mV, significantly larger than the value of 30 mV expected for a two-electron, one-step reversible reaction [12,13]. We therefore believe that the overall reaction involves two sequential one-electron steps with standard potentials separated by a measurable difference.

Polcyn and Shain [14] examined the expected cyclic voltammetric response for cases of this sort and defined the results in terms of the difference in standard (or formal) potentials $E_2^0 - E_1^0$, where the subscripts refer, in the present case, to the couples involving loss of the first and second electrons, respectively, in oxidation, *i.e.*,



For $E_2^0 - E_1^0 > 100$ mV, separate peaks are expected, but for smaller splittings, a nearly merged response should be seen. Only for $E_2^0 - E_1^0 > -100$ mV, *i.e.*, the second oxidation being much easier than the first, does one expect the characteristic voltammetric response of a two-electron, one-step process. Between these limits, one obtains a wide peak splitting and a lower, broader response, manifesting the difference in $E_2^0 - E_1^0$. When $E_2^0 - E_1^0 = 0$, the expected splitting $E_{pa} - E_{pc} = 42$ mV, which is still smaller than the limiting value for **2** extrapolated to zero current.

Thus, we conclude that $E_2^0 - E_1^0$ is about 35 mV, so removal of the second electron is only slightly more difficult than removal of the first. Taking (E_{pa}

+ E_{pc})/2 = 1.00 V vs. SCE as the effective standard potential for the composite wave, we estimate E_1^0 as 0.98 V and E_2^0 as 1.02 V vs. SCE in acetonitrile.

The data in Table 3 for i_{pc}/i_{pa} show that the product of the two-electron oxidation of **2** is stable over most of the cyclic voltammetric time-scale. At sweep rates slower than 100 mV/s, there is a deviation from unity in i_{pc}/i_{pa} that indicates either slight instability in the two-electron oxidation product or convective losses of that product from the diffusion layer.

The consistency of $i_{pa}/n^{1/2}$ with scan rate is sufficiently good to indicate that the oxidation of **2** is diffusion controlled. The falloff in values at high n is probably related to distortions in the ramp waveform caused by IR losses, and the rise at very low n probably reflects convective contributions or nonlinear diffusion to the unshielded disk.

DISCUSSION

The similarities in the electrooxidative behavior of **2** and **5** suggest cooperative interactions between the substituents present. The ease with which the first electron is removed suggests that the charge density in the one-electron oxidized forms of **2** and **5** is, to a considerable extent, located outside the anthracene nucleus. The dissimilarities between **2** and **5** in electrooxidative behavior, manifested in the greater ease in the removal of the second electron in **2** relative to **5** and the greater stability of the two-electron oxidation product of **2** relative to **5**, suggest an important function of the second *para*-tolylthio group in the electrooxidative chemistry of **2** relative to **5**.

A plausible explanation for the lowering of the potential necessary for the first oxidations of **2** and **5** relative to anthracenes **3** and **4** is the nonbonding interaction of the lone pairs of electrons of the sulfur atom(s) with the electrons of the 2,6-dimethoxyphenyl group π -orbital HOMO. These groups are closely juxtaposed as a result of the geometric constraints provided by their attachment to the anthracene nucleus, making interaction between them inescapable in the preferred conformation. The result of the antibonding interaction between the filled molecular orbitals of these groups is a ground-state destabilizing interaction. This interaction can be viewed in a simplified manner by considering only a single filled *p*-orbital of the central carbon and a filled *p*-orbital on each sulfur of **2** and **5**. The interaction is a two-orbital four-electron interaction for **5** and is a three-orbital six-electron interaction for **2**, as shown in Figures 4 and 5. The approximation in Figure 5 is commonly called the hypervalent [15] bonding scheme when only the two lower orbitals are occupied. These ground-state interactions raise the energy of the HOMO facilitating removal of an electron. The interaction of the three neighboring groups in **2** is expected quali-

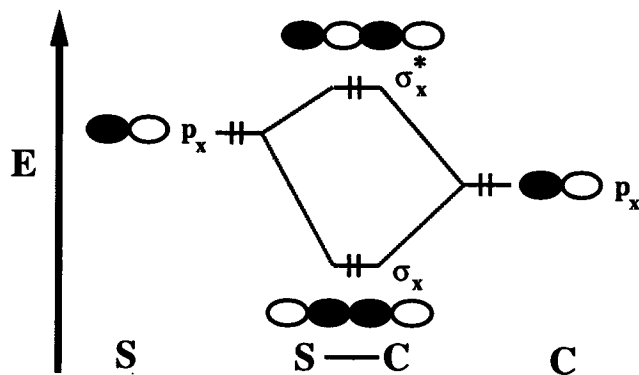


FIGURE 4 Simplified molecular orbital scheme for interaction of a filled p -orbital of carbon and a filled p -orbital of sulfur in **5**.

tatively to be greater than that of the two groups in **5**. This is in accord with the observed lower potential for the one-electron oxidation of **2** relative to **5**. Anthracene **2** is oxidized at 0.1 V lower potential than **5**.

One-electron oxidation of **5** removes this destabilizing interaction by forming a bond between sulfur and carbon **1**. Radical cation **7** is the product expected from one-electron oxidation of **5**. The unpaired electron in **7** is in an approximately non-bonding π -orbital of the pentadienyl system. The removal of this electron creates a dicationic species in which two positive charges are closely juxtaposed. The resulting unfavorable electrostatic interaction manifests itself in the much higher potential for the second oxidation of **5** observed in the voltammetric studies (Table 1). In keeping with this, the product (**8**) from this second oxidation of **5** is shown to be very reactive by the fact that its formation is irreversible in cyclic voltammetry (Figure 2). This lack of stability was observed earlier [2] for chemically generated dication **8**, a species whose solutions in strongly acidic sulfuryl chloride fluoride were stable for periods long enough to allow characterization by ^1H NMR only

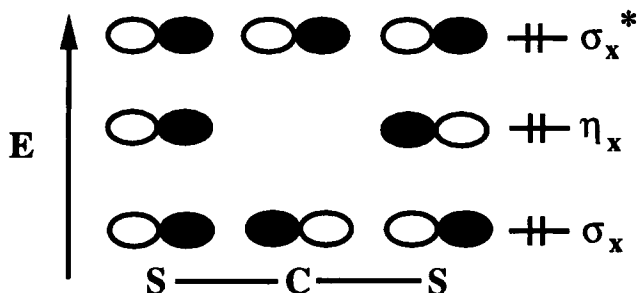


FIGURE 5 Simplified molecular orbital picture for the linear interaction of two p_x -orbitals of two sulfurs flanking the p_x -orbital of a carbon in **2**, typical for hypervalent species when two electrons are removed from orbital σ_x^* .

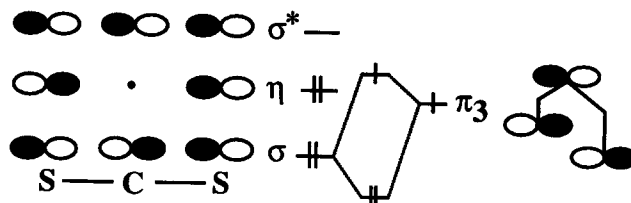
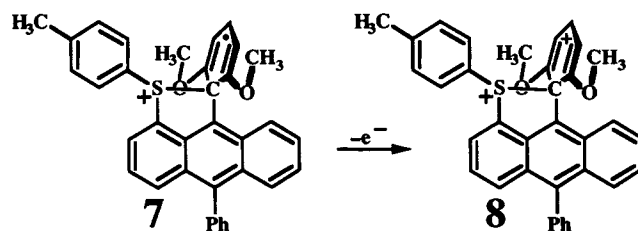


FIGURE 6 A PMO picture for **9** based on a consideration of the interaction of the SOMO of the pentadienyl fragment with a filled hypervalent three-center orbital of this radical-cation.

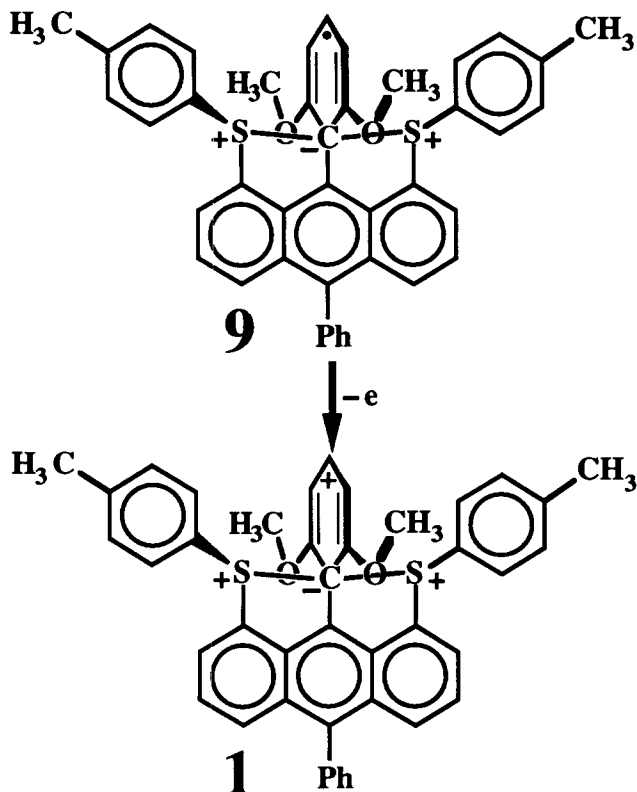
at -50°C or below. Attempts to obtain NMR spectra of **8** were successful in only a few of many experiments [2].



The ease with which the first electron is removed from **2** suggests the importance of the three-center interaction of Figure 5. The removal of a second electron to give dication **1** is easier than for the analogous oxidation of **7** because of the greater delocalization of positive charge in dication **1** than in its two-center analog, **8** (note the formal negative charge on C_1 of **1** and **9**). The features of **1** which provide stability for this 10-C-5 two-electron oxidation product of **2** are discussed in an earlier article in this series [2].

Another way of developing the same conclusion uses a PMO argument which views radical cation **9** in terms of a pentadienyl radical interacting with the lowest of the hypervalent three-center orbitals, as pictured in Figure 6. Removal of the unpaired electron, found primarily in the π non-bonding orbital, π_3 of the pentadienyl system gives dication **1**. In the pictured geometry, the SOMO orbital π_3 of the pentadienyl fragment interacts with the bonding (σ) orbital of the three-center four-electron (hypervalent) bond linking the sulfurs to carbon (Figure 6). The result of this interaction is to raise in energy the pentadienyl orbital π_3 . This results in decreasing the energy necessary to remove the single electron in it. These effects are reflected in a second oxidation potential for **2** which is separated from the first by only approximately 35 mV. The second oxidation potential for **2** ($E_2^0 = 1.02$ V) is greatly reduced ($\Delta V = 0.32$ V) from the second electrooxidative potential of **5** ($E_2^0 = 1.34$ V) as would be anticipated from this analysis.

The replacement of the three-center repulsive interactions of **2** with the bonding S-C-S interactions of **1** is expected to result in a decrease in C-S internuclear distances. This change in geometry would, of course, increase the orbital interactions in the two-electron oxidation product relative to those in neutral anthracene **2**. This provides further stabilization of **1** relative to the stability which would be observed for a Franck-Condon two-electron oxidation product from **2**.



SUMMARY

The ease with which the two-electron oxidation of **2** is effected results from the removal of the antibonding interaction of electron pairs on the sulfurs with the electron-rich 2,6-dimethoxyphenyl group of **2** in favor of a bonding interaction of these groups in **1**. This provides evidence for the ultimate formation of a three-center four-electron (hypervalent) bond to carbon in **1**. The interaction in **1** of an unfilled π -acceptor equatorial bidentate ligand (represented by the pentadienyl π_3 orbital of Fig-

ure 6 minus one electron) with the hypervalent three-center bond results in significant stabilization of this species. The unpaired electron in radical cation **9**, therefore, is destabilizing and easily removed to give dication **1**. In anthracene **5**, the first electron is also more easily removed than in the cases of the other anthracenes studied, as a result of a two-orbital four-electron interaction related to the three-orbital interaction important in **2**. The second oxidation of **2** (**9** \rightarrow **1**), however, is much more facile than that of **5** (**7** \rightarrow **8**) as a result of the importance of the three-center bond to hypervalent carbon in **1**, a type of bonding not possible for dication **8**.

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