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*J. Phys. Chem.*, **1969**, 73 (4), 779-788 • DOI: 10.1021/j100724a004 • Publication Date (Web): 01 May 2002

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## Electron Spin Resonance Studies of Hyperconjugation in 2,3-, 2,6-, and 2,7-Dimethylantracene Cation and Anion Radicals

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The electron spin resonance (esr) spectra of the 2,3-, 2,6-, and 2,7-dimethylantracene cation and anion radicals, prepared by oxidation with sulfuric acid and by reduction with either potassium metal in dimethoxyethane or electrochemically in dimethylformamide, are given. The experimental coupling constants arising from the interaction of the unpaired electron with the ring protons were found to be in good agreement with those calculated using simple Hückel molecular orbital theory. The experimental coupling constants arising from the interaction of the unpaired electron with the methyl protons were found to be in good agreement with those calculated using simple Hückel molecular orbital theory considering a hyperconjugative model and Levy's formula. Polarographic reduction half-wave potentials of 30 methyl-substituted anthracenes and naphthalenes were correlated with the energies of the lowest vacant  $\pi$ -molecular orbital. Molecular orbital calculations using different models (inductive, heteroatom, hyperconjugation) showed that the best results were obtained with the hyperconjugation model with a small inductive effect; this model also yielded spin densities which were in good agreement with the electron spin resonance results.

The effects that are produced by the substitution of a methyl group for a hydrogen into an aromatic hydrocarbon have been discussed in terms of inductive and hyperconjugative models. The inductive effect of a methyl group upon an aromatic hydrocarbon is considered as a direct electrostatic effect modifying the electric potential in the aromatic ring, with the carbon of the aromatic ring adjacent to the methyl group made more electropositive. The latter effect causes a charge redistribution around this ring carbon, but no transference of actual charge is allowed between the aromatic ring and the methyl group.<sup>2</sup> On the other hand, the hyperconjugative effect has been defined in the most general sense as the conjugation of alkyl groups with a multiple bond.<sup>3,4</sup> Among the alkyl groups, the methyl group, due to its higher symmetry, can conjugate more effectively with multiple bonds than other alkyl groups. For example, the hyperconjugative effect for a methyl group and an aromatic hydrocarbon can be explained theoretically, on the basis of molecular orbital theory, in the following way. It is possible to construct, by a proper combination, orbitals for a methyl group which possess  $\pi$  symmetry and can combine with the  $\pi$  orbitals of the aromatic ring. This combination allows a flow of electrons between the methyl group and the aromatic ring, producing a redistribution of electrons in the aromatic ring.

The assessment of the alkyl substitution effects in terms of an inductive or a hyperconjugative model has been discussed extensively.<sup>5</sup> Among the experimental techniques used to study this problem, electron spin resonance (esr) seems to be one of the best for ion and neutral radicals which involve alkyl substitution effects.<sup>2b,6,7</sup> The main value of esr in these studies is

based on the fact that hyperfine splitting from methyl protons will be observed only if the unpaired spin density penetrates in some way into the methyl group and interacts with the protons of this group. Experimentally this effect has been observed several times, for example in 9-methyl- and 9,10-dimethylantracene cation and anion radicals,<sup>2b,8</sup> and in several dimethylnaphthalene anion radicals.<sup>9</sup>

The observation of hyperfine splittings arising from methyl protons can be explained by a hyperconjugative mechanism, since the combination of the methyl group  $\pi$ -electron orbitals (pseudo  $\pi$  orbitals)<sup>7</sup> with the  $\pi$  orbitals of the aromatic rings allows the delocalization of the unpaired electron (unpaired spin density) onto the methyl groups. This leads directly to hyperfine splittings from the interactions of this unpaired spin density with the methyl protons.

The experimental observation of hyperfine splittings from methyl protons apparently rules out the impor-

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(2) (a) G. W. Wheland and L. Pauling, *J. Amer. Chem. Soc.*, **57**, 2086 (1935); (b) J. R. Bolton, A. Carrington, and A. D. McLachlan, *Mol. Phys.*, **5**, 31 (1962).

(3) (a) R. S. Mulliken, *J. Chem. Phys.*, **7**, 339 (1939); (b) R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Amer. Chem. Soc.*, **63**, 41 (1941).

(4) C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, 2052 (1953).

(5) (a) "Conference on Hyperconjugation," Indiana University, June, 1958, in *Tetrahedron*, **5**, 105 (1959); (b) R. S. Mulliken, *ibid.*, **6**, 68 (1959); (c) M. J. S. Dewar, "Hyperconjugation," The Ronald Press Company, New York, N. Y., 1962.

(6) M. C. R. Symons, *Tetrahedron*, **18**, 333 (1962).

(7) J. P. Colpa and E. de Boer, *Mol. Phys.*, **7**, 333 (1964).

(8) J. A. Brivati, R. Hulme, and M. C. R. Symons, *Proc. Chem. Soc.*, 384 (1961).

(9) F. Gerson, B. Weidmann, and E. Heilbronner, *Helv. Chim. Acta*, **47**, 1951 (1964).

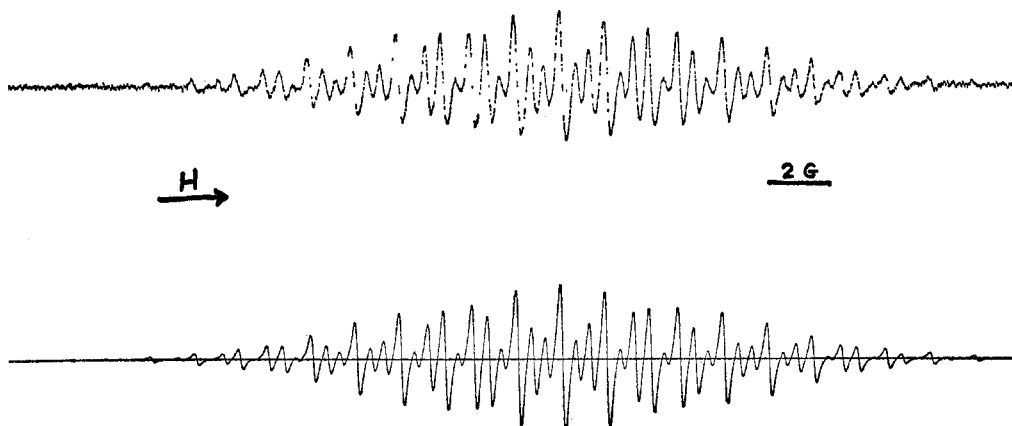


Figure 1. Top: esr spectrum of 2,3-dimethylantracene anion radical prepared by potassium metal reduction in DME and examined at  $-80^{\circ}$ . Bottom: theoretical simulated esr spectrum using the coupling constants listed in Table I and a line width of 0.160 G.

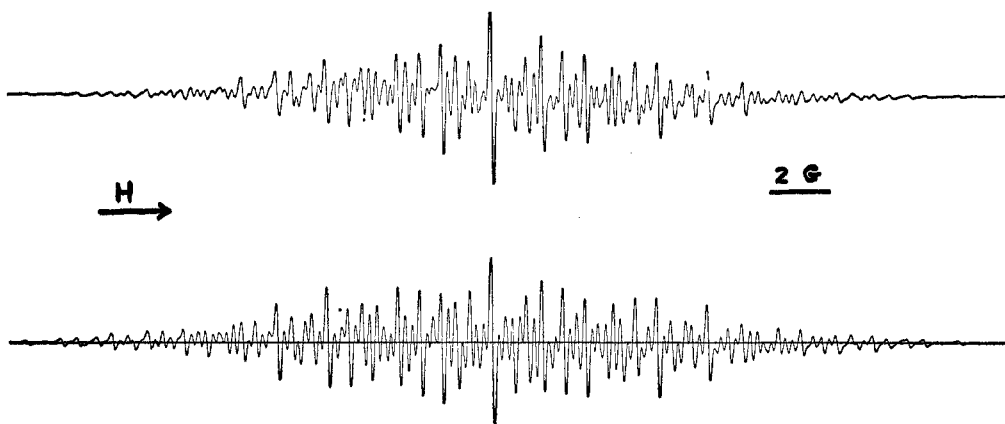


Figure 2. Top: esr spectrum of 2,3-dimethylantracene cation radical prepared by sulfuric acid oxidation. Bottom: theoretical simulated esr spectrum using the coupling constants given in the Table I and a line width of 0.160 G.

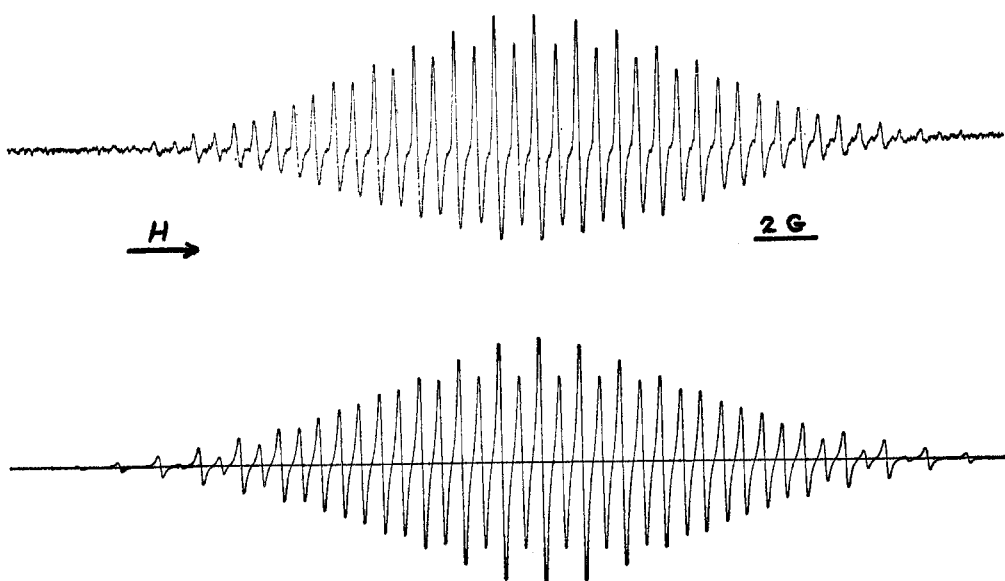


Figure 3. Top: esr spectrum of 2,6-dimethylantracene anion radical prepared by electrochemical reduction in DMF and examined at  $-50^{\circ}$ . Bottom: theoretical simulated esr spectrum using the coupling constants listed in Table I and a line width of 0.130 G.

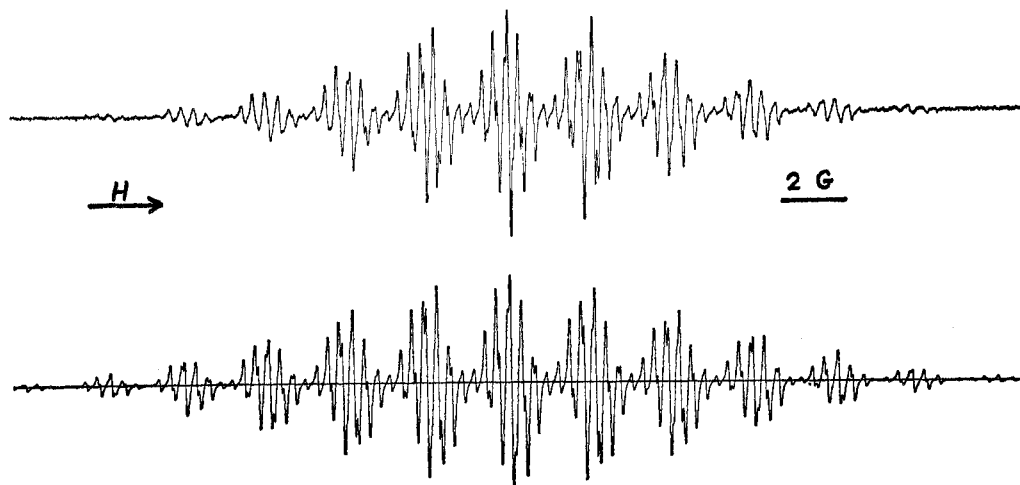
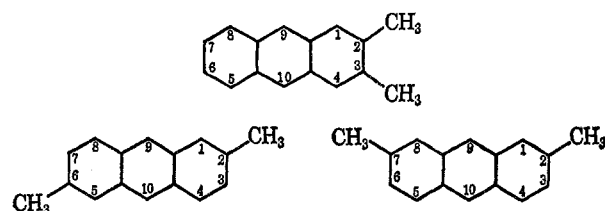


Figure 4: Top: esr spectrum of 2,6-dimethylantracene cation radical prepared by sulfuric acid oxidation. Bottom: theoretical simulated esr spectrum using the coupling constants given in Table I and a line width of 0.090 G.

tance of an inductive model to explain the methyl substitution effects, since there is no provision in this model for a charge transference between the aromatic ring and the methyl group. However, those hyperfine splittings from the methyl protons could also arise through a spin-exchange polarization mechanism similar to that which produces proton hyperfine splittings in aromatic ion radicals, which arise by spin-exchange polarization between the unpaired  $\pi$  electron and the  $\sigma$  electrons in the C-H bond.<sup>10,11</sup> In the case of methyl proton hyperfine splittings Colpa and de Boer<sup>7</sup> suggested that "spin polarization merely rearranges the spins in the  $\sigma$  orbitals of the aliphatic C-C and C-H bonds, without a net transfer of spin into these orbitals, spin density now arises through correlation effects between the unpaired electron and the paired electron in the  $\sigma$  bonds." However, if the methyl proton coupling constants arise only from a spin-exchange polarization mechanism, one would expect these coupling constants to be very similar in the cation and anion radicals of a given alternant hydrocarbon. This is because, in the case of a spin polarization mechanism, the hyperfine splittings arising from the methyl protons should be proportional to the unpaired spin density in the substituted ring carbon. Molecular orbital calculations show that the spin densities in the substituted ring carbons in cations and anions are very similar. Experimentally, Bolton, *et al.*,<sup>2b</sup> and Colpa and de Boer<sup>7</sup> have shown that the methyl (and also methylene) proton coupling constants are nearly twice as large for the cation radicals as the corresponding constants for the anion radicals (for example, 8.00 and 3.88 G in 9,10-dimethylantracene, 7.79 and 4.27 G in 9-methylantracene, and 12.80 and 6.58 G in pyracene cation and anion radicals, respectively). Hence the experimental facts cannot be explained exclusively by spin-exchange polarization, and it is also necessary to consider an alternate mechanism, *e.g.*, hyperconjugation,

to account for them. Indeed, the hyperconjugative model can predict correctly that the methyl (or methylene) proton coupling constants in the cation radical will be nearly twice as large as in the anion radicals of these aromatic hydrocarbons, and the contribution of spin polarization to the methyl or methylene splitting is very small, probably no more than a few per cent of the total observed hyperfine splittings.<sup>7,12</sup>

The objectives of the present work were: (1) to examine the esr spectra of the 2,3, 2,6-, and 2,7-dimethylantracene (DMA) cation and anion radicals



(2) to discuss the different models used in the molecular orbital calculations of methyl-substituted aromatic hydrocarbons and to correlate the experimental coupling constants arising from the interaction of the unpaired electron with both the ring protons and the methyl protons; (3) to correlate polarographic reduction half-wave potentials of methyl-substituted anthracenes and naphthalenes with molecular orbital theory to test the different models considered in these calculations.

## Results

*Preparation of Radicals.* Anion radicals were prepared either by exhaustive controlled-potential electrolysis in an external cell at a mercury pool electrode

(10) (a) H. M. McConnell, *J. Chem. Phys.*, **24**, 632, 764 (1956); (b) H. M. McConnell and H. H. Dearman, *ibid.*, **28**, 51 (1958); (c) H. M. McConnell and D. B. Chesnut, *ibid.*, **28**, 107 (1958).

(11) (a) S. I. Weissman, *ibid.*, **25**, 890 (1956); (b) H. S. Jarret, *ibid.*, **25**, 1289 (1956).

(12) D. H. Levy, *Mol. Phys.*, **10**, 233 (1966).

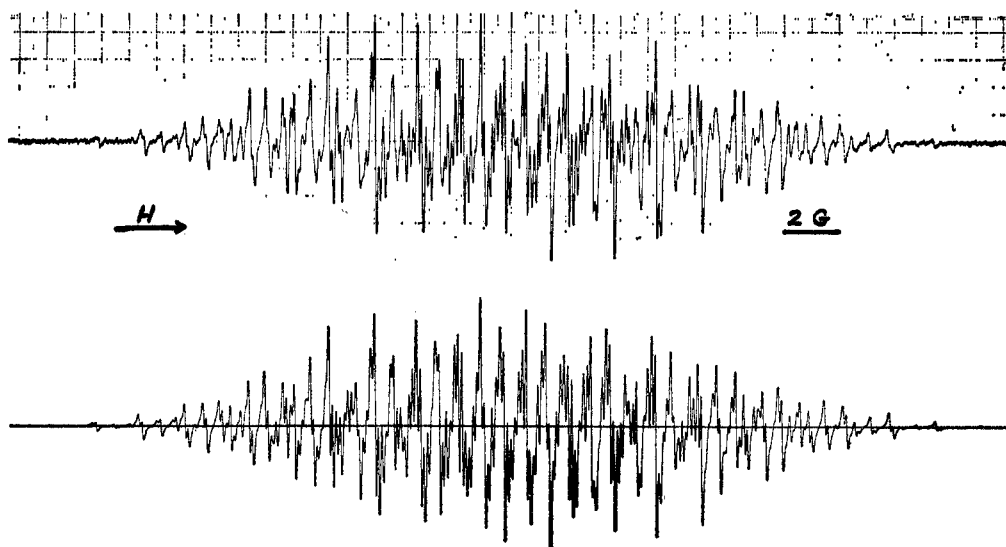


Figure 5. Top: esr spectrum of 2,7-dimethylantracene anion radical prepared by potassium metal reduction in DME and examined at  $-80^\circ$ . Bottom: theoretical simulated esr spectrum using the coupling constants listed in Table I and a line width of 0.096 G.

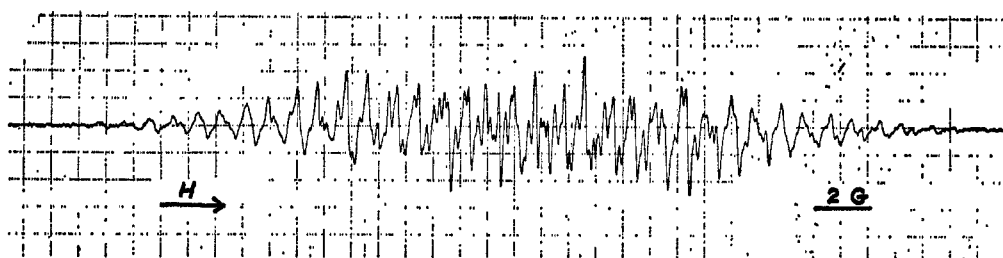


Figure 6. ESR spectrum of 2,7-dimethylantracene cation radical prepared by sulfuric acid oxidation.

in dimethylformamide (DMF) solutions containing 0.1 *M* tetra-*n*-butylammonium iodide (TBAI) as supporting electrolyte and concentrations of the hydrocarbons of  $2$  to  $6 \times 10^{-4}$  *M* or by potassium metal reduction in dimethoxyethane (DME). Cation radicals were obtained by dissolving a few milligrams of the hydrocarbon in concentrated sulfuric acid at room temperature. Hydrocarbon concentrations of 0.001 to 0.02 *M* were employed. Details are given in the Experimental Section.

The spectra of the anion radicals prepared by electrolytic reduction in DMF and potassium metal reduction in DME were virtually identical. Typical spectra for 2,3-DMA, 2,6-DMA, and 2,7-DMA anion and cation radicals are shown in Figures 1 through 6.

*Assignment of the ESR Spectra.* The coupling constants for the radicals were assigned by comparing the experimental spectra with those simulated by a computer. The values of the assigned coupling constants are given in Table I. The computer-simulated spectra based on the coupling constants, assuming a Lorentzian line shape, are shown in Figures 1 through 5. Line-width variations and lack of good resolution in the experimental spectrum of 2,7-DMA cation radical prevented a complete assignment of coupling constants. The approximate values given in Table I were obtained

by inspection of an esr spectrum produced by over-modulation.

## Discussion

*Molecular Orbital Treatment of Methyl-Substituted Aromatic Hydrocarbons.* To account for the effects produced by a methyl group substitution in an aromatic hydrocarbon, three models are commonly used in molecular orbital theory: (1) the inductive model,<sup>1</sup> (2) the heteroatom model,<sup>13</sup> and (3) the hyperconjugation model.<sup>3</sup>

*Inductive Model.* The substitution of a methyl group for a hydrogen atom in an aromatic hydrocarbon produces a change in the magnitude of the coulomb integral of the substituted aromatic carbon due to the electron-donating inductive effect of the methyl group. This inductive effect is treated in Hückel molecular orbital (HMO) theory<sup>14</sup> by assigning a small negative value to the coulomb parameter  $h_r$  for the carbon atom *r* of the  $\pi$  system to which the methyl group has been attached. It has been found that suitable values for

(13) F. A. Matsen, *J. Amer. Chem. Soc.*, **72**, 5243 (1950).

(14) E. Hückel, *Z. Physik*, **70**, 204 (1931).

**Table I:** Experimental Coupling Constants of ESR Spectra of 2,3-, 2,6-, and 3,7-Dimethylanthracene Cation and Anion Radicals

	Ring position									
	1	2	3	4	5	6	7	8	9	10
2,3-DMA <sup>+</sup>	3.60	1.95 <sup>a</sup>	1.95 <sup>a</sup>	3.60	2.76	1.35	1.35	2.76	6.38	6.38
2,3-DMA <sup>-</sup>	2.37	1.46 <sup>a</sup>	1.46 <sup>a</sup>	2.37	2.87	1.46	1.46	2.87	5.30	5.30
2,6-DMA <sup>+</sup>	3.18	2.76 <sup>a</sup>	0.56	3.18	3.18	2.76 <sup>a</sup>	0.56	3.18	6.33	6.33
2,6-DMA <sup>-</sup>	2.67	1.33 <sup>a</sup>	1.33	3.32	2.67	1.33 <sup>a</sup>	1.33	3.32	5.25	5.25
2,7-DMA <sup>+</sup>	2.7	2.7 <sup>a</sup>	0.9	2.7	2.7	0.9	2.7 <sup>a</sup>	2.7	6.3	5.5
2,7-DMA <sup>-</sup>	2.40	1.72 <sup>a</sup>	1.60	3.00	3.00	1.60	1.72 <sup>a</sup>	2.40	4.83	5.66

<sup>a</sup> Denotes a methyl proton hyperfine splitting.

$h_r$  range from  $-0.3$  to  $-0.5$ .<sup>15</sup> In this work the coulomb integral parameter,  $h_r$ , was given a value of  $-0.3$ .<sup>2b</sup>

**Heteroatom Model.** In this model, the methyl group is regarded as a pseudo-heteroatom,  $m$ , which contributes a pair of electrons to the  $\pi$  system. Therefore, two parameters have to be considered: (1) a resonance integral parameter,  $k_{rm}$ , for the evaluation of the resonance integral,  $\beta_{rm}$ , corresponding to the bond between the carbon of the pseudo-heteroatom (methyl group),  $m$ , and the substituted carbon atom of the  $\pi$  system,  $r$ , and (2) a coulomb integral parameter,  $h_m$ , to calculate the coulomb integral,  $\alpha_m$ , of the pseudo-heteroatom,  $m$ . Parameter values covering the ranges 1.4–3.3 and 0.5–0.8 have been used for  $h_m$  and  $k_{rm}$ , respectively. In this work, the resonance integral parameter,  $k_{rm}$ , was given a value of 0.5, and the coulomb integral parameter,  $h_m$ , was given a value of 1.5.<sup>2b</sup>

**Hyperconjugation Model.** In this model, the methyl group is treated as a modified vinyl group,  $C'-C-H_3$ , where  $C'$  is the substituted carbon atom belonging to the original  $\pi$  system,  $C$  corresponds to the carbon atom of the methyl group, and  $H_3$  is the pseudo-atom corresponding to a group of three hydrogens. In this model, there are several parameters to consider: the coulomb integral parameters,  $h_{C'}$ ,  $h_C$ , and  $h_{H_3}$ , and the resonance integral parameters,  $k_{C'C}$  and  $k_{CH_3}$ . Mulliken, *et al.*,<sup>3</sup> in their original calculations using this model, assumed  $h_{C'}$ ,  $h_C$ , and  $h_{H_3}$  were zero, and  $k_{C'C} = 0.8$  and  $k_{CH_3} = 5$ . Coulson and Crawford<sup>4</sup> modified these original parameters based on the following arguments. (1) The *ortho-para* directing property of the methyl substituent in electrophilic reactions implies that a  $\pi$ -electron migration from the methyl group into the aromatic hydrocarbon must be involved. To account for this effect, the coulomb integral parameter for the pseudo-atom,  $h_{H_3}$ , was given a value of  $-0.5$ , making it more electropositive than the ring carbon atom,  $C'$ . The electropositive nature of  $H_3$  was also assumed to be shared with the adjacent carbon atom,  $C$ , whose coulomb integral parameter was then given a value of  $-0.1$ . (2) The resonance integrals were assumed to vary with distance and be proportional to the overlap

integrals;  $k_{C'C} = 0.7$  and  $k_{CH_3} = 2.5$  were used. Coulson and Crawford's parameters were chosen in order to reproduce the dipole moment of toluene. This set of parameters with small variations has been employed by the majority of researchers in this field. In this work Levy's values of the coulombs integral parameters,  $h_{C'} = 0$ ,  $h_C = -0.1$ , and  $h_{H_3} = -0.5$ , and the resonance integral parameters,  $k_{C'C} = 0.76$  and  $k_{CH_3} = 2.00$ , were employed.

It has been suggested from electronic spectra studies<sup>16</sup> and from the interpretation of esr spectra of toluene and other anions<sup>17</sup> that it is necessary to introduce a small inductive effect together with hyperconjugation. In this work, we have also considered this possibility by giving to the coulomb integral parameter,  $h_{C'}$ , a value of  $-0.1$ .

**Calculated Coupling Constants. Ring Protons.** Values of the spin densities ( $\rho$ ) were calculated using the different models; the results are listed in Table II. The calculated  $\rho$  values were compared with those derived from the experimental coupling constants ( $a_H$ ) using the following relations: (1) the McConnell relation:<sup>10</sup>  $a_H = Q\rho$ , with  $Q = 32$  for cations, and  $Q = 28$  for anions; (2) the Colpa-Bolton relation:<sup>18</sup>  $a_H = (Q\rho \pm K\rho^2)$ , where  $Q = 27$  and  $K = 12$ ; (3) the Giacometti-Nordio-Pavan relation:<sup>19</sup>  $a_H = Q_1\rho \pm Q_2 |\sum_j c_i c_j|$ , where  $Q_1 = 31.5$  and  $Q_2 = 7.0$ . Values of the ring coupling constants for the different models and the above relations are given in Tables III to V. Since there are no major differences among the magnitudes of the spin densities of a specific ring position calculated using the different models (Table II), when the same relation (*e.g.* McConnell) is used for the calculation of the theoretical coupling constants of a specific ring position, no major differences are found

(15) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

(16) A. Denis and A. Pullman, *Theoret. Chim. Acta*, **7**, 110 (1967).

(17) (a) J. P. Malrieu, A. Pullman, and M. Rossi, *ibid.*, **3**, 261 (1965); (b) D. Lazdins and M. Karplus, *J. Amer. Chem. Soc.*, **87**, 920 (1965); (c) E. de Boer and J. P. Colpa, *J. Phys. Chem.*, **71**, 21 (1967).

(18) (a) J. P. Colpa and J. R. Bolton, *Mol. Phys.*, **6**, 273 (1963); (b) J. R. Bolton, *J. Chem. Phys.*, **43**, 309 (1965).

(19) G. Giacometti, P. L. Nordio, and M. V. Pavan, *Theoret. Chim. Acta*, **1**, 404 (1963).

**Table II:** Hückel Spin Densities of the Ring Carbon Atoms of Dimethylantracene Cation and Anion Radicals Calculated Using Several Models

Carbon atom	Model			
	Inductive	Hetero-atom	Hyperconjugation With inductive effect	Without inductive effect
2,3-Dimethylantracene				
Cation radical				
1	0.1162	0.1098	0.1108	0.1046
5	0.0897	0.0897	0.0892	0.0913
6	0.0466	0.0462	0.0460	0.0465
9	0.1918	0.1890	0.1887	0.1890
Anion radical				
1	0.0741	0.0866	0.0874	0.0945
5	0.1054	0.0995	0.0982	0.0957
6	0.0504	0.0489	0.0484	0.0478
9	0.1938	0.1924	0.1909	0.1908
2,6-Dimethylantracene				
Cation radical				
1	0.1137	0.1069	0.1077	0.1023
3	0.0304	0.0339	0.0328	0.0385
4	0.0931	0.0922	0.0917	0.0931
9	0.1907	0.1875	0.1869	0.1881
Anion radical				
1	0.0822	0.0895	0.0899	0.0947
3	0.0669	0.0561	0.0545	0.0484
4	0.0982	0.0970	0.0962	0.0955
9	0.1931	0.1924	0.1911	0.1908
2,7-Dimethylantracene				
Cation radical				
1	0.1195	0.1115	0.1127	0.1053
3	0.0376	0.0394	0.0387	0.0420
4	0.0877	0.0883	0.0876	0.0905
9	0.2113	0.2028	0.2036	0.1979
10	0.1726	0.1743	0.1728	0.1794
Anion radical				
1	0.0761	0.0869	0.0876	0.0945
3	0.0641	0.0530	0.0519	0.0481
4	0.1045	0.0996	0.0984	0.0957
9	0.1755	0.1844	0.1842	0.1900
10	0.2127	0.2007	0.1980	0.1915

from one model to another. Hence a study of only the ring proton coupling constants is not useful for deciding the magnitude of hyperconjugation or inductive effects in these dimethylantracenes. This argument can be extended to other methyl-substituted anthracenes using perturbation theory.<sup>2</sup>

*Calculated Coupling Constants. Methyl Protons.* The experimental methyl proton coupling constants are listed in Table VI. The methyl proton coupling constants of 9-methyl- and 9,10-dimethylantracenes are also listed in Table VI. Note that the methyl proton coupling constants for the cation radicals are larger

than the corresponding anion radicals, and the ratio of cation to anion coupling constants is, in most cases, close to a factor of 2. The experimental findings suggest that the large differences in the cation and anion coupling constants are due to a predominantly hyperconjugative mechanism. Therefore, since an inductive model in which the methyl proton hyperfine splittings arise exclusively through a spin-exchange polarization mechanism could not account for these differences in methyl proton coupling constants, the hyperconjugation models were tested. Bolton, *et al.*,<sup>2</sup> observed that the

**Table III:** Experimental and Theoretical Ring Proton Coupling Constants in 2,3-Dimethylantracene Cation and Anion Radicals Assuming Different Models and Relations

Carbon atom	$a_H$   , G				Exptl
	In-ductive	Het-ero-atom	Hyperconjugation With inductive effect	Without inductive effect	
McConnell Relation					
Cation radical					
1	3.72	3.51	3.55	3.35	3.60 <sup>a</sup>
5	2.87	2.87	2.85	2.92	2.76 <sup>a</sup>
6	1.49	1.48	1.47	1.49	1.35
9	6.14	6.05	6.04	6.05	6.38
Anion radical					
1	2.07	2.43	2.45	2.65	2.37 <sup>a</sup>
5	2.95	2.78	2.75	2.73	2.87 <sup>a</sup>
6	1.41	1.37	1.35	1.40	1.46
9	5.43	5.39	5.35	5.67	5.30
Giacometti-Nordio-Pavan Relation					
Cation radical					
1	3.98	3.76	3.80	3.59	3.60 <sup>a</sup>
5	3.07	3.07	3.06	3.13	2.76
6	1.59	1.58	1.58	1.60	1.35
9	6.56	6.47	6.46	6.48	6.38
Anion radical					
1	2.10	2.47	2.49	2.70	2.37 <sup>a</sup>
5	3.32	2.84	2.80	2.74	2.87 <sup>a</sup>
6	1.43	1.39	1.38	1.37	1.46
9	5.50	5.49	5.46	5.45	5.30
Colpa-Bolton Relation					
Cation radical					
1	3.30	3.11	3.14	2.96	3.60 <sup>a</sup>
5	2.52	2.52	2.51	2.56	2.76 <sup>a</sup>
6	1.28	1.27	1.30	1.28	1.35
9	5.62	5.53	5.52	5.53	6.38
Anion radical					
1	1.93	2.25	2.27	2.45	2.37 <sup>a</sup>
5	2.71	2.57	2.54	2.47	2.87 <sup>a</sup>
6	1.33	1.29	1.28	1.26	1.46
9	4.78	4.75	4.72	4.71	5.30

<sup>a</sup> Assigned to this position on the basis of MO theory.

heteroatom model could predict fairly well the ratios of the methyl proton coupling constants of the cation and anion radicals of 9-methyl- and 9,10-dimethylanthracenes. The following theoretical and experimental ratios, respectively, were obtained:<sup>2</sup> 9-methylanthracene, 3.638 and 1.82, and 9,10-dimethylanthracene, 3.095 and 2.06. In the present work the following theoretical and experimental ratios were found: 2,3-dimethylanthracene, 2.471 and 1.34; 2,6-dimethylanthracene, 3.657 and 2.08; and 2,7-dimethylanthracene, 3.078 and 1.57. Note that the experimental ratio for 2,3-dimethylanthracene is lower than for the other

**Table IV:** Experimental and Theoretical Ring Proton Coupling Constants in 2,6-Dimethylanthracene Cation and Anion Radicals Assuming Different Models and Relations

Carbon atom	a <sub>H</sub>  , G				Exptl
	In-ductive	Het-ero-atom	Hyperconjugation With inductive effect	Without inductive effect	
McConnell Relation					
Cation radical					
1	3.64	3.42	3.45	3.27	3.18
3	0.97	1.08	1.05	1.23	0.54
4	2.98	2.95	2.93	2.98	3.18
9	6.10	6.00	5.98	6.02	6.33
Anion radical					
1	2.30	2.51	2.52	2.65	2.67 <sup>a</sup>
3	1.87	1.57	1.53	1.39	1.33
4	2.75	2.72	2.69	2.73	3.32 <sup>a</sup>
9	5.41	5.39	5.35	5.46	5.25
Giacometti-Nordio-Pavan Relation					
Cation radical					
1	3.89	3.66	3.69	3.51	3.18
3	1.04	1.16	1.12	1.32	0.54
4	3.18	3.16	3.14	3.19	3.18
9	6.52	6.42	6.40	6.45	6.33
Anion radical					
1	2.34	2.55	2.56	2.71	2.67 <sup>a</sup>
3	1.90	1.60	1.57	1.39	1.33
4	2.79	2.77	2.75	2.73	3.32 <sup>a</sup>
9	5.49	5.49	5.45	5.46	5.25
Colpa-Bolton Relation					
Cation radical					
1	3.22	3.02	3.05	2.89	3.18
3	0.83	0.93	0.90	1.05	0.54
4	2.62	2.59	2.58	2.62	3.18
9	5.58	5.48	5.47	5.50	6.33
Anion radical					
1	2.14	2.32	2.33	2.45	2.67 <sup>a</sup>
3	1.75	1.48	1.44	1.28	1.33
4	2.54	2.51	2.49	2.47	3.32 <sup>a</sup>
9	5.49	4.75	4.72	4.72	5.25

<sup>a</sup> Assigned to this position on the basis of MO theory.

**Table V:** Experimental and Theoretical Ring Proton Coupling Constants in 2,7-Dimethylanthracene Cation and Anion Radicals Assuming Different Models and Relations

Carbon atom	a <sub>H</sub>  , G				Exptl
	In-ductive	Het-ero-atom	Hyperconjugation With inductive effect	Without inductive effect	
McConnell Relation					
Cation radical					
1	3.82	3.57	3.61	3.37	2.7
3	1.20	1.26	1.24	1.34	0.9
4	2.81	2.83	2.80	2.90	2.7
9	6.76	6.49	6.52	6.33	6.3 <sup>a</sup>
10	5.52	5.58	5.53	5.74	5.5 <sup>a</sup>
Anion radical					
1	2.13	2.43	2.45	2.65	2.40 <sup>a</sup>
3	1.68	1.48	1.45	1.35	1.60
4	2.93	2.79	2.76	2.68	3.00 <sup>a</sup>
9	4.91	5.16	5.16	5.32	4.83 <sup>a</sup>
10	5.96	5.62	5.55	5.36	5.66 <sup>a</sup>
Giacometti-Nordio-Pavan Relation					
Cation radical					
1	4.09	3.82	3.86	3.61	2.7
3	1.29	1.35	1.32	1.44	0.9
4	3.00	3.02	3.00	3.10	2.7
9	7.23	6.95	6.97	6.79	6.3
10	5.90	5.97	5.92	6.16	5.5
Anion radical					
1	2.16	2.48	2.45	2.70	2.40 <sup>a</sup>
3	1.71	1.51	1.48	1.38	1.60
4	2.97	2.84	2.81	2.74	3.00 <sup>a</sup>
9	4.99	5.26	5.26	5.43	4.83 <sup>a</sup>
10	6.04	5.72	5.65	5.48	5.66 <sup>a</sup>
Colpa-Bolton Relation					
Cation radical					
1	3.40	3.16	3.20	2.98	2.7
3	1.03	1.08	1.05	1.16	0.9
4	2.46	2.48	2.46	2.54	2.7
9	6.24	5.97	6.00	5.81	6.3 <sup>a</sup>
10	5.02	5.07	5.02	5.23	5.5 <sup>a</sup>
Anion radical					
1	1.99	2.26	2.27	2.44	2.40 <sup>a</sup>
3	1.58	1.40	1.37	1.27	1.60
4	2.69	2.57	2.54	2.47	3.00 <sup>a</sup>
9	4.37	4.57	4.57	4.70	4.83 <sup>a</sup>
10	5.20	4.94	4.88	4.73	5.66 <sup>a</sup>

<sup>a</sup> Assigned to this position on the basis of MO theory.

members of the group, probably because the steric interaction between the methyl groups in positions 2 and 3 reduces to some extent the conjugation between the methyl groups and the aromatic ring. However, although this model predicts the methyl proton coupling constant ratios in the right direction, there is a serious discrepancy between the observed and predicted split-



tings themselves, as noted by Colpa and de Boer<sup>7</sup>. They found, for example, that the heteroatom model for the ions of 9,10-DMA gave values for the methyl coupling constants that were roughly too low by a factor of 4. This same disparity was found for the DMA ion radicals in this study.

Levy<sup>12</sup> derived the following general formula for the calculation of methyl proton hyperfine splittings to be

**Table VI:** Experimental and Theoretical Methyl Proton Coupling Constants of Methylanthracene Cation and Anion Radicals. The Theoretical Methyl Proton Coupling Constants Have Been Calculated by Using Levy's Formula and the Hyperconjugation Model (with and without a Small Inductive Effect)

Hydrocarbon	$ a_H , G$		Exptl
	Levy's formula without inductive effect	Levy's formula with inductive effect	
Cation radical			
9-Methylanthracene	7.85	7.46	7.79 <sup>a</sup>
9,10-Dimethylanthracene	7.97	7.85	8.00 <sup>a</sup>
2,3-Dimethylanthracene	1.95	1.83	1.95
2,6-Dimethylanthracene	2.30	2.39	2.76
2,7-Dimethylanthracene	2.14	2.12	2.7
Anion radical			
9-Methanthracene	5.16	5.25	4.27 <sup>a</sup>
9,10-Dimethylanthracene	4.99	4.78	3.88 <sup>a</sup>
2,3-Dimethylanthracene	1.31	1.38	1.46
2,6-Dimethylanthracene	1.30	1.22	1.33
2,7-Dimethylanthracene	1.30	1.29	1.72

<sup>a</sup> Taken from ref 2b.

used with Mulliken's hyperconjugation model<sup>3</sup> with or without overlap

$$a_{\text{methyl}} = 219.8c_H^2 + 13.17c_C^2 + 107.0c_{HC}c_C + 3.997c_{HC}c_{C'} + 0.973c_{CC'} - 3.09c_{C'}^2$$

where  $c_H$  is the coefficient of the pseudo orbital ( $H_s$ ),  $c_C$  is the coefficient of the methyl carbon (C) in the modified vinyl group, and  $c_{C'}$  is the coefficient of the carbon atom (C') of the original  $\pi$  system to which the methyl group is attached. In addition to the hyperconjugation contribution, a small spin polarization contribution is considered in this formula, given by a term  $3.09c_{C'}^2$ . Levy used this formula only for anion radicals, but we have extended it to cation radicals with good success; the results are listed in Table VI. Coefficients were calculated by the HMO method without overlap using Mulliken's hyperconjugation model with and without a small inductive effect and the parameters listed previously. We have also carried out calculations of methyl proton coupling constants of several dimethylnaphthalene (DMN) anion radicals using

**Table VII:** Experimental and Theoretical Methyl Proton Coupling Constants of Dimethylnaphthalene Anion Radicals. The Theoretical Methyl Proton Coupling Constants Have Been Calculated by Using Levy's Formula and the Hyperconjugation Model (with or without a Small Inductive Effect)

Hydrocarbon	$ a_H , G$		Exptl <sup>a</sup>
	Levy's formula without inductive effect	Levy's formula with inductive effect	
1,4-Dimethylnaphthalene	4.71	4.43	3.26
1,5-Dimethylnaphthalene	4.65	4.76	4.41
1,8-Dimethylnaphthalene	4.63	4.82	4.61
2,3-Dimethylnaphthalene	1.82	1.94	1.69
2,6-Dimethylnaphthalene	1.89	1.63	1.22
2,7-Dimethylnaphthalene	1.85	1.81	2.16

<sup>a</sup> From ref 9.

Levy's formula. These results are listed in Table VII. The agreement found between the experimental and theoretically calculated coupling constants was excellent in most of the cases.

**Polarographic Correlations.** ESR-HMO correlations only serve to compare the experimental coupling constants with the theoretical spin densities, *i.e.*, the square of the various elements of the eigenvector associated with the  $\pi$ -MO where the unpaired electron moves. It is also of interest to attempt a correlation of polarographic reduction half-wave potentials with the eigenvalue of the lowest available antibonding  $\pi$ -MO. In this way both the eigenvector and the eigenvalue of a model can be tested.<sup>20</sup>

The usual correlation equation is given by<sup>15</sup>

$$E_{1/2} = -bm_{m+1} + c$$

where  $E_{1/2}$  is the polarographic reduction half-wave potential,  $m_{m+1}$  is the energy of the lowest vacant  $\pi$ -MO in units of  $\beta_{CC}$ , and  $b$ , the slope of the correlation line, is regarded as the effective value of  $\beta$  for the system under study. In the present work,  $E_{1/2}$  for 12 methylanthracenes and anthracene itself and 16 dimethylnaphthalenes and naphthalene itself, measured in 75% aqueous dioxane by Klemm, *et al.*,<sup>21</sup> have been correlated. The  $m_{m+1}$  energies were calculated from HMO theory using, as previously, the inductive, the heteroatom, and the hyperconjugation, with and without inductive effect, models. The  $E_{1/2}$  and  $m_{m+1}$  values are listed in Table VIII. The following correlation equations were obtained: *inductive model*,  $E_{1/2} = (2.085 \pm 0.125)m_{m+1} - 1.025 \pm 0.076$ ; *heteroatom model*,  $E_{1/2} = (2.387 \pm 0.057)m_{m+1} - 0.941 \pm 0.032$ ; *hyperconjugation*

(20) A. J. Bard, K. S. V. Santhanam, J. T. Maloy, J. Phelps, and L. O. Wheeler, *Discussions Faraday Soc.*, **45**, 167 (1968).

(21) (a) L. H. Klemm, A. J. Kohlik, and K. B. Desai, *J. Org. Chem.*, **28**, 625 (1963); (b) L. H. Klemm and A. J. Kohlik, *ibid.*, **28**, 2044 (1963).

**Table VIII:** Polarographic Reduction Half-Wave Potentials for Methylanthralenes and Energies of Lowest Vacant Molecular Orbitals Calculated Using Various Models

Hydrocarbon	$-E_{1/2},^a$ V vs. sce	$-m_{m+1}$ in $\beta_{CC}$ units			
		Inductive	Heteroatom	Hyperconjugation	
				Without inductive effect	With inductive effect
Anthracene	1.925	0.414	0.414	0.414	0.414
1-MA	1.937	0.442	0.427	0.415	0.428
2-MA	1.956	0.428	0.420	0.415	0.419
9-MA	1.940	0.474	0.439	0.417	0.436
2,3-DMA	1.991	0.446	0.427	0.415	0.425
2,6-DMA	1.988	0.441	0.426	0.415	0.425
2,7-DMA	1.991	0.443	0.427	0.415	0.425
9,10-DMA	1.976	0.523	0.462	0.419	0.455
2,3,9-TMA	2.007	0.505	0.452	0.418	0.446
2,6,9-TMA	2.003	0.500	0.451	0.418	0.445
2,3,6,7-TeMA	2.054	0.478	0.440	0.417	0.436
2,3,9,10-TeMA	2.044	0.554	0.475	0.420	0.465
2,3,6,7,9,10-HMA	2.109	0.589	0.487	0.421	0.474
Naphthalene	2.437	0.618	0.618	0.618	0.618
1-MN	2.458	0.671	0.639	0.615	0.633
2 MN	2.460	0.636	0.626	0.617	0.624
1,2-DMN	2.479	0.682	0.645	0.614	0.637
1,3-DMN	2.483	0.690	0.647	0.614	0.638
1,4-DMN	2.471	0.714	0.658	0.612	0.646
1,5-DMN	2.475	0.730	0.660	0.612	0.647
1,6-DMN	2.476	0.692	0.647	0.614	0.638
1,7-DMN	2.469	0.688	0.646	0.614	0.638
1,8-DMN	2.521	0.732	0.661	0.612	0.647
2,3-DMN	2.501	0.664	0.635	0.616	0.530
2,6-DMN	2.476	0.651	0.633	0.616	0.629
2,7-DMN	2.485	0.658	0.634	0.616	0.629
1,3,7-TMN	2.496	0.703	0.654	0.613	0.643
1,4,5-TMN	2.529	0.783	0.681	0.609	0.660
2,3,5-TMN	2.515	0.720	0.656	0.613	0.644
2,3,6-TMN	2.523	0.682	0.642	0.615	0.635

<sup>a</sup> From ref 21.

tion model (without a small inductive effect),  $E_{1/2} = (2.494 \pm 0.072)m_{m+1} - 0.055 \pm 0.037$ ; *hyperconjugation model* (with a small inductive effect,  $E_{1/2} = (2.456 \pm 0.051)m_{m+1} - 0.920 \pm 0.028$ .

The best least-squares fit (*i.e.*, the smallest standard deviation in the coefficient of  $m_{m+1}$ ) was obtained with the hyperconjugation model employing a small inductive effect. Note that the hyperconjugation model without a small inductive effect predicts nearly the same energy eigenvalue for each type of molecule considered, even though this model gives a fairly good overall least-squares correlation. These results support the suggestion based on studies of electronic spectra and esr spectra of toluene and other anions, that is the introduction of a small inductive effect together with hyperconjugation produces more satisfactory results.

### Conclusions

(1) The methyl proton hyperfine splittings arise in these dimethylanthracenes predominantly from a hyperconjugative mechanism rather than from a spin-

exchange polarization mechanism. This effect is more pronounced in cation radicals than in anion radicals.

(2) A hyperconjugation model (with or without a small inductive effect) where the methyl group is treated as a modified vinyl group and using slightly modified Coulson and Crawford parameters and Levy's formula is very satisfactory in accounting for methyl proton hyperfine splittings.

(3) A study of the correlations between the polarographic reduction half-wave potentials of methyl substituted anthracenes and naphthalenes *vs.* the energies of the lowest vacant  $\pi$ -MO's showed that a hyperconjugation model with a small inductive effect correlated very well.

### Experimental Section

*Electrochemical Experiments.* The electrochemical cell and the vacuum line used were essentially the same as reported by Santhanam and Bard.<sup>22</sup> The electro-

(22) K. S. V. Santhanam and A. J. Bard, *J. Amer. Chem. Soc.*, **88**, 2669 (1966).

chemical reduction was carried out in the following way. Mercury, TBAI (0.1 M), and stirring bar were introduced into the electrochemical cell. The auxiliary compartment was introduced, and the cell was connected to the vacuum line by means of O-ring ball joint. The cell was evacuated overnight to remove traces of air and water. Evacuation to about  $10^{-5}$  mm was considered satisfactory for performing the electrochemical experiment and the esr examinations. After the evacuation process the stopcocks which connect the main body of the cell with the side arms (3-mm Pyrex tubing) were closed. Then the cell was cooled down at liquid nitrogen temperature and the solvent (DMF) was distilled into it from a storage flask. After the distillation had been completed, the cell was warmed to room temperature without ceasing continuous evacuation. As soon as the room temperature had been reached, the cell was brought to the atmospheric pressure by introducing helium through the vacuum line. A helium blanket was kept over the cell during the entire experiment to prevent air from coming into contact with the solution. The cell prepared in this way was ready for electrochemical measurements. The reference electrode (sce) and the working electrode (hanging mercury drop electrode) were introduced at this moment. A cyclic voltammogram of the background was recorded to check the purity of the solution. Then, the hanging mercury drop electrode was removed and the mercury pool was connected to serve as a working electrode. As soon as this step had been completed a weighed sample was introduced into the cell by means of a small glass tube. When the sample had dissolved in the DMF, new cyclic voltammetric measurements were carried out, and finally controlled potential coulometry was performed. When the coulometry had been completed, the evacuated bulb of one of the stopcocks which was connected with the esr tube was opened to the cell. A few milliliters was pulled into this bulb to be subsequently discarded. This was carried out to get a homogeneous solution between the cell and the stopcock. The 3-mm evacuated side arm was cooled down and the stopcock was opened for a brief time to this tube. After this the 3-mm Pyrex tubing was sealed and cut with a torch. A second sample was usually taken at a different stage of the reduction in order to study the changes in the esr spectra.

Tetra-*n*-butylammonium iodide (TBAI) was obtained from Southwestern Analytical Chemicals (Austin, Texas) and was used without further purification. *N,N*-Dimethylformamide (DMF) was obtained from Eastman Organic Chemicals. It was purified by storing overnight over anhydrous copper sulfate and then was distilled under vacuum.<sup>22</sup> Helium of 99.995% purity was obtained from the Matheson Co. (La Porte, Texas). It was passed successively through anhydrous magnesium perchlorate, copper turnings heated to 350°, activated charcoal at liquid nitrogen temperature,

and finally to the vacuum line. The reference electrode employed was an aqueous saturated calomel electrode (sce) with a fresh 3% agar-1 M potassium nitrate salt bridge. The end of the sce which was immersed in the electrolytic solution was closed by a medium porosity sintered glass disk. The auxiliary electrode was a silver wire.

*Alkali Metal Reductions.* Alkali metal reductions were carried out in an apparatus described by Wheeler, *et al.*;<sup>23</sup> details of the technique have been described.<sup>24</sup> Dimethoxyethane (DME) was obtained from the Ansul Co. It was stored over calcium hydride for 12 hr with continuous stirring and was then refluxed over lithium aluminum hydride for 16 hr. Then it was distilled under nitrogen and stored in the vacuum line.<sup>25</sup>

Potassium metal was obtained from Matheson Coleman and Bell. It was stored under mineral oil and was carefully washed with purified solvent at the time of the experiment.

*Compounds.* 2,3-, 2,6-, and 2,7-dimethylantracenes (ca. 0.050 g of each one) were donated by Dr. L. H. Klemm (The University of Oregon) and were used as received.

*Electron Spin Resonance Spectrometer.* A Varian Associates V-4502 spectrometer employing 100 kcps field modulation and a Varian V-153C Klystron (output 300 mW) were used. The field sweep was calibrated by using Fremy salt in one side of a V-4532 dual sample cavity. The high- and low-field coupling constants for the Fremy salt were taken as  $13.160 \pm 0.008$  and  $13.101 \pm 0.004$  G.<sup>26</sup> A Moseley 7100 dual channel recorder was used to record the spectra. A Varian V-4540 variable temperature unit was used for low-temperature studies.

*Computer Calculations.* The molecular orbital calculations were done on a Control Data Corporation (CDC) 6600 Computer. The theoretical simulated spectra were calculated on the CDC 6600 Computer and plotted on the CDC 160 plotter.

*Acknowledgments.* The support of this research by the Robert A. Welch Foundation and the National Science Foundation (GP-6688X) is gratefully acknowledged. The esr instrument was purchased with funds provided by the National Science Foundation (Grant No. GP-2090). We extend these acknowledgements to Mr. T. V. Atkinson for helpful discussions and Dr. L. H. Klemm (The University of Oregon) for the samples of 2,3-, 2,6-, and 2,7-dimethylantracene.

(23) L. O. Wheeler, K. S. V. Santhanam, and A. J. Bard, *J. Phys. Chem.*, **71**, 2223 (1967).

(24) (a) D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Amer. Chem. Soc.*, **78**, 116 (1956); (b) P. Balk, G. J. Holjtink, and J. W. H. Schreurs, *Rec. Trav. Chim.*, **76**, 813 (1957).

(25) D. F. Scriver, D. E. Smith, and P. Smith, *J. Amer. Chem. Soc.*, **86**, 5153 (1964).

(26) J. A. Valenzuela and A. J. Bard, *J. Phys. Chem.*, **72**, 286 (1968).