Homolytic Bond Dissociation Energies of the Acidic C–H Bonds in α-Substituted and 10-Substituted 9-Methylanthracenes and Their Related Radical Anions

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Equilibrium acidities (pK_{HA}), reduction potentials E_{re}(HA), oxidation potentials E_{ox}(HA), and oxidation potentials of the conjugate anions $E_{ox}(A^-)$ have been measured in dimethyl sulfoxide (DMSO) solution for 13 α-substituted 9-methylanthracenes (9-GCH$_2$An) and 11 10-substituted 9-methylanthracenes (10-G-9-MeAn). The equilibrium acidities have been shown to be linearly correlated with Hammett σ^- constants. The similar ρ^- values for the linear correlations of pK_{HA} vs σ^- for 9-GCH$_2$An ($\rho^- = 13.8$) and 10-G-9-MeAn ($\rho^- = 14.2$) demonstrate that the like substituents in 9-GCH$_2$An and 10-G-9-MeAn have similar large effects on the equilibrium acidities. Suitable combinations of these equilibrium acidities with the reduction and oxidation potentials led to estimates of (a) the homolytic bond dissociation energies (BDE$_{HA}$) of the acidic C–H bonds in 9-GCH$_2$An and 10-G-9-MeAn, (b) the homolytic bond dissociation energies (BDE$_{HA^{\bullet-}}$) of the acidic C-H bonds in 9-GCH$_2$An$^{\bullet-}$ and 10-G-9-MeAn$^{\bullet-}$ radical anions, and (c) the radical cation acidities ($pK_{HA^{\bullet+}}$) of the 9-GCH$_2$An$^{\bullet+}$ and 10-G-9-MeAn$^{\bullet+}$ radical cations. Introduction of α-CN and α-NO$_2$ groups had opposite effects on the strengths (BDE$_{HA}$) of the acidic C–H bonds in 9-GCH$_2$An; the α-CN group decreased the BDE$_{HA}$ value by 2.5 kcal/mol and the α-NO$_2$ increased the BDE$_{HA}$ value by 4.5 kcal/mol, but they both weakened the acidic C–H bonds in 9-GCH$_2$An$^{\bullet-}$ radical anions (by 10.6 and 12.5 kcal/mol, respectively). The BDEs of the acidic C–H bonds in 10-G-9-MeAn were estimated to be 81.3 ± 1.3 kcal/mol and those in the corresponding radical anions were estimated to be 58.5 ± 2.5 kcal/mol. The 9-GCH$_2$An$^{\bullet+}$ and 10-G-9-MeAn$^{\bullet+}$ radical cations are strongly acidic with the $pK_{HA^{\bullet+}}$ values estimated in the range of −5 to −11 $pK_{HA^{\bullet+}}$ units. Seven linear free energy relationships have been observed.

Introduction

Equilibrium acidity measurements of weak acids, HA, in the gas phase have provided quantitative information concerning intrinsic anion stabilities, and equilibrium acidity measurements in various solvents (H$_2$O, DMSO, CH$_3$CN, THF, DMF, CHA) have provided quantitative information concerning the enormous and varied effects of solvent and counterion on A$^-$ anion stabilities.[1] The most extensive acidity scale established to date is that in DMSO, which covers the pK_{HA} range from 2 to 32 and has more than 1500 entries.[1] These studies furnish measures of heterolytic bond dissociation energies ($\Delta G°$) for these weak acids. Homolytic bond dissociation energies (BDE$_{HA}$s) of the acidic H–A bonds in weak acids ($\Delta H°$) have generally been considered to provide the best quantitative estimates of the radical stabilization energies (RSEs) of the corresponding A$^\bullet$ radicals.[2] For example, BDE$_{HA}$ values for variously substituted methanes, GCH$_2$–H, have recently been collected.[3a] These values give RSEs (ΔBDEs relative to CH$_3$–H) for 21 GCH$_2^\bullet$ radicals. Although most of the data for this list were obtained from gas-phase studies, BDE$_{HA}$s from solution studies were also included because there is evidence to indicate that BDE$_{HA}$s determined in solution do not differ appreciably from these determined in the gas phase.[4]

Recently, we have combined the pK_{HA} values with the oxidation potentials $E_{ox}(A^-)$, of their conjugate bases to estimate the BDE$_{HA}$s of the acidic H–A bonds in weak acids (eq 1).[3b]

$$\mathrm{BDE_{HA}} = 1.37pK_{HA} + 23.1E_{ox}(A^-) + 73.3 \qquad (1)$$

The pK_{HA} values are believed to be accurate to ±0.1 pK units (0.15 kcal/mol), or better.[1] (Henceforth, kcal/mol will be abbreviated as kcal.) The $E_{ox}(A^-)$ values of the conjugate anions were measured by cyclic voltammetry (CV). Despite the fact that most of the CV waves formed in measuring the oxidation potentials of the conjugate anions under the usual experimental condition (scan rate: 100 mV/s) are irreversible, they were reproducible to ±20 mV (0.5 kcal).[3b] Furthermore, the $E_{ox}(A^-)$ values obtained from the irreversible CV waves have also been shown to agree within 50–100 mV with most of the $E_{ox}(A^-)$ values of the conjugate anions tried to date, as measured by second harmonic alternating current voltammetry (SHACV)[5] or high-speed cyclic voltammetry (200–10000 V/s).[6,7] The BDE$_{HA}$ values of the acidic H–A bonds in weak acids estimated by using eq 1, although empirical, have been found to be in agreement with the best gas-phase literature values to within ±2 kcal for most of the compounds where literature BDE values are available.[3b] Recently, thermodynamic cycles have been devised in several laboratories to estimate homolytic bond dissociation energies for radical

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[3] (a) Bordwell, F. G.; Zhang, X.-M.; Alnajjar, M. S. *J. Am. Chem. Soc.* 1992, *114*, 7623. (b) Bordwell, F. G.; Cheng, J.-P.; Ji, G.-Z.; Satish, A. V.; Zhang, X.-M. *J. Am. Chem. Soc.* 1991, *113*, 9790.

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[6] Bausch, M. J.; Gostowski, R. *J. Org. Chem.* 1991, *56*, 6260.

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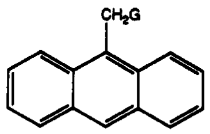
anions.[8] In a previous paper, we have used eq 2 to estimate the homolytic bond dissociation energies (BDE$_{HA^{\cdot-}}$ s) for the acidic C–H bonds in 35 radical anions derived from variously substituted fluorenes, diphenylmethanes, triphenylmethanes, and xanthenes.[8e] The strengths of the acidic C–H bonds in these radical anions were found to be weakened by ca. 20–40 kcal relative to those in the corresponding neutral molecules.

$$\mathrm{BDE}_{\mathrm{HA}^{\cdot-}} = 1.37\mathrm{p}K_{\mathrm{HA}} + 23.1E_{\mathrm{re}}(\mathrm{HA}) + 73.3 \qquad (2)$$

Bausch and his colleagues have examined the relative homolytic bond dissociation energies of the acidic C–H bonds in 9-methylanthracenes substituted at the α- and 10-positions (9-GCH$_2$-10-G′-An) and found that the effects of the electron donor OMe and acceptor CN groups on the RSEs are more than additive when G = OMe and G′ = CN.[9] They also found the E_{re}(HA) values of some 10-substituted 9-methylanthracenes (10-G-9-MeAn) to be linearly correlated with their pK_{HA} values.[10]

In the present paper, we extend our studies to 13 α-substituted 9-methylanthracenes (9-GCH$_2$An) (1) and 11 10-substituted 9-methylanthracenes (10-G-9-MeAn) (2).



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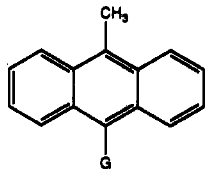

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Results and Discussion

The pK_{HA}, E_{re}(HA), and E_{ox}(HA) values for members of the families 1 and 2, together with the E_{ox}(A$^-$) values for the corresponding conjugate anions, are summarized in Tables I and II.

Table I. Equilibrium Acidities, Oxidation Potentials, and Reduction Potentials of α-Substituted 9-Methylanthracenes (9-GCH$_2$An) and the Oxidation Potentials of Their Conjugate Anions

substituents	pK_{HA}[a]	E_{ox}(A$^-$)[c]	E_{re}(HA)[e]	E_{ox}(HA)[g]	(σ^-)[h]
H	31.1	−1.489	−2.417	0.745	0.0
Me	32.4				−0.17
MeO	30.6	−1.635[d]	−2.295[d]		−0.26
PhO	30.2	−1.513	−2.153[d]	0.933	−0.10
n-hexylthio	29.9				0.06 (SMe)
p-tolylthio	28.8				
PhS	28.6	−1.362	−2.089[f]	0.825	0.18
PhCO	18.86[b]	−0.645	−2.271	0.796	0.83
p-BrPhS	28.2				
PhSO$_2$	21.6	−0.786	−1.929[f]	0.886	1.06[i]
CN	19.8	−0.930	−2.203	0.885	1.00
10-Me-9-CN	20.6				
NO$_2$	12.8	−0.205	−1.87[f]	0.993	1.63

[a] Equilibrium acidities in DMSO solution measured by the method described previously,[1] in pK_{HA} units. [b] Unpublished results from this laboratory. [c] Irreversible oxidation potentials (in volts) of the conjugate anions in DMSO measured by cyclic voltammetry and referred to the ferrocenium/ferrocene (Fc$^+$/Fc) couple.[3b] [d] From refs 9 and 10. [e] Reversible reduction potentials (in volts) in DMSO of the neutral molecules measured by the cyclic voltammetry and referred to the Fc$^+$/Fc couple. These potentials agreed to within ±100 mV with those given in ref 10. [f] Irreversible. [g] Irreversible oxidation potentials (in volts) in DMSO of the neutral molecules measured by the cyclic voltammetry in DMSO and referred to the (Fc$^+$/Fc) couple. [h] Taken from ref 15, unless otherwise indicated. [i] Obtained from the pK_{HA} value of 4-(phenylsulfonyl)phenylacetonitriles in DMSO (Bares, J. E. Ph.D. Dissertation, Northwestern University, Evanston, IL, 1976, p 154).

Table II. Equilibrium Acidities, Oxidation Potentials, and Reduction Potentials of 10-Substituted 9-Methylanthracenes (10-G-9-MeAn) and the Oxidation Potentials of Their Conjugate Anions

substituents	pK_{HA}[a]	E_{ox}(A$^-$)[b]	E_{re}(HA)[c]	E_{ox}(HA)[e]	(σ^-)[g]
H	31.1	−1.489	−2.417[d]	0.745	0.0
Me	31.8	−1.515	−2.465	0.665	−0.17
MeO	31.8	−1.537	−2.389	0.595	−0.26
Ph	30.75	−1.456	−2.340	0.715	0.02
Br	28.4				0.25
Cl	28.2	−1.347	−2.207[d]	0.835	0.19
PhS	25.5	−1.188	−2.102	0.815	0.18
PhCO	22.2	−0.928	−2.071	0.835	0.83
CHO	16.6	−0.675	−1.740	0.895	1.03
CN	20.0	−0.895	−1.877	1.085[f]	1.00
NO$_2$	13.2	−0.379	−1.475	1.075[f]	1.63

[a] Equilibrium acidities in DMSO solution measured by the method described previously,[1] in pK_{HA} units. [b] Irreversible oxidation potentials (in volts) of the conjugate anions in DMSO measured by cyclic voltammetry and referred to the Fc$^+$/Fc couple. [c] Reversible reduction potentials (in volts) in DMSO of the neutral molecules measured by the cyclic voltammetry and referred to the Fc$^+$/Fc couple. [d] Irreversible. [e] Irreversible oxidation potentials (in volts) in DMSO of the neutral molecules measured by the cyclic voltammetry in DMSO and referred to the (Fc$^+$/Fc) couple, unless otherwise indicated. [f] Measured in acetonitrile. [g] Taken from ref 15.

Equilibrium Acidities of α-Substituted and 10-Substituted 9-Methylanthracenes. The pK_{HA} value (31.1) of 9-MeAn (3) is ca. 12 pK units (16.5 kcal) lower than that of toluene, the pK_{HA} value of which is estimated to be 43 in DMSO.[1] The relatively high acidity of 3 is associated with the extensive delocalization of the negative charge over the anthryl ring in the anion (3a–d). The differences in pK_{HA} values between α-substituted derivatives of 3 and α-substituted derivatives of toluene are much smaller. For example, the pK_{HA} values of 9-PhSCH$_2$An, 9-PhSO$_2$CH$_2$An, and 9-CNCH$_2$An (Table I) are only 2.2, 1.8, and 2.1 pK_{HA} units lower than those of PhSCH$_2$Ph (pK_{HA} = 30.8), PhSO$_2$CH$_2$Ph (pK_{HA} = 23.4), and PhCH$_2$CN (pK_{HA} = 21.9), respectively.[1] This diminution is caused by steric effects in the derivatives of 3, which lower their acidities. Thus, the importance of the contributors 4c and 4d in delocalizing the negative charge into the anthryl ring is diminished by the steric interactions of the substituents (G) with the peri-hydrogen atoms at C-1 and C-8 positions, which prevent the coplanarity of the p orbitals of the carbanions with the aromatic system and hamper resonance stabilization of the anions by the substituents. Steric interference of this type is greatly enhanced when bulkier substituents, such as NO$_2$ or PhCO, are introduced into the α-position. For example, the methylene group in the 9-AnCH$_2^-$ anion has been shown to be twisted by ca. 17° from the plane of the anthryl ring,[11] and X-ray data indicate that NO$_2$[12] or CH$_3$CO[13] groups in the α positions of 9-GCH$_2$An are twisted out of

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(8) (a) Griller, D.; Simoes, J. A. M.; Mulder, P.; Sim, B. A.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1989**, *111*, 7872. (b) Maslak, P.; Narvaez, J. N. *J. Chem. Soc., Chem. Commun.* **1989**, 138 and references cited therein. (c) Andrieux, C. P.; Gallardo, I.; Savéant, J. M.; Su, K.-B. *J. Am. Chem. Soc.* **1986**, *108*, 638 and references cited therein. (d) Arnett, E. M.; Amarnath, K.; Harvey, N. G.; Cheng, J.-P. *Science* **1990**, *247*, 423 and references cited therein. (e) Zhang, X.-M.; Bordwell, F. G. *J. Am. Chem. Soc.* **1992**, *114*, 9787.

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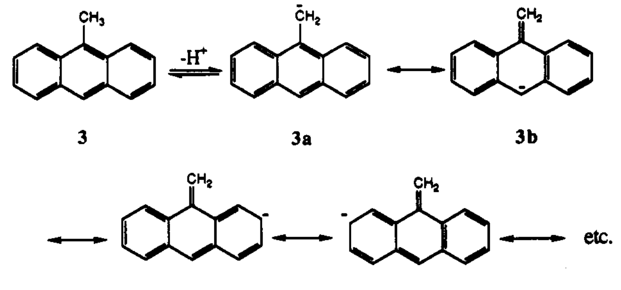
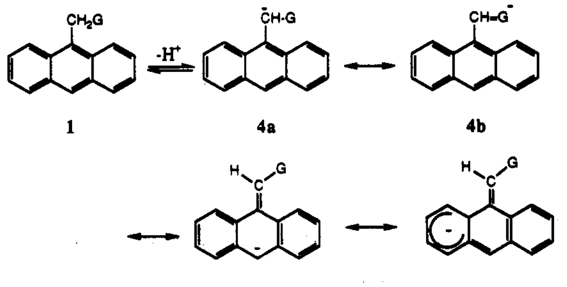


3 3a 3b

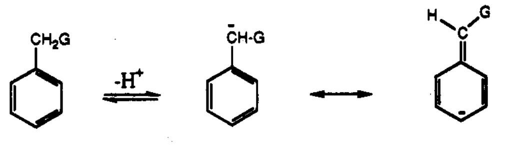
3c 3d



1 4a 4b

4c 4d

the anthryl plane by 49–85°. Steric interactions of this type are absent when the anthryl ring is replaced by the much smaller phenyl ring (**5a–b**). Therefore, it is not surprising to find that the pK_{HA} values of 9-NO_2CH_2An (12.8) and 9-$PhCOCH_2An$ (18.86) are 0.5 and 1.2 pK units *higher* than those for $PhCH_2NO_2$ (pK_{HA} = 12.3)[1] and $PhCOCH_2Ph$ (pK_{HA} = 17.7),[14] respectively.



5 5a 5b

In spite of the severe steric interactions with some substituents, the pK_{HA} values of compounds in the type **1** family are linearly correlated with Hammett σ^- constants (Figure 1). The slope for the regression line (ρ^- = 13.8, R^2 = 0.95) is slightly larger than that reported for toluene (ρ^- = 12).[16a,b] The large ρ^- value indicates that the negative charge in the conjugate anion is localized to a considerable extent on the methylene carbon atom in 9-$GCHAn^-$ ion, as in **4a**.

Of the resonance contributors (**3a–d**) for the 9-anthrylmethide anion (9-$AnCH_2^-$), **3b** has the lowest energy since both of the outer benzene rings retain their aromatic character. Heat of combustion data indicate that anthracene has a resonance energy of 84 kcal.[16c] If we assume that delocalization of a negative charge into each benzene ring occurs at the expense of ca. 36 kcal of resonance energy, it follows that anion **3** has lost less than 11.5 kcal of this resonance energy.

Examination of Tables I and II indicates that the substituents in the α positions of **1** and the C-10 positions of **2** have similar effects on the pK_{HA} values. For example, the pK_{HA} value of 10-NO_2-9-MeAn (13.2) is only 0.4 pK units higher than that of 9-NO_2CH_2An (12.8), and the pK_{HA} value of 10-CN-9-MeAn (20.0) is only 0.2 pK units higher than that of 9-$CNCH_2An$ (19.8). It is not surprising, then, to find that the pK_{HA} values of type **2** weak acids are also linearly correlated with Hammett σ^- constants, and that the ρ^- value (14.2) is remarkably close to that found for type **1** weak acids. This linear correlation indicates that resonance contributors of type **6c** are important and demonstrates that transmission of the electronic effects of substituents is more effective across and through the central ring of anthracene than across and through a benzene ring, where ρ^- has been shown to be about 12 kcal.[16a,b] The unusual effectiveness of the transmission of the effect of the donor MeO group to the acceptor CN group in radical **7** can be used to rationalize the greater than additive effect observed in this radical.[9] Nearly additive, but not greater than additive, effects have been observed for donor–acceptor interactions in other radicals such as $PhS\dot{C}HCN$.[3a]

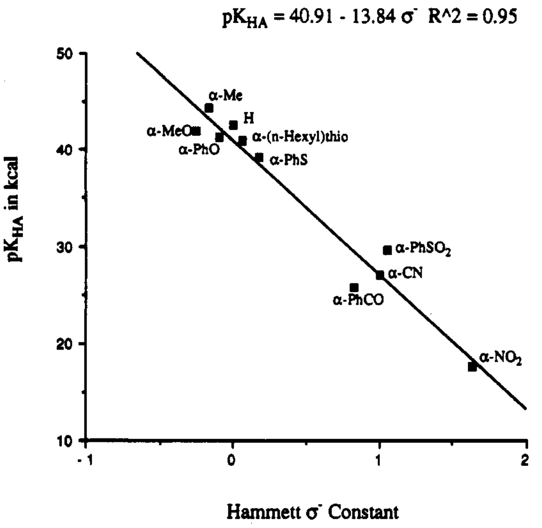
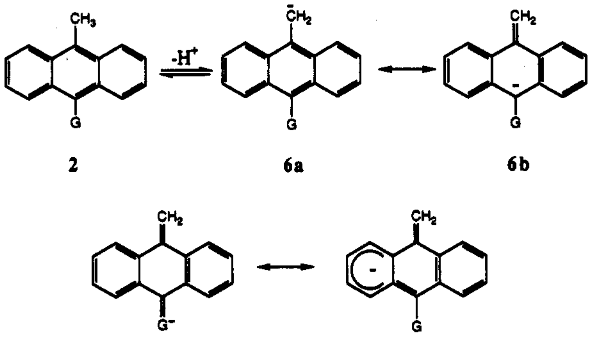
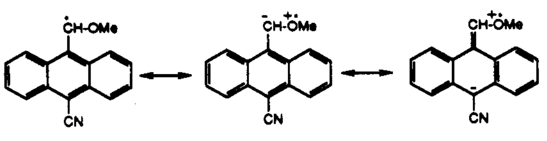


Figure 1. Plot of the equilibrium acidities (pK_{HA}) of 9-GCH_2An versus Hammett σ^- constants.



2 6a 6b

6c 6d



7a 7b 7c

The near identity of the ρ^- values for the linear correlations of the pK_{HA} values versus Hammett σ^- constants for families **1** and **2** requires that a plot of the pK_{HA} values for family **1** weak acids versus those for family

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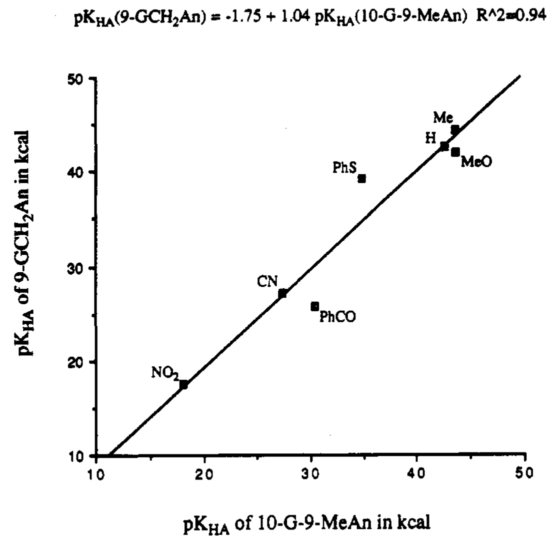

Figure 2. Plot of the equilibrium acidities of 9-GCH$_2$An versus the equilibrium acidities of 10-G-9-MeAn in DMSO.

2 weak acids be linear. The near unity slope of this plot (Figure 2) ($R^2 = 0.94$) reveals that the electron densities at the C-10 position (e.g. contributor **6b**) and at the methylene carbon position (e.g. contributor **4a**) are approximately equal in 10-G-9-AnCH$_2^-$ and 9-GAnCH$^-$ anions. Extended Hückel calculations also show that there are nearly equal amounts of π electron density delocalized at the C-10 and the methylene carbon positions in these anions.[17]

Oxidation Potentials of the Conjugate Anions Derived from α-Substituted and 10-Substituted 9-Methylanthracenes. Examination of Tables I and II shows that like substituents have similar effects on the oxidation potential values [$E_{ox}(A^-)$] of the conjugate anions **4** and **6** derived from the deprotonation of family 1 weak acids and family 2 weak acids. For example, the introduction of the electron-withdrawing NO$_2$ group into the α- or the C-10 position of 9-MeAn increases the $E_{ox}(A^-)$ values of the corresponding conjugate anions by 29.7 and 25.6 kcal, respectively, and the introduction of the CN group into the α or the C-10 position of 9-MeAn increases the $E_{ox}(A^-)$ values of the conjugate anions by 12.9 or 13.7 kcal, respectively. The $E_{ox}(A^-)$ values of the anions **4** and **6** are each linearly correlated with Hammett σ^- constants; the ρ^- values are 16.8 and 14.2 kcal, respectively. The high ρ^- value for the anions **4** (16.8) shows that the oxidation potentials of the anions are even more sensitive to substituent changes than are their basicities ($\rho^- = 13.8$). The slope of a plot of $E_{ox}(A^-)$ for 9-GCH$_2$An$^-$ (4$^-$) versus $E_{ox}(A^-)$ for 10-G-9-AnCH$_2^-$ (6$^-$) is 1.24 (Figure 3), indicating that the odd electron density at the α-position of the radicals derived from anions **4** is slightly higher than that at the C-10 position of the radicals derived from anions **6**.

Homolytic Bond Dissociation Energies of the Acidic C-H Bonds in α-Substituted and 10-Substituted 9-Methylanthracenes. The homolytic bond dissociation energies of the acidic C–H bonds in the members of families 1 and 2 weak acids were estimated by using eq 1. The results are summarized in Tables III and IV. The BDEs in Tables III and IV are given to 3 significant figures, but the reader should keep in mind that the accuracy of the estimates is ±2 kcal.[3b]

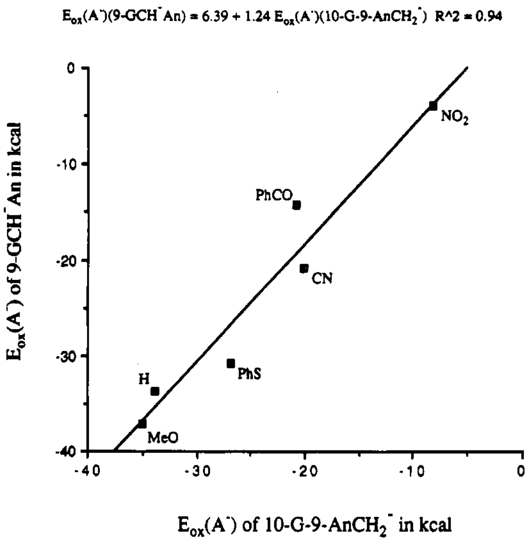

Figure 3. Plot of the oxidation potentials of 9-GCH$^-$An anions versus the oxidation potentials of 10-G-9-AnCH$_2^-$ anions.

Table III. Equilibrium Acidities, Radical Cation Acidities, and Homolytic Bond Dissociation Energies of the Acidic C–H Bonds in α-Substituted 9-Methylanthracenes (9-GCH$_2$An) and Their Radical Anions

substituents	pK_{HA}	$pK_{HA^{\bullet+}}$[a]	BDE_{HA}[b]	$BDE_{HA^{\bullet-}}$[c]
H	31.1	−6.4	81.5	60.1
MeO	30.6		77.5	62.2
PhO	30.2	−11.0	79.9	64.9
PhS	28.6	−8.3	81.0	64.2
PhSO$_2$	21.6	−6.6	84.7	58.3
CN	19.8	−10.8	78.9	49.5
PhCO	18.86	−5.4	84.2	46.6
NO$_2$	12.8	−7.4	86.1	47.6

[a] In kcal/mol; estimated by using of eq 4. [b] In kcal/mol; estimated by using eq 1. [c] In kcal/mol; estimated by using of eq 2.

Table IV. Equilibrium Acidities, Radical Cation Acidities, and Homolytic Bond Dissociation Energies of the Acidic C–H Bonds in 10-Substituted 9-Methylanthracenes (10-G-9-MeAn) and Their Radical Anions

substituents	pK_{HA}	$pK_{HA^{\bullet+}}$[a]	BDE_{HA}[b]	$BDE_{HA^{\bullet-}}$[c]
H	31.1	−6.4	81.5	60.1
Me	31.8	−5.0	81.8	59.9
MeO	31.8	−4.2	81.4	61.7
Ph	30.75	−5.9	81.8	61.3
Cl	28.2	−8.2	80.8	61.0
PhS	25.5	−8.3	80.8	59.7
PhCO	22.2	−7.5	82.3	55.9
CHO	16.6	−9.8	80.4	55.8
CN	20.0	−13.4	80.0	57.3
NO$_2$	13.2	−11.3	82.6	57.3

[a] In kcal/mol; estimated by using of eq 4. [b] In kcal/mol; estimated by using eq 1. [c] In kcal/mol; estimated by using of eq 2.

The BDE value of the acidic C–H bond in 9-MeAn is estimated to be 81.5 kcal, which is in good agreement with the literature value of 81.8 ± 1.8 kcal.[2a] The BDE value of the acidic C–H bond in 9-MeAn is lower than those in toluene (88 kcal) and 1-methylnaphthalene (85 kcal) by 6.5 and 3.5 kcal, respectively.[2a] These differences are in accord with the greater resonance stabilization of benzyl-type radicals by the anthryl ring than by the phenyl and naphthyl rings.

We have shown elsewhere that the substituents in a molecule play a dual role toward radicals: (a) destabilizing by virtue of their group electronegativities (*F* effects) and (b) stabilizing to the extent of their ability to delocalize an odd electron by a resonance effect (*R* effect). For example, in the proximate type Me$_3$N$^+\dot{C}$H–G radicals,

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(17) Streitwieser, A.; Brauman, J. I. *Supplemental Tables of Molecular Orbital Calculations*; Pergamon Press: New York, 1965; p 377.

where G = PhCO, CN, and CO_2Et, the *F* effects of the trimethylammonium groups destabilize the corresponding radicals by 2–3 kcal. On the other hand, the *R* effects of the pyridinium groups in the corresponding $c\text{-}C_5H_5\text{-}N^+\dot{C}H\text{-}G$ radicals overshadow the *F* effects and stabilize the radicals formed by 3–5 kcal.[18]

For groups in the 10-position of 9-methylanthracene, bond-weakening delocalizing effects are balanced for most part by bond-strengthening *F* effects leading to an average BDE of 81.3 ± 1.3 kcal. Electron-withdrawing groups in the 10-position with large steric demands, such as NO_2 and PhCO, cannot achieve coplanarity with the anthracene ring, and their *F* effects cause small bond-strengthening effects, whereas the CN and CHO groups, although electron-withdrawing, cause bond weakening effects because they *can* achieve coplanarity or near coplanarity with the anthracene ring. Donor groups also appear to have small bond-weakening effects.

The average of BDEs for $9\text{-}\alpha\text{-}GCH_2$-anthracenes is 81.7 ± 4.3 kcal. Here the donors, MeO, PhO, PhS, and the acceptor CN groups cause 4.0, 1.6, 0.5, and 2.6 kcal bond-weakening effects, respectively, whereas the more sterically demanding acceptor groups $PhSO_2$, PhCO, and NO_2 cause bond strengthening effects of 3.2, 2.7, and 4.6 kcal, respectively, because of repulsive interactions between the substituents and the perihydrogen atoms in C-1 and C-8 positions in the anthryl ring. These steric interactions are decreased when the bulky anthryl ring is replaced by a much smaller phenyl ring. For example, the BDE values of the acidic C–H bonds in $PhCH_2COPh$ and $PhCH_2NO_2$ are 82.5 and 84.5 kcal,[14] respectively, compared to 84 and 86 kcal for the acidic C–H bonds in $9\text{-}PhCOCH_2An$ and $9\text{-}NO_2CH_2An$, respectively. The $PhSO_2$ group often exerts unusually strong steric and stereoelectronic demands. For example, unlike the PhCO and NO_2 groups, the $PhSO_2$ group in $PhSO_2CH_2Ph$ causes the BDE value of the acidic C–H bond to *increase* by 2 kcal, relative to that of toluene.[19a] In the earlier pK_{HA} comparisons we saw that groups operating from the (remote) 10-position in 9-MeAn exert effects on anion stabilities that rival those from α-positions. But in the present instance, we see that the α-substituent effects on the BDEs are substantially greater than are the remote (C-10) substituent effects. In $\alpha\text{-}GCH_2An$, the substituents can usually adopt a conformation where the stereoelectronic effects of G can be at least partially operative, whereas substituents in the 10-position are much more restricted in the conformations that they can adopt.

In contrast to the effects of $PhSO_2$, PhCO, and NO_2 groups, the effect of the CN group in $9\text{-}CNCH_2An$ is to *weaken* the acidic C–H bond by 2.6 kcal. The replacement of a hydrogen atom by the smaller and linear CN group in the α-position of 9-MeAn evidently introduces smaller steric interactions than for the other electron-withdrawing groups. Nevertheless, the 2.6 kcal ΔBDE value observed, relative to 9-MeAn, is much smaller than the 6 kcal ΔBDE value observed for the introduction of the CN group into the α-position of toluene. This may be attributed in part to a saturation effect since the $9\text{-}AnCH_2^\bullet$ radical is 6.5 kcal more stable than the benzyl radical.

The apparent 1 kcal lower BDE_{HA} value for $\alpha\text{-}PhOCH_2An$ than for $\alpha\text{-}PhSCH_2An$ can be interpreted as indicating a larger stabilizing effect of α-RO than α-RS functions on $AnCH_2^\bullet$ radicals. This is consistent with the observation of a larger effect of α-RO than α-RS functions in stabilizing $9\text{-}GFl^\bullet$ radicals.[19] It is contrary, however, to the BDE data for $3\text{-}GFl^\bullet$ radicals,[19a] or for $GCH_2^\bullet$ radicals,[3a] where 3-RO vs 3-RS and α-RO vs α-RS effects have been found to be about equal. It is also contrary to the effects of para substituents on benzyl radicals found in the $\sigma_\alpha^\bullet$ scale where ESR hyperfine coupling constants show that $p\text{-}MeSC_6H_4CH_2^\bullet$ radicals have the highest spin density of all the benzyl radicals studied and are much higher than for the $p\text{-}MeOC_6H_4CH_2^\bullet$ radicals.[20] Other ESR studies also point to spin densities of α-RS carbon-centered radicals being much higher than those of α-RO carbon-centered radicals,[21] but Rüchardt has pointed out that no clear relationship between spin density and radical stability has been formulated.[22] Substituent effects on radical stabilities have recently been shown to be subject to large thermodynamic stereoelectronic effects—much larger than those on analogous anions.[23] In sterically congested systems, such as $9\text{-}G\text{-}Fl^\bullet$ radicals and the anthryl radicals, substituent effects will be perturbed by steric, as well as stereoelectronic, effects which we believe accounts for the divergent results cited above. We conclude that α-RS and α-RO effects on radical stabilities do not differ appreciably in noncongested substrates.

Correlations of Anion Oxidation Potentials for Families with pK_{HA}s. In earlier studies, we have found linear correlations between the oxidation potentials, $E_{ox}(A^-)$ of the conjugate bases in several families of weak acids with their pK_{HA} values. The slopes were near unity for carbon acids. Examples include (a) families where the anion basicities were changed by meta substituents, as in 2- and 2,7-substituted fluorenes (slope ≅ 1.0),[19b] and meta-substituted arylacetonitriles (slope ≅ 1.2),[24a] and (b) families where steric congestion around the anion and the corresponding radical sites was severe, as in $3\text{-}(p\text{-}GC_6H_4)$-1,1,5,5-tetraphenyl-1,4-pentadienes,[24b] and para-substituted triphenylmethanes, $p\text{-}GC_6H_4CHPh$.[24d] Plots of $E_{ox}(A^-)$ for $\alpha\text{-}GCHAn^-$ or $10\text{-}G\text{-}9\text{-}AnCH_2^-$ anions vs the corresponding pK_{HA} values are linear with slopes of 1.0 and 1.2 (Figures 4 and 5). Examples have now been obtained in sufficient number and variety to indicate the existence of *an inherent linear relationship between oxidation potentials of carbanions and their basicities, a 1 kcal/mol increase in anion basicity leading to approximately a 1 kcal/mol more negative potential.* [A linear plot for $E_{ox}(A^-)$ versus pK_{HA} has also been observed for meta-substituted phenoxide ions, but here the slope of plot is close to 2.[25]] *Linear plots of this type can be expected whenever the substituent effects on the radicals being generated are small.*

Reduction Potentials and Homolytic Bond Dissociation Energies of the Acidic C–H Bond in Radical Anions Derived from α-Substituted and 10-Substi-

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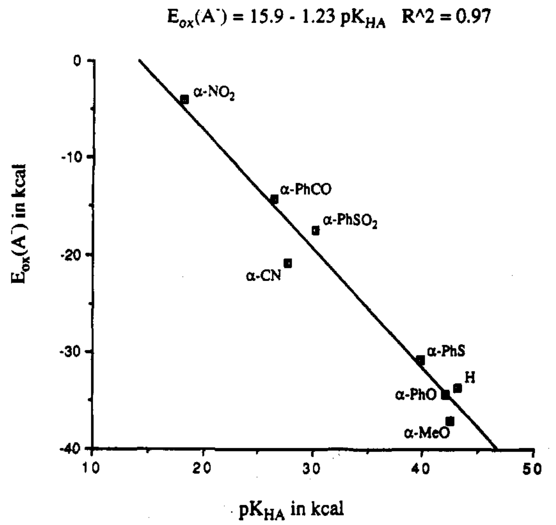


Figure 4. Plot of the oxidation potentials of 9-GCH$^-$An anions versus the equilibrium acidities of their conjugate acids.

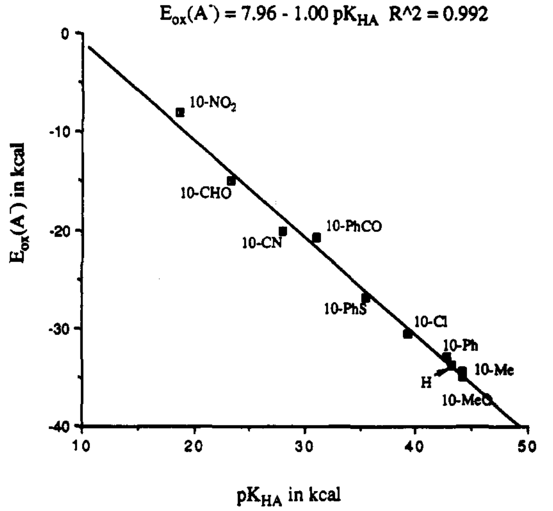


Figure 5. Plot of the oxidation potentials of 10-G-9-AnCH$_2^-$ anions versus the equilibrium acidities of their conjugate acids.

tuted 9-Methylanthracenes. Equation 2 shows that combination of the equilibrium acidity with the reduction potential will provide an estimate of the homolytic bond dissociation energy of the H–A bond in a radical anion, i.e.

$$\text{H–A} \xrightarrow{(+e^-)} \text{H–A}^{\bullet -} \rightarrow \text{H}^\bullet + \text{A}^-$$

Examination of the E_{re}(HA) values of type 1 and type 2 acids in Tables I and II shows that the average reduction potential of 9-NO$_2$CH$_2$An, 9-NCCH$_2$An, and 9-PhCOCH$_2$-An is about 0.3 V (7 kcal) less positive than the average reduction potentials for 10-NO$_2$-9-CH$_3$An, 10-NC-9-CH$_3$-An, and 10-PhCO-9-CH$_3$An. This difference is caused by the presence of the methylene group in the 9-GCH$_2$An$^{\bullet -}$ radical anions, which separates the substituents from the aromatic ring. As a consequence, neither the negative charge nor the odd electron present in the ring can be effectively stabilized by delocalization into the substituents (**8a–c**). On the other hand, the negative charge and the odd electron in the 10-G-9-MeAn$^{\bullet -}$ radical anions can be effectively stabilized by delocalization into the substituents by resonance (**9a–c**). As a result there is a good linear correlation between the E_{re}(HA)s and pK_{HA}s for 10-G-9-MeAn (R^2 = 0.98; ρ^- = 0.80)[10] (Figure 6) and no linear correlation for 9-GCH$_2$An (Figure 7).

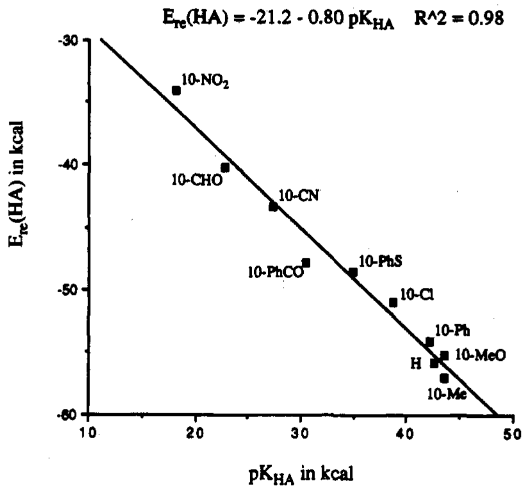


Figure 6. Plot of the reduction potentials of 10-G-9-MeAn versus their equilibrium acidities. A similar linear plot with a slope of 0.77 has been reported previously.[10]

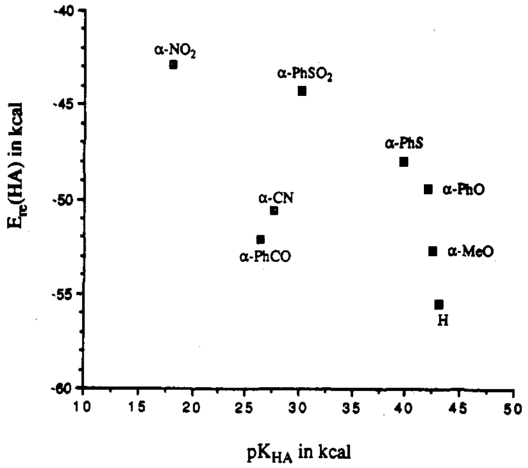


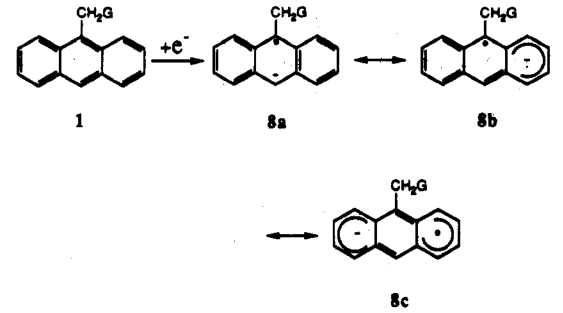
Figure 7. Plot of the reduction potentials of 9-GCH$_2$An versus the equilibrium acidities of 9-GCH$_2$An.

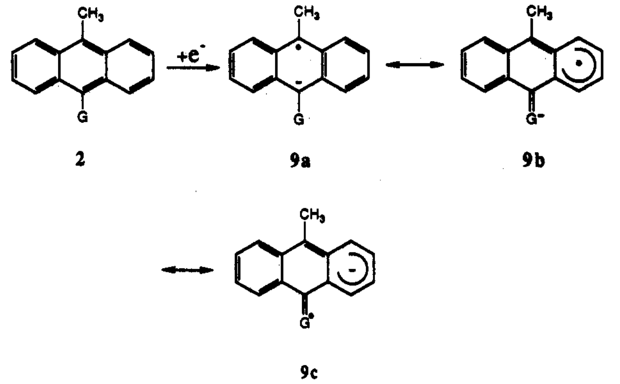
The linear correlation in Figure 6 shows that in families where the charge in radical anions can be delocalized to the substituents, the basicities of the radical carbanions play a role similar to that played by nonradical carbanions (Figures 4 and 5). The slope of the plot is smaller (0.80 rather than ~1), but this may be due to the base-weakening effect of the odd electron.

Examination of Table III reveals that the BDE$_{HA^{\bullet -}}$ value for 9-MeAn$^{\bullet -}$ radical anion is estimated to be 60 kcal, i.e. about 20 kcal lower than the BDE$_{HA}$ value of the parent weak acid. The electron-donor groups, α-MeO, α-PhO, and α-PhS, strengthen these acidic C–H bonds by about 2–3 kcal and the electron-acceptor groups, α-PhSO$_2$, α-CN, α-NO$_2$, and α-PhCO, weaken the corresponding acidic C–H bonds by about 2, 10.5, 12.5, and 13.5 kcal, respectively. Similarly, from Table IV we see that the acceptor groups, PhCO, CHO, CN, and NO$_2$, exert 3–4 kcal bond-*weakening* effects on the acidic C–H bond in 10-G-9-MeAn$^{\bullet -}$ radical anions, whereas the donor groups Me, MeO, Ph, Cl, and PhS, exert 0–2 kcal bond-*strengthening* effects.

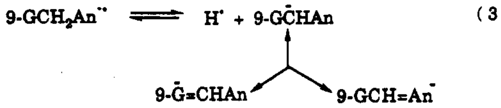
There are relatively little data in the literature with which to compare these effects. Although there have been several recent studies on CX$^{\bullet -}$ type radical anions, where X = C, Cl, O, S etc.,[8] the only examples where X = H of which we are aware are those in our earlier paper.[8e]

Substituents can affect the BDE$_{HA^{\bullet -}}$ values for radical anions either by stabilizing the radical anion (bond





strengthening) or stabilizing the product anion (bond weakening). Stabilization of the charge in the radical anion by a field/inductive (F) effects will explain the small bond strengthening effects of the donors in the 9-$GCH_2An^{\bullet-}$ and 10-G-9-$MeAn^{\bullet-}$ radical anions. Similar small effects have been observed for the 9-EtO, 9-EtS, and 9-Me_2N donor groups in substituted fluorene radical anions.[8e] The much larger bond-weakening effects of the acceptor groups described above can be explained by their stabilizing (delocalizing) effects on the product anions (eq 3). Similar effects have been observed for the effects of the CO_2Et group in the 9-$CO_2EtFlH^{\bullet-}$ radical anion and for the CN group in the 9-cyanoxanthene radical anion.[8e]



$$9\text{-}GCH_2An^{\bullet-} \rightleftharpoons H^{\bullet} + 9\text{-}G\bar{C}HAn \longleftrightarrow 9\text{-}\bar{G}{=}CHAn,\ 9\text{-}GCH{=}An^{-} \qquad (3)$$

In contrast, the 3-CF_3, 3-NO_2, 4-NO_2, and 4-$PhSO_2$ groups in triphenylmethane radical anions and the 9-$PhSO_2$, 2-$PhSO_2$, 2-CN, and 2-NO_2 groups in fluorene radical anions are bond-strengthening (by 5, 11, 10, and 27 kcal, respectively). Evidently in these radical anions the stabilizing F effect on the radical anion is the dominant factor.

The unusually large effect for the nitro group in 2-$NO_2FlH_2^{\bullet-}$ radical anion is believed to be due to its unique ability to accept and internally stabilize an electron in the reduction process. The nitro group stabilizes the odd electron in the radical anion and increases the $BDE_{HA^{\bullet-}}$ by making the reduction potential more positive (eq 2). Similarly, the E_{re}(HA) values for 10 nitro triphenylmethanes were found to be near −1.5 V (vs the ferrocenium/ferrocene couple), regardless of the structure of the rest of the molecule;[24d] this constancy is consistent with addition of the electron to the NO_2 moiety.[8e]

Although the BDE_{HA} values of the acidic C–H bonds in 9-MeAn and fluorene are nearly the same (81.5 and 80 kcal, respectively), the $BDE_{HA^{\bullet-}}$ value for the acidic C–H bond in the 9-$MeAn^{\bullet-}$ radical anion is about 25 kcal higher than that of the comparable acidic C–H bond in the $H_2Fl^{\bullet-}$ radical anion. This is a consequence largely of the unusual ease of reducing the central aromatic ring in anthracene. In terms of eq 2, the 25 kcal higher $BDE_{HA^{\bullet-}}$ value is caused by a 0.59 V (13.6 kcal) more positive E_{re}(HA) value and an 8.5 unit (11.6 kcal) lower acidity.

The unusual ease of reducing the central ring in anthracene also negates the special role in reductions usually played by a NO_2 group. Whereas the nitro group in 2-NO_2FlH_2 accepts an electron internally and increases the $BDE_{HA^{\bullet-}}$ value of the acidic C–H bond from 35 to 64 kcal,[8e] the presence of the nitro group in the α position or the C-10 position of 9-MeAn *decreases* the $BDE_{HA^{\bullet-}}$ values by 13 and 3 kcal, respectively. Examination of the reduction potentials in Tables I and II shows that the effect of the presence of a nitro group in making E_{re}(HA) more positive is not exalted, but instead is comparable to those of other electron-withdrawing groups. These nitro groups evoke lower $BDE_{HA^{\bullet-}}$ values by stabilizing the anion products more than they stabilize the radical anions. Their effects are, therefore, just the opposite in this regard to that of NO_2 and other remote electron-withdrawing groups in fluorene, diphenylmethane, or triphenylmethane.[8e]

Radical Cation Acidities of in α-Substituted and 10-Substituted 9-Methylanthracenes. The equilibrium acidities ($pK_{HA^{\bullet+}}$s) of the radical cations derived from type 1 and type 2 acids by loss of one electron were estimated by eq 4.[26] The results are summarized in Tables III and IV.

$$pK_{HA^{\bullet+}} = pK_{HA} + 16.8[E_{ox}(A^-) - E_{ox}(HA)] \qquad (4)$$

Examination of the $pK_{HA^{\bullet+}}$ values in Tables III and IV indicates that all the radical cations derived from 1 and 2 are strongly acidic and fall in the range of −5.5 to −13 $pK_{HA^{\bullet+}}$ units. Their acidities are somewhat weaker than those of the corresponding fluorene radical cations, however. The weaker acidities are in accord with the lower oxidation potentials [E_{ox}(HA)] since the positive charge in radical cations $10^{\bullet+}$ and $11^{\bullet+}$ can delocalize over the larger aromatic system (anthryl ring). For example, the E_{ox}(HA) value of 9-MeAn is 0.53 V (12.2 kcal) less positive than that of fluorene, and the $pK_{HA^{\bullet+}}$ value of 9-$MeAn^{\bullet+}$ radical cation (−6.4) is ca. 10 $pK_{HA^{\bullet+}}$ units lower than that of $FlH_2^{\bullet+}$ radical cation (−17).[26]

We have seen earlier that a plot of E_{re}(HA) vs pK_{HA} is linear (slope = 0.80) for 10-G-9-MeAn family (Figure 6) because the effects of substituent in delocalizing the negative charge and the odd electron in 10-G-9-$MeAn^{\bullet-}$ radical anions and the negative charge in A^- anions are comparable to their effects in delocalizing the negative charge in the 10-G-9-$CHAn^-$ anions. It is not surprising to find then that a plot of E_{ox}(HA) vs $pK_{HA^{\bullet+}}$ is linear (R^2 = 0.96) for 10-G-9-MeAn family (Figure 8) because the effects of substituents in delocalizing the positive charge in the 10-G-9-$MeAn^{\bullet+}$ radical cations being formed are comparable to their effects on the acidities of the radical cations. In other words, the substituents are exerting their effect by delocalizing the positive charge and odd electron in the $HA^{\bullet+}$ radical cation (**10a–c**).

$$10\text{-}G\text{-}9\text{-}MeAn^{\bullet+} \rightleftharpoons H^+ + 10\text{-}G\dot{C}HAn \qquad (5)$$

We have shown in earlier studies that substituent effects on equilibria such as eq 5 generally affect the stability of

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[26] Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 2473.

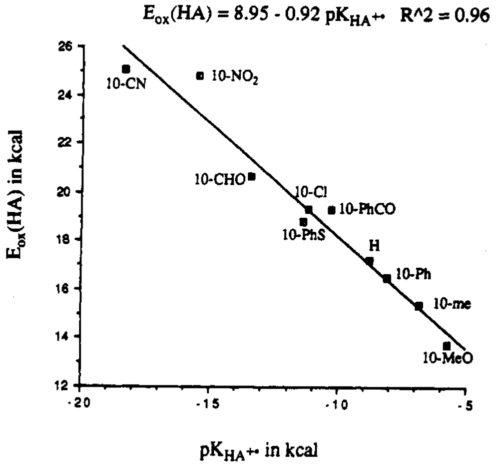
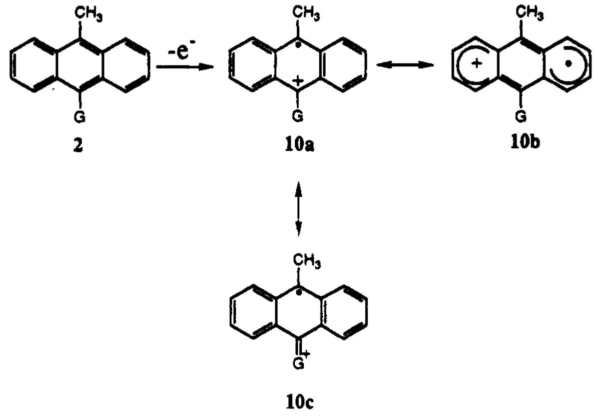
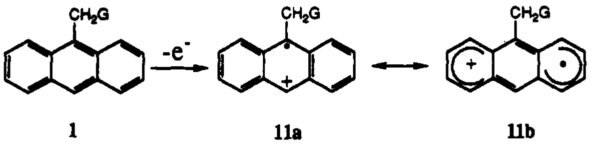


Figure 8. Plot of the oxidation potentials of 10-G-9-MeAn versus the acidities of 10-G-9-MeAn$^{\bullet+}$ radical cations.

the radical cation much more than they affect the stability of the product radical. The dominant role in charge delocalization in these instances is expected since in DMSO solution the stabilizing effects of substituents on charges are generally much greater than on radicals. As expected, a scatter plot was obtained for E_{ox}(HA) of 9-GCH$_2$An vs the p$K_{HA^{\bullet+}}$ values for 9-GCH$_2$An$^{\bullet+}$ radical cations since the positive charge and the odd electron in 9-GCH$_2$An$^{\bullet+}$ radical cations cannot be effectively delocalized to the substituents due to the separation by the methylene group (**11a**–**b**). Linear plots of E_{ox}(HA) vs the p$K_{HA^{\bullet+}}$ values have been observed in several other instances, however.[24]





Experimental Section

General. NMR spectra were recorded on a Varian T60 instrument in CDCl$_3$ or CCl$_4$ with tetramethylsilane as internal standard. IR spectra were recorded on a Beckman IR-5 spectrophotometer with the polystyrene peak at 1601 cm^{-1} as the standard. Melting points were measured on a Fisher-Johns melting apparatus or a Thomas-Hoover melting point apparatus. All melting points were uncorrected. Elemental analyses were performed by Micro-Tech Laboratories of Skokie, IL.

Materials. The synthesis of 9-((phenylsulfonyl)methyl)anthracene has been described in a previous paper.[27] Pure samples of 9-MeOCH$_2$An, 9-PhOCH$_2$An, 9-(n-C$_6$C$_{11}$)SCH$_2$An, 9-(p-CH$_3$C$_6$H$_4$)SCH$_2$An, 9-PhSCH$_2$An, and 9-(p-BrC$_6$H$_4$)SCH$_2$An were kindly provided by N. Kornblum and A. Scott.

9-Methylanthracene (Aldrich) was purified by treatment with activated charcoal in refluxing ethanol, followed by repeated recrystallization from 95% ethanol to give pale yellow plates: mp 79 °C [lit.[28] mp 81.5 °C].

9-Ethylanthracene was prepared following the literature method.[29] The product was purified by column chromatography on neutral alumina eluting with 10% ether–hexane. Repeated recrystallization from ethanol gave cream plates: mp 58 °C [lit.[29] mp 56–58 °C]; NMR (CDCl$_3$) δ 1.62 (t, 3 H, CH$_3$), 3.77 (q, 2 H, –CH$_2$–), 7.4–7.8 (m, 4 H, Ar), 8.0–8.5 (m, 5 H, Ar).

10-Methyl-9-(iodomethyl)anthracene was prepared by the literature method,[30] and was used immediately in the synthesis of 9,10-dimethylanthracene and 10-methyl-9-(cyanomethyl)anthracene.

9,10-Dimethylanthracene was prepared by the literature method.[30] Recrystallization from ethanol followed by sublimation gave bright yellow crystals: mp 181.5–182 °C [lit.[31] mp 179–180 °C].

10-Methyl-9-(cyanomethyl)anthracene. To 5.0 g of 10-Me-9-ICH$_2$An in 75 mL of DMSO was added 0.8 g of sodium cyanide. The mixture was heated at 70 °C for 1.5 h and then diluted 5-fold with water and extracted with chloroform. The chloroform extracts were washed with water and brine. Drying with anhydrous MgSO$_4$ and removal of solvent under reduced pressure gave a yellow solid: mp 206–206.5 °C; NMR (CDCl$_3$) δ 3.03 (s, 3 H, CH$_3$), 4.46 (s, 2 H, CH$_2$CN), 7.4–7.75 (m, 4 H, Ar), 8.0–8.5 (m, 4 H, Ar). Anal. Calcd for C$_{17}$H$_{13}$N: C, 88.28; H, 5.67. Found: C, 88.12; H, 5.67.

9-(Cyanomethyl)anthracene was prepared in the same manner as 10-methyl-9-(cyanomethyl)anthracene except 9-(chloromethyl)anthracene was substituted for 9-(iodomethyl)-10-methylanthracene as starting material and the mixture stirred for 3 h at room temperature. The crude product was sublimed to produce yellow needles: mp 164–165 °C [lit.[32] mp 163.5–164.5 °C]; NMR (CDCl$_3$) δ 4.53 (s, 2 H, –CH$_2$–), 7.9–8.3 (m, 4 H, Ar), 8.5 (s, 1 H, Ar); IR (Nujol mull) 2235 (CN).

9-(Phenylthio)anthracene. To 10 g of anthrone dissolved in 500 mL of refluxing acetic acid under nitrogen was added 13 g (2.2 equiv) of thiophenol and 10 g of concentrated sulfuric acid. The reaction was held at reflux for 24 h, and then 350 ml of water/acetic acid was removed by distillation. Upon cooling, 9.5 g (65%) of solid crystallized and was collected. The crude product was purified by chromatography on silica gel eluting with hexane, followed by recrystallization from methanol and then hexane to give plates: mp 94–7 °C [lit.[33] mp 100.5–102 °C]; NMR (CDCl$_3$) δ 6.95 (m, 5 H, SC$_6$H$_5$), 7.4–7.6 (m, 4 H, Ar), 7.9–8.1 (m, 2 H, Ar), 8.5 (s, 1 H, 10-CH), 8.7–8.9 (m, 2 H, peri-H's).

10-(Phenylthio)-9-bromoanthracene. To a stirred solution of 1.5 g (5.9 mmol) of 9-(phenylthio)anthracene in 80 mL of acetic acid held at room temperature under nitrogen was dropwise added 1.04 g (6.45 mmol) of bromine in 20 mL of acetic acid. Upon completion of the addition the reaction was allowed to cool to room temperature, resulting in the crystallization of yellow plates. The crude product was recrystallized from acetic acid: NMR (CDCl$_3$) δ 6.9–7.1 (m, 5 H, C$_6$H$_5$), 7.5–7.7 (m, 4 H, C$_6$H$_5$), 8.5–8.7 (m, 2 H, 1,8-H's), 8.8–9.0 (m, 2 H, 4,5-H's).

10-(Phenylthio)-9-methylanthracene. To 5 mL of 1.8 M phenyllithium solution in 5 mL of anhydrous ether was added 1.0 g of 10-(phenylthio)-9-bromoanthracene in ether under nitrogen. The mixture was stirred for 15 min at room temperature, and 1.5 g of methyl iodide in 5 mL of ether was added. After 1 h, the yellow precipitate was collected on a filter, and the filtrate was diluted with ether and washed with water and brine. Drying the ether layer with Na$_2$SO$_4$ and removal of solvent under reduced pressure gave a yellow solid. The yellow solids were combined and recrystallized once from benenze/ethanol and then twice from acetic acid to give yellow needles. The compound was further purified on a Waters 660 liquid chromatography using

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a semipreparative reverse-phase C18 column eluted with 18% H_2O/MeOH at 5 mL/min. Recrystallization from ethanol gave yellow needles: mp 157–158 °C; NMR ($CDCl_3$) δ 3.15 (s, 3 H, CH_3), 6.95–7.1 (m, 5 H, C_6H_5), 7.4–7.7 (m, 4 H, C_6H_5), 8.2–8.6 (m, 2 H, 1,8-H's), 8.8–9.1 (m, 2 H, 4,5-H's).

9-(Nitromethyl)anthracene. This compound was kindly synthesized by J. E. Bartmess. 9-Formylanthracene was converted to its oxime (in 93% yield), yellow needles: mp 159–162 °C [lit.[34] mp 165–165.5 °C]. This was converted to the nitro compound by oxidizing 4.4 g (0.02 mol) of the oxime with the trifluoroperacetic acid made from 7.5 mL (0.05 mol) of trifluoroacetic anhydride and 1.2 mL (0.04 mol) of 90% hydrogen peroxide. The crude product was triturated with five 200-mL portions of hot hexane. Removal of the hexane under reduced pressure gave 1.0 g of yellow solid. Recrystallization from ethanol gave golden needles: mp 178.5–179.5 °C; NMR ($CDCl_3$) δ 6.36 (s, 2 H), 7.3–7.6 (m, 4 H), 7.8–8.3 (m, 4 H), 8.2–8.3 (m, 1 H); IR (mull) 1550 and 1380 cm^{-1} (NO_2). Anal. Calcd for $C_{13}H_{11}NO_2$: C, 75.94; H, 4.67. Found: C, 75.72; H, 4.74.

10-Methoxy-9-methylanthracene was prepared following the literature method.[35] Recrystallization from ethanol gave pale green crystals: mp 147 °C [lit.[36] mp 147 °C]; NMR ($CDCl_3$) δ 3.01 (s, 3 H, CH_3), 4.09 (s, 3 H, OCH_3), 7.3–7.5 (m, 4 H, Ar), 8.1–8.4 (m, 4 H, Ar).

10-Chloro-9-methylanthracene was prepared following the literature method.[37] Recrystallization from hexane followed by column chromatography on neutral alumina with hexane as eluant and repeated recrystallizations from hexane gave yellow needles: mp 180 °C [lit.[37] mp 180–181 °C]; NMR ($CDCl_3$) δ 3.03 (s, 3 H, CH_3), 7.5–7.7 (m, 4 H, Ar), 8.2–8.7 (m, 4 H, Ar).

10-Bromo-9-methylanthracene was prepared following the literature method.[37] The crude product was recrystallized from hexane. A portion was purified by means of column chromatography on a neutral alumina eluted with hexane to give yellow needles: mp 171–172 °C [lit.[37] mp 170–172 °C]; NMR ($CDCl_3$) δ 3.02 (s, 3 H, CH_3), 7.5–7.7 (m, 4 H, Ar), and 8.2–8.6 (m, 4 H, Ar).

9-Phenylanthracene. Anthrone (5.0 g, 0.026 mol) was extracted into a solution of phenylmagnesium bromide prepared from 11.9 g (0.076 mol) of bromobenzene and 1.8 g (0.077 mol) of magnesium in 100 mL of anhydrous ethyl ether. The mixture was allowed to reflux for 5 h, and the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane and hydrolyzed with aqueous ammonium chloride. The organic layer was washed with 2 N NaOH, 2 N HCl, and saturated sodium bicarbonate and dried over magnesium sulfate. Removal of solvent under reduced pressure gave a yellow liquid. Heating at 100 °C under vacuum for 4 h to remove excess bromobenzene caused the product to solidify. The crude product was triturated with pentane to remove biphenyl and gave 5.56 g (84%) of a yellow solid. Recrystallization from absolute ethanol gave pale yellow plates: mp 152–6 °C [lit.[38] mp 154–6 °C]; NMR ($CDCl_3$) δ 7.3–7.7 (m, 11 H, -Ar), 7.95–8.05 (m, 2 H, peri-H's), 8.45 (s, 1 H, 9-H).

10-Phenyl-9-bromoanthracene. To a stirred solution of 1.5 g (5.9 mmol) of 9-phenylanthracene in 80 mL of acetic acid held at 65 °C under nitrogen was added dropwise a solution of 1.04 g (6.5 mmol) of bromine in 20 mL of acetic acid. Upon completion of the addition the reaction mixture was allowed to cool to room temperature, and the crystals were collected. Removal of the acetic acid under reduced pressure gave a yellow solid. The solid was recrystallized from acetic acid and then combined with the previously collected crystals to give 1.8 g (92%): mp 153–5 °C [lit.[39] mp 154–5 °C]; NMR ($CDCl_3$) δ 7.2–7.7 (m, 11 H, Ar), 8.15–8.65 (m, 2 H, peri-H's).

10-Phenyl-9-methylanthracene. To 5 mL of 1.8 M phenyllithium in benzene–ether mixed solution at room temperature under nitrogen was added 1 g of 10-phenyl-9-bromoanthracene in 8 mL of dry benzene. The solution was stirred for 3 h and then added dropwise to 1.5 mL of methyl iodide in 2 mL of dry benzene. This mixture was stirred for 4 h, diluted with benzene, and washed with water, 10% HCl, saturated sodium bicarbonate, and brine. Drying with Na_2SO_4 and removal of solvent under reduced pressure gave 1.4 g of yellow liquid. The crude product was purified by chromatography on a Waters 660 LC using a reverse-phase C18 semi-prep column eluted with 80% MeOH/water at 6.5 mL/min. Repeated recrystallization from ethanol gave yellow plates: mp 115–8 °C [lit.[39] mp 112–3 °C]; NMR ($CDCl_3$) δ 3.01 (s, 3 H, CH_3), 7.05–7.7 (m, 11 H, Ar), 8.1–8.3 (m, 2 H, peri-H's).

10-Formyl-9-methylanthracene was prepared following the literature method.[40] The dark brown needles were recrystallized from 75 mL of glacial acetic acid and washed with methanol to give amber needles: mp 169–170 °C [lit.[40] mp 173 °C]; NMR ($CDCl_3$) δ 3.05 (s, 3 H, CH_3), 7.4–7.8 (m, 4 H, Ar), 8.1–8.4 (m, 2 H, Ar), 8.7–8.9 (m, 2 H, Ar), and 11.35 (s, 1 H, CHO).

10-Benzoyl-9-methylanthracene was prepared following the literature method.[41] Recrystallization from acetic acid and then ethanol gave bright yellow needles: mp 177–178 °C; NMR ($CDCl_3$) δ 3.13 (s, 3 H, CH_3), 7.15–7.9 (m, 11 H, Ar), 8.2–8.5 (m, 2 H, Ar): IR (Nujol mull) 1670 cm^{-1} (C=O). Anal. Calcd for $C_{22}H_{16}O$: C, 89.16; H, 5.44. Found: C, 89.12; H, 5.46.

10-Cyano-9-methylanthracene. To 2.1 g of 10-formyl-9-methylanthracene suspended in 50 mL of 95% ethanol was added 0.75 g of hydroxylamine hydrochloride (neutralized with sodium carbonate) in 7 mL of warm (75 °C) water. The mixture was heated on a steam bath for 15 min, cooled, and diluted with water. The solid was collected on a filter and heated in 10% sodium hydroxide for 10 min. The solution was cooled and diluted with water, and the solid material was collected on a filter. Recrystallization from ethanol gave yellow plates of the oxime, mp 210–212 °C dec [lit.[42] mp 170–180 °C]. To 1.2 g of the oxime was added 25 mL of acetic anhydride. The resulting solution was refluxed for 15 min and then filtered while still hot. Upon cooling orange crystals appear in the filtrate. Recrystallization from 50% benzene–hexane gave 0.9 g of brilliant gold needles: mp 208–210 °C [lit.[42] mp 208–210 °C]; NMR ($CDCl_3$) δ 3.04 (s, 3 H, CH_3), 7.5–7.8 (m, 4 H, Ar), 8.2–8.5 (m, 4 H, Ar).

10-Nitro-9-methylanthracene was prepared following the literature method.[43] Column chromatography on neutral alumina eluting with 10% ether–hexane and repeated recrystallization from amyl alcohol gave orange needles: mp 203–205 °C; NMR ($CDCl_3$) δ 3.15 (s, 3 H, CH_3), 7.45–8.0 (m, 6 H, Ar), 8.15–8.45 (m, 2 H, Ar). Anal. Calcd for $C_{15}H_{11}NO_2$: C, 75.94; H, 4.67; N, 5.90. Found: C, 75.93; H, 4.67; N, 5.98.

The equilibrium acidities were determined by the overlapping indicator method as describe previously.[1] 9-Methylanthracene and 9,10-dimethylanthracene are too weakly acidic to be fully deprotonated by dimsylate anion in DMSO solution. Therefore, a modification of the usual method was used to measure the pK_{HA} values.[44] The redox potentials were measured by cyclic voltammetry. The working electrode (BAS) consisted of a 1.5-mm-diameter platinum disk embedded in a cobalt glass seal. It was polished with a 0.05-μm Fisher polishing aluminum and rinsed with ethanol before each run. The counter electrode (BAS) was platinum wire (BAS). The reference electrode was Ag/AgI, and the reported potentials were referenced to ferrocenium/ferrocene couple ($E_{1/2}$ = 0.875 V vs the Ag/AgI couple).[4] Most electrochemical experiments were conducted in a standard glass cell (BAS). For measurements with highly basic anions ($pK_{HA} > 27$), an air-tight cell was used. Tetraethylammonium tetrafluoroborate was used as the supporting electrolyte. All electrochemical experiments were carried out under argon.

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