with equimolar amounts of octylamine in methanol.

All products were crystallized or precipitated from methanol. All products gave satisfactory spectra (IR, ^{1}H NMR, mass spectra, chemical ionization). Satisfactory elemental analysis were only obtained from compounds **1–5** and **9–11**. The idon-, allon-, and altronamides did not solidify, and carbon values were low.

Gelation Procedures. A. Hydrogels. (i) Galactonamides. **1** (50 mg) was dissolved in 10 mL of boiling water and cooled in an ice bath. A turbid gel of low mechanical strength was formed within a few seconds and did not change its appearance after 3 months. Slow cooling did not produce gels but flaky precipitates. Concentrations greater than half a percent (w/v) could not be obtained; lower concentrations gave even less solid gels. The racemate, **1** + **9**, was less soluble (≃30 mg/10 mL) and formed also stable gels of low tensile strength.

(ii) Mannonamides. **2** or **10** (100 mg) was dissolved in 10 mL of refluxing water and again cooled with an ice bath. Solidification to a white gel of medium mechanical stability occurred within a few seconds. Concentration of up to 300 mg in 10 mL of hot water could be obtained. Concentrations below 0.5% (w/v), or slow cooling, resulted in flaky precipitates. The racemate (100 mg/10 mL) **2** + **10** gave a white gel on rapid cooling, which behaved similarly to the gels from the pure enantiomers.

(iii) Gluconamides. **3** or **11** (100 mg) was dissolved in 10 mL of water on heating to 75 °C. The solutions were then left standing, and a compact, clear gel was formed within 2–3 min. After about 30 min, the gels became turbid, and crystals formed within a few days. This sequence of events appeared in a concentration range of 0.5–50% (w/v). The racemate **3** + **11** dissolved only above 85 °C and precipitated on cooling. The solubility of the racemate in boiling water is of the same order as for the enantiomers.

(iv) Talonamide. **4** (100 mg) was dissolved in 2 mL of water at 60 °C. A clear, solid gel was formed within a few minutes at room temperature, but crystals appeared rapidly. The concentration range for formation of gels was 0.5–70% (w/v).

(v) Gulonamide. The solubility of **5** in boiling water was higher than 100% (w/v). No gelation was observed. **B. Organogels. (i) Galactonamides.** **1** and **9** were practically insoluble in refluxing xylene. **(ii) Mannonamides.** **2** or **10** (100 mg each) was dissolved in 20 mL of refluxing 1,2-xylene and cooled in an ice bath. Viscous and turbid solutions were obtained, which did not solidify or produce precipitates. From xylene solutions of racemic **2** + **10** precipitated white flakes on cooling. 1,3-Xylene did not work because its boiling point is slightly too low to dissolve **2**. **(iii) Gluconamides.** **3** or **11** (100 mg) was dissolved in 10 mL of refluxing 1,2-xylene and cooled to room temperature. Clear, compact gels were obtained from which crystals precipitated within 3 or 4 days. The useful concentration range for the formation of clear gels was 1–7% (w/v). The racemate **3** + **11** behaved identically with the pure enantiomers.

(iv) Talonamide. **4** (50 mg) was dissolved in 50 mL of 1,2-xylene at 100 °C. A clear, compact gel was obtained on cooling. Crystallization occurred only after days. The concentration range for gelation was 1–100% (w/v).

(v) Gulonamide. Similar behavior to talonamide.

Electron Microscopy Grids. Carbon-coated copper grids were dipped into freshly prepared gels or hot viscous solutions (talonamide in water, mannonamide in xylene). The samples were shadowed with platinum–carbon at an elevation angle of about 30° with an Edwards coating system E 306A. Negatively stained gels (e.g., Figure 2b) were prepared with 2% (w/v) phosphotungstic acid. The pH was adjusted to 7 with sodium hydroxide. In order to determine the handedness of helix or ribbon twistings, great care was taken in exposing heavy metal-shadowed surfaces directly to the electron beam.

Freeze etching (Figure 2 (parts c and d)) was carried out with a Balzer BA 360 freeze-etching device. A small droplet of freshly prepared 3% hydrogel of **2** without any cryoprotectants was mounted on a specimen support. It was rapidly immersed into liquid Freon A 13 (Messer-Griesheim) cooled by liquid nitrogen. The probe was fractured at 173 K in vacuo in small steps down to a final depth of about 40 nm. This was followed by etching at 173 K for 30 s. Immediately thereafter, the etched surface was shadowed with platinum–carbon at an elevation angle of 30°. Subsequently it was covered by a layer of pure carbon at an elevation angle of 90°. The replica was floated off from the specimen support and loaded onto a copper grid. Electron microscopy was carried out with a Siemens Elmiscope 1 at a direct magnification of 40 000.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft (SFB 312 "Gerichtete Membranprozesse"), the FNK of the Freie Universität Berlin, and the Fonds der Chemischen Industrie. We thank Prof. E. Zeitler for his continuous interest and help.

Acidities of Radical Cations Derived from Remotely Substituted and Phenyl-Substituted Fluorenes

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Abstract: Estimates of the acidities of the radical cations derived from remotely substituted and phenyl-substituted fluorenes have been made from measurements of the acidities and oxidation potentials of the fluorenes and the oxidation potentials of their conjugate bases. The radical cation acidities of fluorene, 2-bromofluorene, and 4-azafluorene were all estimated to be −17. The $\text{p}K_{\text{HA}^{\cdot+}}$ values for fluorenes bearing remote donor substituents were as follows: 3-Me (−15); 2-Me (−15); 3-MeO (−13.5); 2-PhS (−12); 3,6-$(\text{MeO})_2$ (−12); 2-MeO (−10); 2,7-$(\text{PhS})_2$ (−9.5); 2,7-$(\text{MeO})_2$ (−6); 2,3,6,7-$(\text{MeO})_4$ (−2); 2-Me_2N (+1). A plot of $E_{\text{ox}}(\text{HA})$ for the fluorenes vs the acidities of the corresponding radical cations, $\text{p}K_{\text{HA}^{\cdot+}}$, is linear (slope = 0.93; $R^2 = 0.995$). The introduction of a phenyl or aryl group into the 9-position of fluorene, as in 9-Ph, 9-*p*-tolyl, 9-*m*-ClC_6H_4, or 9-mesitylfluorenes and fluoradene, increased the radical cation acidity ($\text{p}K_{\text{HA}^{\cdot+}}$ = −21 to −23). A similar Ph effect was observed on the acidities of 2,7- or 3,6-dimethoxyfluorene radical cations. These acidity increases are associated with decreases in the 9-C–H bond dissociation energies (BDEs) of 4–9 kcal/mol, relative to that of fluorene. On the other hand, fusion of a benzene ring onto the 1,2- or 2,3-positions lowers the acidity of fluorene by 6 and 5 $\text{p}K_{\text{HA}^{\cdot+}}$ units, respectively, an effect which overshadows the small acid-strengthening effects caused by the ~1 kcal/mol lower 9-C–H BDEs.

The acidities of only a few radical cations have been determined because of the difficulty in measuring the position of an equilibrium involving two highly reactive radical species, such as those in eq 1.[1] Nevertheless, acidities of about a dozen nitrogen and oxygen radical cation acids have been measured, including those for $\text{PhNH}_2^{\cdot+}$,[2] $\text{Me}_2\text{NH}^{\cdot+}$,[3] and $\text{PhOH}^{\cdot+}$,[4] which have $\text{p}K_{\text{HA}^{\cdot+}}$ values of 7, 6.5–7, and −2, respectively. Typically, the radical cations were generated by photolysis or pulse radiolysis in an

$$\text{H–A}^{\cdot+} + \text{H}_2\text{O} \rightleftarrows \text{H}_3\text{O}^+ + \text{A}^{\cdot} \qquad (1)$$

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(1) For reviews, see: Hammerich, O.; Parker, V. D. *Adv. Phys. Org. Chem.* **1984**, *20*, 55–189 and references cited therein.

(2) Land, E. J.; Porter, G. *Trans. Faraday Soc.* **1963**, *59*, 2027.

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aqueous buffer, and the concentration of the radical formed on deprotonation was determined spectroscopically. The $pK_{HA^{\bullet+}}$ of one carbon radical cation acid, $(CH_3CH_2)_3N^{\bullet+}$, has been determined in this way to be 8.0.[5]

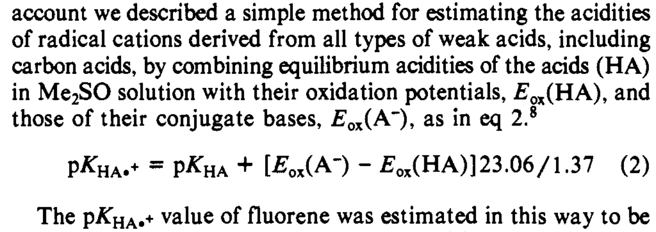
Methods of this type appear to be inapplicable to hydrocarbon radical cations, however, because of their much higher acidities. For example, calculations indicate that the radical cation of toluene has a $pK_{HA^{\bullet+}}$ of about −12 in acetonitrile,[6] and the high kinetic acidities of polymethylbenzene radical cations toward pyridine bases also point to high equilibrium acidities.[7] In a preliminary account we described a simple method for estimating the acidities of radical cations derived from all types of weak acids, including carbon acids, by combining equilibrium acidities of the acids (HA) in Me_2SO solution with their oxidation potentials, $E_{ox}(HA)$, and those of their conjugate bases, $E_{ox}(A^-)$, as in eq 2.[8]

$$pK_{HA^{\bullet+}} = pK_{HA} + [E_{ox}(A^-) - E_{ox}(HA)]23.06/1.37 \quad (2)$$

The $pK_{HA^{\bullet+}}$ value of fluorene was estimated in this way to be −16 in Me_2SO solution, and the values of its 2-methoxy and 2,7-dimethoxy derivatives were estimated to be −11 and −6, respectively. The oxidation potential of 2,7-dimethoxyfluorene was observed to be reversible in MeCN but irreversible in Me_2SO, presumably because deprotonation occurred in the more basic solvent. This was consistent with the change from an irreversible oxidation in CH_2Cl_2 to a reversible oxidation when F_3CCO_2H was added.[9] In the present paper we report the effect on reversibility of adding pyridine, describe the effects of substituents on the acidities of radical cations derived from fluorenes, and relate the latter to their effects on oxidation potentials and C–H homolytic bond dissociation energies (BDEs) of the fluorenes.

Results and Discussion

Effect of Added Base on Reversible Oxidation Cyclic Voltammetric (CV) Waves. If the switch from reversible to irreversible oxidative CV waves for 2,7-dimethoxyfluorene (1) on changing solvents from MeCN to Me_2SO is caused by increased solvent basicity, as was assumed,[8] it is reasonable to expect a similar change to occur in the CV scan in MeCN by adding base. The scan for ferrocene–ferrocenium ion is shown at the upper right and that for 1 at the upper left in Figure 1. Peak A at 1.55 V (vs Ag/AgI) in the latter scan is believed to correspond to the formation of the radical cation from the neutral species upon one-electron removal (1 to 2) and peak B to the formation of the dication 3. The $E_{ox}(HA)$ value of 1.88 V for peak B agrees with the average value of 1.93 in MeCN reported earlier for this peak.[10] When the scan was repeated in the presence of excess 0.3% pyridine, there was a 30 mV cathodic shift in the position of peak A and the scan was no longer reversible. A similar effect was observed by addition of Me_2SO to the solution, but here reversibility was restored by addition of trifluoroacetic acid. It seemed likely that loss of reversibility was associated with the action of pyridine or of Me_2SO, acting as a base, to remove a proton from 2, which according to our estimate is a strong acid ($pK_{HA^{\bullet+}}$ = −6 in Me_2SO). The resulting radical (4) could then couple rapidly with the radical cation to form cation 5 (or the like).



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2 3

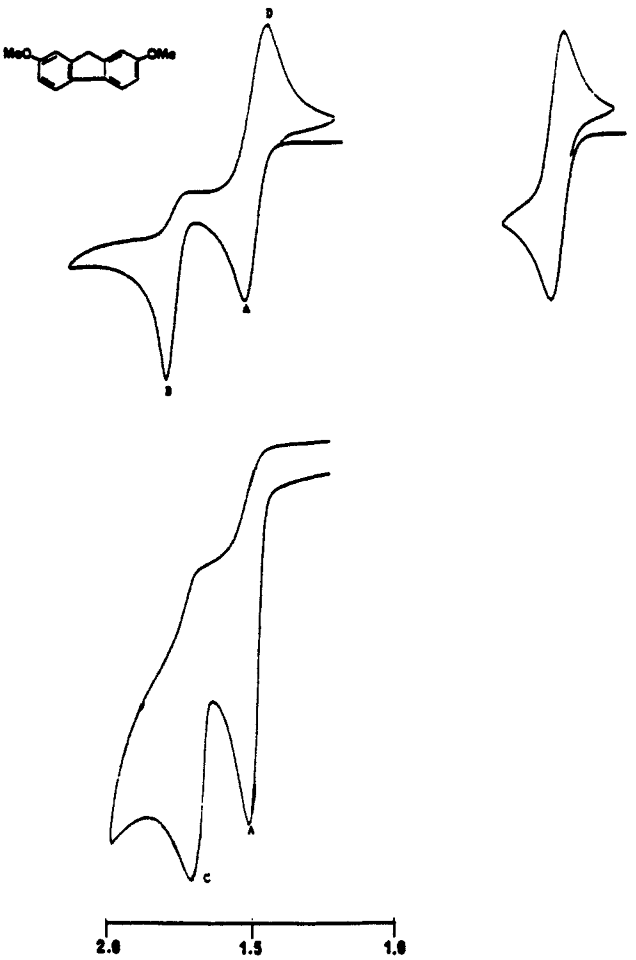
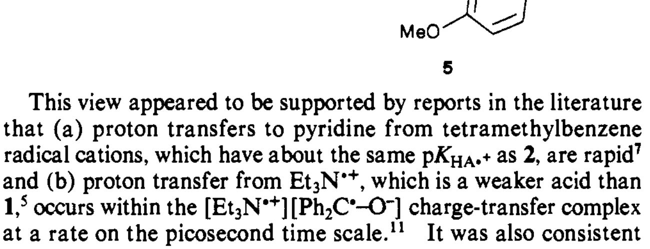


Figure 1. Cyclic voltammetric oxidative scans in MeCN for (a) ferrocene (upper right), (b) 2,7-dimethoxyfluorene (upper left), and (c) 2,7-dimethoxyfluorene with excess 0.3% pyridine in MeCN added (bottom).



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This view appeared to be supported by reports in the literature that (a) proton transfers to pyridine from tetramethylbenzene radical cations, which have about the same $pK_{HA^{\bullet+}}$ as 2, are rapid[7] and (b) proton transfer from $Et_3N^{\bullet+}$, which is a weaker acid than 1,[5] occurs within the $[Et_3N^{\bullet+}][Ph_2C^{\bullet}–O^-]$ charge-transfer complex at a rate on the picosecond time scale.[11] It was also consistent with our observation that the reversibility of the electrochemical

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Table I. Acidity and Oxidation Potential Data for Remotely Substituted Fluorenes (G-FlH$_2$) in Dimethyl Sulfoxide and Acetonitrile Solutions

G	pK_{HA}[a]	E_{ox}(HA)[b] MeCN	E_{ox}(HA)[b] Me$_2$SO	E_{ox}(A$^-$)[j]	p$K_{HA}$$^{\bullet+}$[k]	BDE[l]
H	22.6	2.15[c,d] (60)		−0.194 (45)	−17	79.5
2-Br	20.0	2.14[e] (40)		−0.038 (45)	−17	79.5
4-aza	20.55	2.19[f] (85)		−0.018 (50)	−17	80.7
3-Me	23.4	2.04 (25)		−0.259 (40)	−15	79.1
2-Me	23.1	2.04[c] (60)		−0.200 (45)	−15	80.0
3-MeO	23.95	1.91 (40)		−0.316 (40)	−13.5	78.5
2-PhS	20.5	1.90 (50)	1.86 (75)	−0.047 (45)	−12	80.0
3,6-(MeO)$_2$	25.3	1.85 (70)	1.88 (75)	−0.384 (45)	−12	78.8
2-MeO	22.7	1.79[g] (40)	1.80	−0.189 (40)	−10	79.7
2,7-(PhS)$_2$	18.5	1.73[h] (50)	1.72 (50)	0.068 (50)	−9.5	79.9
2,7-(MeO)$_2$	22.95	1.55[h,i] (40)	1.60 (70)	−0.195 (45)	−6	79.9
2,3,6,7-(MeO)$_4$	25.4	1.33[h] (55)	1.38[c] (65)	−0.295 (60)	−2	80.9
2-Me$_2$N	24.2	1.14[h] (60)	1.13[h]	−0.248 (40)	+1	80.4

[a] Measured in Me$_2$SO; reported in ref 10 or measured as part of the present study. [b] Obtained by cyclic voltammetric measurements at room temperature in a solution containing 0.1 M Et$_4$N$^+$BF$_4^-$ as a supporting electrolyte with a Pt electrode at a sweep rate of 100 mV/s. The potentials are reported vs a Ag/AgI reference electrode, using the ferrocene redox pair as an internal standard (0.875 V vs Ag/AgI). Wave widths (mV) as defined by ($E_p - E_{p/2}$) are shown in parentheses. Waves are irreversible unless otherwise noted. [c] Appeared as a shoulder. [d] 2.17 in MeCN[16] (SCE value +0.36 V); 2.07 in NaOAc/HOAc[17] (NHE value +0.125 V); 2.02 in NaOAc/HOAc[18] (SCE value +0.365 V). [e] 2.15 in MeCN[16] (SCE value +0.365 V). [f] Measured at a glassy carbon electrode. [g] 1.71 in MeCN[16] (SCE value +0.365 V). [h] E_p value for a reversible oxidation. [i] 1.54 in CH$_2$Cl$_2$/TFA.[9] [k] Estimated by using eq 1. [j] Oxidation potential of the anion (eV); wave widths (mV) are shown in parentheses. [l] BDE of the 9-C–H bond in the neutral fluorene, estimated by using eq 4 with E_{ox}(A$^-$) related to SHE by adding −0.125 V.

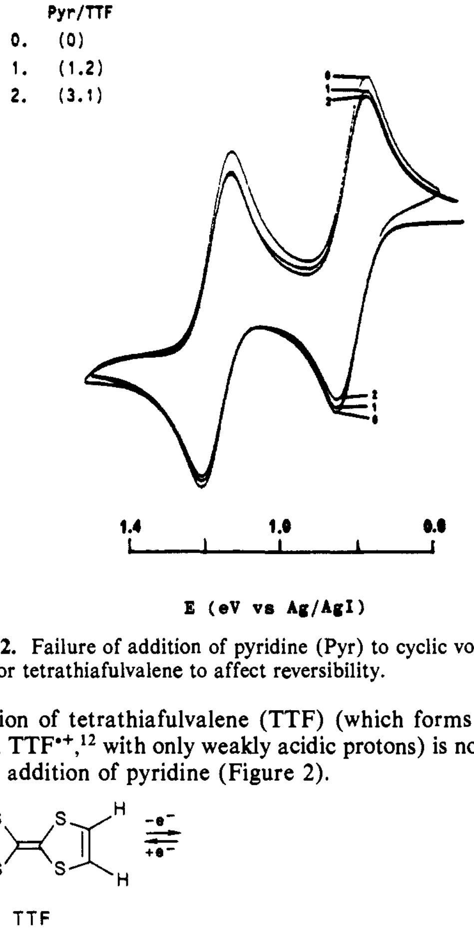
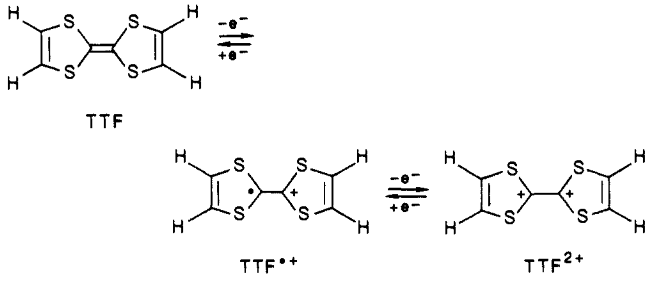


Figure 2. Failure of addition of pyridine (Pyr) to cyclic voltammetric scans for tetrathiafulvalene to affect reversibility.

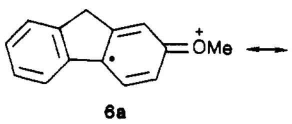
oxidation of tetrathiafulvalene (TTF) (which forms a radical cation, TTF$^{\bullet+}$,[12] with only weakly acidic protons) is not affected by the addition of pyridine (Figure 2).



On the other hand, proton transfer does not occur readily from the solvent-separated radical pair [Et$_3$N$^{\bullet+}$][(*E*)-PhCH=CHPh]$^{\bullet-}$,[13] and deprotonation of the hexamethylbenzene radical cation does not occur by a simple proton transfer from the radical cation.[14] Also, a study of the rates of reaction of the radical cation derived from **1** and its dideuterio derivative with pyridine failed to show a deuterium isotope effect (k_H/k_D) = 1.0 ± 0.2. It is clear from these results that the reaction of **2** with pyridine is complex and that deprotonation does not occur in the rate-determining step.[15]

Radical Cation Acidities of Remotely Substituted Fluorenes. Acidity and oxidation potential data for remotely substituted fluorenes and their radical cations are summarized in Table I.

The radical cations of fluorene, 2-bromofluorene, and 4-azafluorene all have acidities p$K_{HA^{\bullet+}}$ estimated to be −17. We conclude, therefore, that mild electron-withdrawing substituents have little or no effect in stabilizing or destabilizing the fluorene radical cation or its conjugate base, the fluorene radical. On the other hand, the electron-donating substituents, Me, PhS, MeO, and Me$_2$N, stabilize the fluorene radical cation to a progressively greater extent, resulting in acidity decreases. The stabilizing effect of MeO is seen to be larger from the 2-position (Δp$K_{HA^{\bullet+}}$ = 7) than the 3-position (Δp$K_{HA^{\bullet+}}$ = 3.5). This is not surprising, since the odd electron (or positive charge) can be delocalized to the second benzene ring (**6b**) when a 2-MeO substituent is present, while the positive charge is maintained on the oxygen atom of the methoxyl group. This is not possible, however, when the substituent is in the 3-position (**7**).



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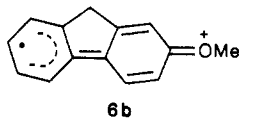

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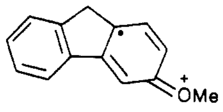

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Introduction of a second "meta" MeO substituent into the 7-position causes a further 4-unit decrease in acidity, accompanied,

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[12] Identification of TTF$^{\bullet+}$ and TTF^{2+} was made by Shuming Nie using surface-enhanced Raman spectroscopy: Nie, S.; Van Duyne, R. P., unpublished results.

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[15] At the Organic Mechanisms Conference in Halifax, Nova Scotia, Aug 1987, Professor V. D. Parker questioned our postulate of deprotonation of **2** by pyridine. He offered to carry out an isotopic rate study and has reported these results to us.

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Table II. Acidity and Oxidation Potential Data for Phenyl-Substituted Fluorenes

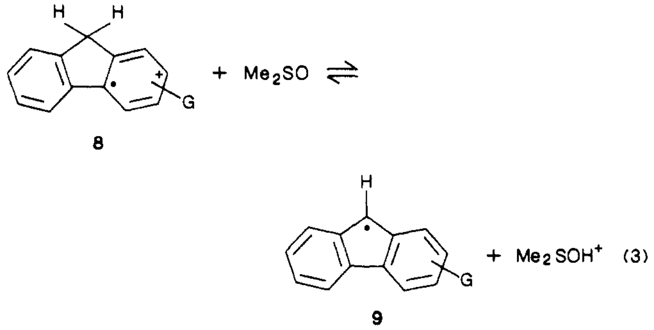
fluorene	pK_{HA}[a]	$E_{ox}(HA)$[c] MeCN	$E_{ox}(HA)$[c] Me_2SO	$E_{ox}(A^-)$[d]	$pK_{HA}{}^{\bullet+}$[f]	BDE[g]
fluorene (FlH_2)	22.6	(see Table I)			−17	79.5
9-Ph-FlH	17.9	2.21 (60)		−0.153 (45)	−22	74.0
9-*p*-MeC_6H_4-FlH	18.3	2.29 (80)		−0.193 (45)	−23	73.6
9-*m*-ClC_6H_4-FlH	16.85	2.27 (80)		−0.063 (45)	−22	74.6
9-mesityl-FlH	18.6	2.21 (75)		−0.140[e] (60)	−21	75.2
fluoradene	10.5[b]	2.12 (90)		+0.130 (45)	−23	70.4
1,2-benzo-FlH_2	19.7		1.75 (55)	−0.056 (50)	−11	78.7
2,3-benzo-FlH_2	23.1		1.81 (70)	−0.269 (50)	−12	78.4
2,7-$(MeO)_2$-9-Ph-FlH	18.3	1.61 (60)		−0.145 (45)	−11	74.7
3,6-$(MeO)_2$-9-mesityl-FlH	21.3	1.86 (50)	1.89 (75)	−0.325 (50)	−15.5	74.6

[a] Measured in Me_2SO by the method previously reported. [b] Reference 19. [c] Obtained by cyclic voltammetry under the conditions described in footnote *b* of Table I. [d] in Me_2SO. [e] Reversible peak reported as an E_p value. [f] Estimated from eq 1. [g] BDE of the 9-C–H bond in the neutral fluorene estimated by using eq 4 with −0.125 added to $E_{ox}(A^-)$ to transfer from the Ag/AgI standard electrode to the standard hydrogen electrode.

in MeCN, by reversibility. A second "para" MeO substituent in the 6-position (to give 3,6-$(MeO)_2FlH_2$) causes 1.5 unit further decreases, but the wave is not reversible. The smaller decreases for the second substitution can be attributed to a saturation effect. The presence of MeO or PhS substituents in both the 2- and 7-positions increases the stability of the radical cations to the point where their lifetimes on the CV time scale become sufficient to allow the reverse waves to appear.

Additivity of the effects of 2,7- and 3,6-dimethoxyl groups would predict a $pK_{HA^{\bullet+}}$ of −1 for 2,3,6,7-tetramethoxyfluorene radical cation, as compared with the −2 value observed. Introduction of a 2-Me_2N group has a larger stabilizing effect on the radical cation of fluorene than the combined effect of the 2-, 3-, 6-, and 7-methoxyl groups (24.7 vs 20.6 kcal/mol). The 2-Me_2N-$Fl^{\bullet+}$ radical cation is sufficiently stable to allow the CV waves to be reversible in Me_2SO as well as MeCN.

Examination of Table I shows that the decrease in $pK_{HA^{\bullet+}}$ values parallels the decrease in $E_{ox}(HA)$ values.[19] A plot of $E_{ox}(HA)$ vs $pK_{HA^{\bullet+}}$ is linear (Figure 3) with a slope of 0.93 (kcal/mol); $R^2 = 0.995$. This plot illustrates the dominant role played by substituent effects in the radical cations on the position of equilibrium 3. It demonstrates that the substituent effects on the fluorenyl radicals, which are measured by the $E_{ox}(A^-)$ and pK_{HA} terms in eq 2, are relatively small. (This is not unexpected, since we have shown earlier that a plot of $E_{ox}(A^-)$ vs pK_{HA} for 2- and 2,7-substituted fluorenes is linear with a slope near unity, indicating that these substituents exert no appreciable stabilizing (or destabilizing) effect on the fluorenyl radical.[20]) On the other hand, the 1 kcal/mol radical stabilizing effect calculated for the 3-MeO substituent by the ΔAOP method[20] should cause a small acid-strengthening effect in the radical cation. We note that the 3-MeO and 3,6-$(MeO)_2$ points are slightly off the line in the direction expected. Phenyl substituents in the 9-position are strongly radical stabilizing, however,[20] and these deviant points were not included in the correlation (Figure 3).



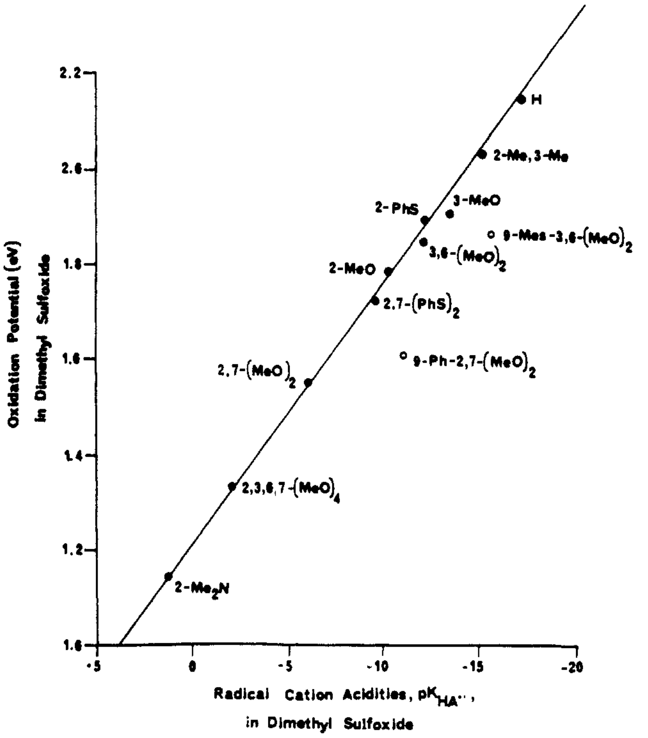


Figure 3. Plot of the oxidation potentials for fluorenes, $E_{ox}(HA)$, vs acidities of radical cations, $pK_{HA^{\bullet+}}$, both in dimethyl sulfoxide solution.

Estimation of homolytic bond dissociation energies (BDEs) by use of eq 4 offers an alternative way to look at these substituent effects.[22] Examination of Table I shows that donor 3-substituents

$$\mathrm{BDE} = 1.37pK_{HA} + 23.06E_{ox}(A^-) + 55.86 \qquad (4)^{21}$$

(3-Me, 3-MeO, 3,6-$(MeO)_2$) lower the BDE of the 9-C–H bond in fluorene slightly, whereas donor 2-substituents (2-Me, 2-PhS, 2-MeO, 2-Me_2N, 2,7-$(PhS)_2$, 2,7-$(MeO)_2$) raise the BDE slightly. The trends are small, however, and may not be significant.

Radical Cation Acidities and BDEs of Phenyl-Substituted Fluorenes. α-Phenyl substituents have been shown to cause large acidifying effects in neutral carbon acids.[23] For example, 9-phenylfluorene is 5 pK_a units more acidic than fluorene, and fluoradene, wherein the 9-phenyl group is constrained to be nearly coplanar with the fluorene ring, is 12.4 units more acidic.[24] Examination of Table II shows that the radical cations of 9-Ph-

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(19) Examination of eq 1 shows that the position of equilibrium 3 depends on pK_{HA} and $E_{ox}(A^-)$, as well as $E_{ox}(HA)$. Usually, the first two effects are small, but examples are given in the accompanying paper where $E_{ox}(A^-)$ plays an important role.

(20) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1979–1985.

(21) $\Delta G°_f(H^\bullet) + \Delta G°_{sol}(H^\bullet) - \Delta G°_{tr}(H^+) + T\Delta S° = 55.86$ kcal/mol at 25 °C (see ref 22). $E_{ox}(A^-)$ is related to the standard hydrogen electrode.

(22) Bordwell, F. G.; Cheng, J.-P.; Harrelson, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 1229–1231.

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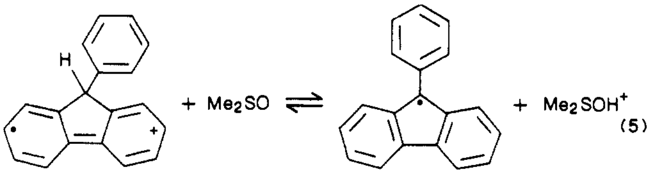
FlH, 9-*p*-MeC$_6$H$_4$-FlH, 9-(*m*-ClC$_6$H$_4$)-FlH, 9-mesityl-FlH, and fluoradene are all more acidic than that from fluorene by 4–6 p$K_{HA\cdot+}$ units. The Ph groups in 9-phenyl-2,7- and 9-phenyl-3,6-dimethoxyfluorenes exert a similar effect on the acidities of the corresponding radical cations. These acidity increases can be explained as a weakening of the 9-C–H bond in these radical cations by the α-Ar group.

Examination of Tables I and II shows that introduction of a 9-Ph group into fluorene makes E_{ox}(HA) more positive by about 60 mV and E_{ox}(A$^-$) less negative by 40 mV. These effects therefore counteract one another and play a negligible role in the observed increase in the acidity of the 9-Ph-Fl$^{\cdot+}$ radical cation by 5 p$K_{HA\cdot+}$ units, relative to HFlH$^{\cdot+}$. Instead, it is the 4.7 unit decrease in pK_{HA} for 9-Ph-FlH vs HFlH that is largely responsible for the enhanced acidity, as calculated by eq 2. The decrease in pK_{HA} is associated with the 5.4 kcal/mol decrease in BDE calculated by eq 4. The BDE decrease corresponds to a stabilization of the radical by the Ph group, which leads to a shift of equilibrium 5 to the right. The other aryl groups exert similar acidifying effects (Table II).



(5)

It may be surprising at first sight that heterolytic BDEs of the type shown in eq 5 can be correlated with homolytic BDEs, since substituents often cause very different effects on the two types of BDEs. Phenyl substituents differ from most other types of substituents in this regard, however, in being only weakly polar and exerting their effects almost completely by delocalization. Since the magnitude of their stabilizing effect on radicals is not greatly different than that on anions, the 5 p$K_{HA\cdot+}$ unit increase in acidity of FlH$_2$$^{\cdot+}$ caused by Ph substitution (Table II) is essentially the same as that caused by Ph substitution in FlH$_2$ (Table I) and the ΔBDE calculated for 9-Ph-FlH vs FlH$_2$ by eq 4.

The methoxyl groups in 2,7-dimethoxy-9-phenyl- and 3,6-dimethoxy-9-mesitylfluorene allow delocalization of the positive charge in the radical cation thereby causing acidity decreases of 11 and 5.5 p$K_{HA\cdot+}$ units, relative to 9-Ph-FlH and 9-mesitylfluorene, respectively, as indicated by the E_{ox}(HA). These points fail to fit on the line in Figure 3, however, because the radical cation acidities are increased by about 5 kcal/mol due to stabilization of the (conjugate base) radical by the aryl group.

Fusion of benzene rings onto the 1,2- or 2,3-positions of fluorene allows extensive further delocalization of the positive charge (or odd electron) and decreases the acidities of these radical cations by 6 and 5 p$K_{HA\cdot+}$ units, respectively, relative to that of FlH$_2$$^{\cdot+}$. These large effects overshadow the small (~1 kcal/mol) weakening BDE effects for the 9-C–H bond (78.7 and 78.4 kcal/mol, respectively).

Summary. The acidities of the radical cations derived by electrochemical oxidation of fluorene and its derivatives are estimated to have p$K_{HA\cdot+}$ values varying from −17 for the parent or its 2-bromo derivative to +1 for its 2-dimethylamino derivative. The progressively larger acidity decreases for 2-PhS, 2-MeO, and 2-Me$_2$N derivatives are associated with progressively larger delocalization of the positive charge and the odd electron in the radical cations by PhS, MeO, and Me$_2$N substituents, respectively. The homolytic bond dissociation energies of the 9-C–H bond in the fluorenes remain essentially constant with these substitutions but are decreased substantially by the introduction of 9-aryl groups. The lower BDEs caused by these aryl groups are responsible for corresponding increases in the acidities of the fluorenes and of the radical cations derived therefrom.

Experimental Section

Materials. The preparation and properties of most of the fluorenes have been described in earlier papers.[18] 2,7-Dimethoxyfluorenone was purchased from Fairchild Chemical Co. The purity of all samples used for CV measurements was established by GC, melting points, NMR, and/or mass spectroscopy.

3,6-Dimethoxy- and 2,3,6,7-Tetramethoxyfluorenones were prepared by the method recently described for polymethoxyfluorenones.[25] The 3,6-dimethoxyfluorenone, which was shown to be identical with a sample provided by Professor G. B. Schuster, was reduced[26] to 3,6-dimethoxyfluorene: colorless needles (EtOH); mp 90.5–91 °C; ^{1}H NMR (CDCl$_3$) δ 3.79 (s, 2 H), 3.90 (s, 6 H), 6.87 (dd, 2 H), 7.29 (d, 2 H), 7.43 (d, 2 H). 2,3,6,7-Tetramethoxyfluorene was prepared similarly. Recrystallization from EtOH (activated carbon) gave colorless needles, mp 196.5–197 °C (lit.[27] mp 193–194 °C).

3,6-Dimethoxy-9-mesitylfluorene. Mesitylmagnesium bromide (0.49 g, 2.2 mol) in dry Et$_2$O was added dropwise under argon to 3,6-dimethoxyfluorenone (0.5 g, 2.1 mmol) dissolved in 4 mL of dry THF. After the resultant mixture was stirred overnight and quenched with saturated aqueous NH$_4$Cl, the organic layer was washed, dried, and evaporated to yield 0.76 g (87%) of crude 9-mesityl-9-hydroxyfluorene. The crude product was mixed with 0.19 g of I$_2$, 0.4 mL of hypophosphorus acid, 0.4 mL of HI, and 10 mL of acetic acid. After a 2-h reflux, addition of aqueous NaHSO$_3$ gave a yellow precipitate. Purification by preparative TLC gave the desired product: mp 132–134 °C; ^{1}H NMR (CDCl$_3$) δ 1.14 (s, 3 H), 2.30 (s, 3 H), 2.67 (s, 3 H), 3.91 (s, 6 H), 5.40 (s, 1 H), 6.7–7.5 (m, 8 H); MS (70 eV) *m/e* 344 (M$^+$), 329 (loss of CH$_3$), 313 (loss of CH$_3$O).

Cyclic Voltammetry. Cyclic voltammetric experiments were performed by using a three-electrode Bioanalytical Systems Inc. (BAS) apparatus (Purdue Research Park, West Lafayette, IN). Voltammograms were recorded on a Bausch and Lomb X-Y recorder. 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 (auxiliary) electrode was a platinum wire (BAS). The Ag/AgI reference electrode was separated from the anolyte by a fitted glass bridge (VYCOR membrane) filled with a saturated tetraethylammonium iodide solution dissolved in the solvent of choice. Most experiments were conducted in a standard glass cell (BAS). For measurements with highly basic species (pK_{HA} >27) an air-tight cell was used. All experiments were carried out under argon; the manipulations are similar to those used for the pK_a measurements described elsewhere.[28] Tetraethylammonium tetrafluoroborate (TEAFB) was used as the supporting electrolyte for most measurements. Tetraethylammonium perchlorate (TEAP) was used on occasion, especially for measurements with highly basic anions. The TEAFB and TEAP, which gave identical results, were both electroanalytical grade; they were dried at 110 °C in vacuo for 24 h prior to use. Analytical grade Me$_2$SO was dried and freed of oxygen by distillation at 60 °C from sodamide at reduced pressure under a blanket of argon; anhydrous acetonitrile (Aldrich gold label) was used as received. Stock solutions were made 0.1 M in electrolyte (TEAFB, TEAP). Concentrations of the solutions were usually 3–4 mM for neutral substrates and 0.1 mM for anionic species.

A typical oxidation potential of an anion, E_{ox}(A$^-$), was determined in the following way. A sample of an acid, HA, sufficient to prepare 5 mL of a 3 mM solution, was weighed and added to the electrical cell. The cell was flushed with argon for ca. 2 min. (For highly basic anions the cell was evacuated and flushed with argon 3 or more times.) A 5-mL aliquot of a 0.1 M solution of TEAFB in Me$_2$SO was then added to the cell via a Hamilton air-tight syringe. The cell was transferred to the CV apparatus, and argon was bubbled in for 2–3 min. A quantity of CH$_3$SOCH$_2$K in Me$_2$SO sufficient to generate a 1 mM solution of the anion, A$^-$, was added via an air-tight syringe while argon was being bubbled into the cell. Most anions were stable in Me$_2$SO under argon for at least several minutes. Anions were generated in a similar manner in MeCN by using a more concentrated CH$_3$SOCH$_2$K in Me$_2$SO solution (>100 mM) in order to minimize the amount of Me$_2$SO introduced. Highly basic anions are less stable in MeCN than Me$_2$SO, and therefore, the voltammograms were recorded immediately after addition of the base.

Oxidation and reduction potentials of neutral compounds were also determined under argon, but here air-tight conditions are less critical.

Voltammograms were recorded at sweep rates of 100 mV/s. In our system, an $E_{1/2}$ value of 0.875 V (vs Ag/AgI) was observed for the ferrocene–ferrocenium redox couple, which served as a standard. This redox couple has been shown to have nearly equal free energies of sol-

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vation in different solvents[29] and has been recommended for use in nonaqueous solvents.[30] For a particular series of experiments the standard $E_{1/2}$ value for this couple could vary by as much as 20 mV. The value needed to correct to 0.875 V was applied in these experiments when appropriate. The potentials were generally reproducible to ±10 mV, ≥5 mV for consecutive scans, and 20 mV for different investigators. The uncertainty in using the X-Y recorder has been estimated to be 5–10 mV.[31]

When oxidation potentials of neutral compounds were recorded, it was often necessary to polish the electrode between each scan to obtain consistent E_{ox} values. This was not a problem in working with anionic species.

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Registry No. 1, 42523-30-8; **2**, 51548-21-1; **7**, 7235-14-5; **8** (G = H), 34985-70-1; **8** (G = 2-Br), 113533-34-9; **8** (G = 4-aza), 113548-07-5; **8** (G = 3-Me), 113533-35-0; **8** (G = 2-Me), 113533-36-1; **8** (G = 3-MeO), 113533-37-2; **8** (G = 2-PhS), 113533-38-3; **8** (G = 3,6-(MeO)$_2$), 113566-63-5; **8** (G = 2-MeO), 101631-12-3; **8** (G = 2,7-(PhS)$_2$), 113533-39-4; **8** (G = 2-Me$_2$N), 113533-40-7; **8** (G = 2,3,6,7-(MeO)$_4$), 65989-21-1; TTF, 31366-25-3; FlH$_2$, 86-73-7; FlH$^-$, 12257-35-1; 2-Br-FlH$_2$, 1133-80-8; 2-Br-FlH$^-$, 85535-20-2; 4-aza-FlH$_2$, 244-99-5; 4-aza-FlH$^-$, 100858-92-2; 3-Me-FlH$_2$, 2523-39-9; 3-Me-FlH, 100858-85-3; 2-Me-FlH$_2$, 1430-97-3; 2-Me-FlH$^-$, 100858-86-4; 3-MeO-FlH$^-$, 100858-84-2; 2-PhS-FlH$_2$, 59014-81-2; 2-PhS-FlH$^-$, 113533-29-2; 3,6-(MeO)$_2$-FlH$_2$, 96617-41-3; 3,6-(MeO)$_2$-FlH$^-$, 113533-30-5; 2-MeO-FlH$_2$, 2523-46-8; 2-MeO-FlH$^-$, 100858-88-6; 2,7-(PhS)$_2$-FlH$_2$, 59014-86-7; 2,7-(PhS)$_2$-FlH$^-$, 113533-31-6; 2,7-(OMe)$_2$-FlH$^-$, 100858-87-5; 2,3,6,7-(MeO)$_4$-FlH$_2$, 51487-65-1; 2,3,6,7-(MeO)$_4$-FlH$^-$, 113533-32-7; 2-Me$_2$N-FlH$_2$, 13261-62-6; 2-Me$_2$N-FlH$^-$, 113533-33-8; 9-Ph-FlH, 789-24-2; 9-Ph-Fl$^-$, 31468-22-1; 9-Ph-Fl$^{\bullet+}$, 113566-64-6; 9-(*p*-MeC$_6$H$_4$)-FlH, 18153-43-0; 9-(*p*-MeC$_6$H$_4$)-Fl$^-$, 42730-14-3; 9-(*p*-MeC$_6$H$_4$)-Fl$^{\bullet+}$, 113533-46-3; 9-(*m*-ClC$_6$H$_4$)-FlH, 32377-11-0; 9-(*m*-ClC$_6$H$_4$)-Fl$^-$, 73872-45-4; 9-(*m*-ClC$_6$H$_4$)-Fl$^{\bullet+}$, 113533-47-4; 9-MeS-FlH, 18153-40-7; 9-MeS-Fl$^-$, 85535-28-0; 9-MeS-Fl$^{\bullet+}$, 113533-48-5; 2,7-(MeO)$_2$-9-Ph-FlH, 113533-41-8; 2,7-(MeO)$_2$-9-Ph-Fl$^-$, 113533-44-1; 2,7-(MeO)$_2$-9-Ph-Fl$^{\bullet+}$, 113533-50-9; 3,6-(MeO)$_2$-9-MeS-FlH, 113533-28-1; 3,6-(MeO)$_2$-9-MeS-Fl$^-$, 113533-45-2; 3,6-(MeO)$_2$-9-MeS-Fl$^{\bullet-}$, 113533-51-0; 1,2-benzo-FlH$_2$, 238-84-6; 1,2-benzo-FlH$^-$, 113533-42-9; 1,2-benzo-Fl$^{\bullet+}$, 113566-65-7; 2,3-benzo-FlH$_2$, 243-17-4; 2,3-benzo-FlH$^-$, 113533-43-0; 2,3-benzo-Fl$^{\bullet+}$, 113566-66-8; pyridine, 110-86-1; deuterium, 7782-39-0; 3,6-dimethoxyfluorenone, 13235-07-9; 2,3,6,7-tetramethoxyfluorenone, 58532-06-2; mesitylmagnesium bromide, 2633-66-1; 9-mesityl-9-hydroxyfluorene, 113533-27-0; fluoradene, 205-94-7; fluoradene anion, 70606-47-2; fluoradene radical cation, 113533-49-6.

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Acidities of Radical Cations Derived from Cyclopentadienes and 3-Aryl-1,1,5,5-tetraphenyl-1,4-pentadienes

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Abstract: Radical cation acidities of nine cyclopentadienes and six 3-aryl-1,1,5,5-tetraphenyl-1,4-pentadienes have been estimated with the equation $pK_{HA^{\bullet+}} = pK_{HA} + [E_{ox}(A^-) - E_{ox}(HA)]23.06/1.37$. Introduction of Ph substituents into the 2- and 5-positions of cyclopentadiene (CpH$_2$) caused the acidity of its radical cation ($pK_{HA^{\bullet+}}$) to decrease from −17 to −8. This decrease is the net result of stabilization (by delocalization) of the positive charge and odd electron in the radical cation (acid weakening) and stabilization of its conjugate base, the radical (acid strengthening). The other effects of structural changes on radical cation acidities observed can be rationalized in a similar manner. Most notable are the 11 and 8.5 $pK_{HA^{\bullet+}}$ unit decreases in the acidities observed for the radical cations derived from 1,2,3,4,5-pentamethyl- and 1,2,3,4,5-pentaphenylcyclopentadienes, respectively, relative to CpH$_2$$^{\bullet+}$. An open-chain analogue of Ph$_5$CpH, 1,1,3,5,5-pentaphenyl-1,4-pentadiene, is 10.9 pK units less acidic because of lesser carbanion stabilization, but its radical cation is 11.5 pK units more acidic because of lesser cation stabilization. A 13 pK unit acid-weakening effect of the 4-Me$_2$N group in 4-Me$_2$NC$_6$H$_4$CH(CH═CPh$_2$)$_2$$^{\bullet+}$ is associated with loss of an electron from the lone pair on nitrogen in 4-Me$_2$NC$_6$H$_4$CH(CH═CPh)$_2$, whereas the parent radical cation, C$_6$H$_5$CH(CH═CPh$_2$)$_2$$^{\bullet+}$, is formed by loss of an electron from an alkene π bond in C$_6$H$_5$CH(CH═CPh$_2$)$_2$. A plot of $E_{ox}(A^-)$ vs pK_{HA} was found to be linear with a slope near unity for 3-aryl-1,1,5,5-tetraphenyl-1,4-pentadienes. Homolytic bond dissociation energies for the acidic C–H bonds in these 15 hydrocarbons are estimated from the pK_{HA} and $E_{ox}(A^-)$ data. Several striking examples of substituents having opposite effects on homolytic and heterolytic BDEs were observed.

The method developed recently to estimate acidities for the radical cations derived from phenothiazines and fluorenes[1] has now been extended to cyclopentadiene, pentamethylcyclopentadiene, cyclopentadienes bearing two, four, or five phenyl rings, and several 3-aryl-1,1,5,5-tetraphenyl-1,4-pentadienes.

Results

Cyclopentadienes. The oxidation potentials of several cyclopentadienide anions, $E_{ox}(A^-)$, the acidities of their conjugate acids, pK_{HA}, and the oxidation potentials of these acids, $E_{ox}(HA)$, are summarized in Table I.

The $pK_{HA^{\bullet+}}$ values in Table I were calculated from eq 1 by using the data in Me$_2$SO whenever possible. It was necessary to use MeCN as the solvent to measure $E_{ox}(HA)$ for cyclopentadiene

$$pK_{HA^{\bullet+}} = pK_{HA} + [E_{ox}(A^-) - E_{ox}(HA)]23.06/1.37 \quad (1)$$

(CpH$_2$) because it oxidizes near the potential for the Me$_2$SO solvent. This increases the uncertainty of the $pK_{HA^{\bullet+}}$ for CpH$_2$$^{\bullet+}$ somewhat, since E_p values in MeCN for $E_{ox}(HA)$ are 70–90 mV more positive for 2,5-diphenylcyclopentadiene and its derivatives in MeCN than in Me$_2$SO (Table I), and this may be true for cyclopentadiene itself. CV measurements with CpH$_2$ required

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