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ACIDITIES OF BENZYL PHENYL SULFONES AND OF THE CORRESPONDING RADICAL CATIONS. HOMOLYTIC BOND DISSOCIATION ENERGIES (BDEs) OF α—C—H BONDS IN BENZYL PHENYL SULFONES

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ABSTRACT

The excellent linearity ($R^2 = 0{\cdot}997$) of a plot of pK_a values for 17 *m*- and *p*-substituted benzyl phenyl sulfones, $GC_6H_4CH_2SO_2Ph$, vs. those for the corresponding arylacetonitrile, $GC_6H_4CH_2CN$, demonstrates that substituent solvation and substituent solvation assisted resonance (SSAR) effects for *p*-CN, *p*-COPh, and *p*-SPh are nearly identical in these two substrates. The $PhSO_2$ group in $PhCH_2SO_2Ph$ increases the BDE of the α—C—H bond by 2 kcal/mol, relative to toluene. The α—C—H bonds in $GC_6H_4CH_2SO_2Ph$ sulfones are stabilized by 1–2 kcal/mol by acceptor G's (*m*-CN, *p*-CN, *m*-CF_3, *p*-CF_3), but weakened by 1 and 5 kcal/mol, respectively, by donors (*p*-OMe and *p*-NMe_2). The $GC_6H_4CH_2SO_2Ph^{+\cdot}$ radical cation with G = H has a $pK_{HA^{+\cdot}} = -25$. Its acidity is increased when G is an acceptor by as much as 9 to 10 kcal/mol (G = 3-CN, 3-CF_3, 4-CF_3, 4-NO_2), but is decreased when G is a donor by as much as 33 kcal/mol (G = NMe_2). When G = 4-SPh the radical cation is stabilized, relative to G = H, by a larger amount (25 kcal/mol) than when G = 4-OMe (18 kcal/mol). Structural changes along the series $PhCH_2SO_2Ph$, 2-naphthyl-CH_2SO_2Ph, 9-anthrylCH_2SO_2Ph cause negligible changes in the acidities of these acids, but sizable decreases in the acidities of the corresponding radical cations. Introduction of a phenylsulfonyl group into the methyl group of 9-methylanthracene or the 9-position of fluorene or xanthene increases the BDEs by 3, 2, and 7 kcal/mol, respectively. These effects of $PhSO_2$ groups are compared and contrasted with those of CN groups.

INTRODUCTION

Relative electronic effects of sulfonyl and cyano groups on anions and radicals

Remote methylsulfonyl and cyano substituents differ but little in their abilities to stabilize oxanions as judged by the size of their Hammett and Taft sigma constants. For example, for CH_3SO_2: $\sigma_m = 0{\cdot}60$, $\sigma_p = 0{\cdot}72$, $\sigma_p^- = 1{\cdot}05$; for CN: $\sigma_m = 0{\cdot}56$, $\sigma_p = 0{\cdot}66$, $\sigma_p^- = 0{\cdot}99$. The effects of methylsulfonyl and cyano groups on adjacent carbanions are also closely similar, as judged by Taft sigma constants ($\sigma_F = 0{\cdot}59$ for CH_3SO_2 and $0{\cdot}60$ for CN)[1] and by the acidities of $CH_3SO_2CH_3$ (pK_a = 31·3 in Me_2SO) and CH_3CN (pK_a = 31·1 in Me_2SO).[2] The two functions differ markedly in their steric bulk and their effect on adjacent radicals, however. Sulfone functions are tetrahedral and their standard free energy (*A*-value) judged by

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conformational analysis, is about 2·5 kcal/mol compared to about 0·2 kcal/mol for the linear cyano function.[3] The appreciable ability of CN to stabilize an adjacent carbon centered radical and the poor ability of RSO_2 functions to do so was revealed long ago in copolymerization studies.[4] Recent rate studies of the thermolysis of $Me_2C(G)N{=}NC(G)Me_2$ azo compounds also point to a large disparity in the ability of these two functions to stabilize radicals. Thus the rate for G = CN is $2{\cdot}9 \times 10^5$ times greater than for G = Me = (1·0), as compared to only 9·2 for G = CH_3SO_2.[5] The apparent stabilizing effect of a *p*-CN group on a benzyl radical is also far greater than that of a *p*-$MeSO_2$ group, as judged by e.s.r. hyperfine coupling constants ($\sigma^{\cdot}_{\alpha}$ = 0·040 for *p*-CN vs. 0·005 for *p*-$MeSO_2$).[6] E.s.r. studies of cyanomethyl radicals indicate substantial spin delocalization ability,[7] whereas α-sulfonyl groups have 'no capacity for spin delocalization.'[8]

By combining data for equilibrium acidities in Me_2SO solution (pK_{HA}) with (a) the oxidation potentials of their conjugate bases, $E_{ox}(A^-)$, and (b) a summation of four constants dictated by a thermodynamic cycle we have devised a method for estimating homolytic bond dissociation energies (BDEs) for weak acids (HA) in Me_2SO solution (equation (1)).[9] In the preceding paper[10] an estimate using equation (1) has shown

$$\mathrm{BDE} = 1{\cdot}37\mathrm{p}K_{\mathrm{HA}} + 23{\cdot}06E_{\mathrm{ox}}(\mathrm{A}^-) + 55{\cdot}86 \qquad (1)$$

that the CN group weakens the adjacent C—H bond in $PhCH_2CN$ by 6 kcal/mol, relative to toluene. Similar bond weakening effects, relative to the parent hydrocarbon, were estimated for 9-cyanomethylanthracene (2·6 kcal/mol), 9-cyanofluorene (6 kcal/mol), and 9-cyanoxanthene (6·5 kcal/mol). On the other hand, the 9-$PhSO_2$ group in 9-phenylsulfonylfluorene appears to strengthen the 9—C—H bond by about 2 kcal/mol.[11] In contrast to its effect on an adjacent C—H bond, the remote CN group in 4-$CNC_6H_4CH_2CN$ appears to strengthen the benzylic C—H bond by about 1 kcal/mol.[10]

In the present paper we report acidity and electrochemical data for benzyl phenyl sulfones, and related compounds, that will allow us to deduce the effects of both remote and proximate structural changes on their acidities and those of the corresponding radical cations. The data will also allow us to estimate the BDEs of the α—C—H bonds in these compounds.

RESULTS AND DISCUSSION

Effects of substituents on acidities in $GC_6H_4CH_2SO_2Ph$ and $GC_6H_4CH_2SO_2CF_3$

Benzyl phenyl sulfones are attractive for study of substituent effects because they are easily prepared by reactions of readily available benzyl chlorides with sodium benzenesulfinate. The equilibrium acidities of 26 3- and 4-$GC_6H_4CH_2SO_2Ph$ compounds, which were prepared in this way, are presented in Table 1. A Hammett plot constructed primarily from *meta* points is shown in Figure 1. The deviations for the *m*-NMe_2, *m*-OMe, and *m*-SPh points, which were not included in the correlation, are probably due to differences in solvent effects on σ's in Me_2SO and in H_2O. (The σ_m for OMe recommended for use in Me_2SO[12] would bring this point close to the line.)

A plot of the pK_{HA} values for $ArCH_2SO_2Ph$ vs. those for $ArCH_2CN$ for 17 substituents shows excellent linearity over a range of 9 pK_{HA} units (Figure 2). Note that the points for *p*-NO_2, *p*-SO_2Ph, *p*-CN, *p*-COPh, and *p*-SPh groups fit the line very nicely. These points would therefore deviate from the line in Figure 1 to the same extent as they deviate from the Hammett plot for $ArCH_2CN$ pK_{HA} values shown in the preceding paper.[10] The cause of these

Table 1. Equilibrium acidities of benzyl phenyl sulfones, $GC_6H_4CH_2SO_2Ph$ in Me_2SO solution at 25 °C

G	pK^{a}_{HA}	G	pK^{a}_{HA}
4-NMe_2	25·9	3-COPh[c]	22·1
4-OMe	25·0	3-Cl[b]	21·5$_5$
4-Me	24·1	3-Br[b]	21·5
4-*t*-Bu	24·0$_5$	3-CF_3[b]	21·3
3-NMe_2	24·2$_5$ ± 0·15	3-CN	20·6
3-Me	23·6$_5$	4-CF_3	20·2
H	23·4	4-S(O)Ph	20·1$_5$
4-F	23·6	4-COPh	18·8
3-OMe	23·1$_5$[b]	4-CN	18·5
4-Cl	22·3[b]	4-SO_2Ph	18·3
3-SPh	22·2	4-NO[c]$_2$	15·8$_5$
3-F	21·7	3-$N^+Me_3OTs^-$	20·1$_5$
4-SPh	21·7 ± 0·15	4-$N^+Me_3Br^-$	20·3
		4-$N^+Me_3OTs^-$	20·2

[a] Average of 3-point titrations with two or more indicators; standard deviations ±0·1 or less, unless otherwise noted.

[b] G. J. McCollum, Ph.D. Dissertation, Northwestern University, 1977.

[c] The CH_3SOCH_2K solution was quenched with known quantity of standard acid with a pK_{HA} value 4 or more units higher. This solution was then titrated with a solution of the unknown using the absorbance of the latter anion as an indicator.

deviations, which require the use of exalted Hammett constants (σ^-) in order to place them on the line in the Hammett correlation, has been recently shown to be due in part to substituent solvation assisted resonance (SSAR) effects.[10,13] The slope of 0·8 for the line in Figure 2 shows that $ArCHCN^-$ ions are somewhat more sensitive to substituent effects, particularly SSAR effects, than are $ArCHSO_2Ph^-$ ions. Plots of pK_{HA} values for phenols vs. anilines[13d] and for $ArNH_2$ vs. $ArCH_2CN$[10] are also linear with slopes near unity. We conclude that SSAR effects in Me_2SO for strong resonance acceptors do not differ greatly for ArO^-, $ArCHSO_2Ph^-$, $ArNH^-$, or $ArCHCN^-$ ions despite the differences in the nature of the atom present at the acidic site (O, N, or C). The SSAR effects in Me_2SO are considerably larger than those in water, however, as may be judged by a comparison of the apparent σ^- values for *p*-NO_2 in Me_2SO for the four anion types (1·40, 1·56, 1·72, and 1·72, respectively), with σ^- values for *p*-NO_2 in H_2O (1·24–1·27). The negative charge density at the anionic site in the $ArCHSO_2Ph^-$ ion may be greater than in the other ArX^- ions because of steric hindrance to solvation, but by the same token resonance relay of charge to the substituent may be less because of steric hindrance to resonance.

The Hammett ρ values for acidities of $ArCH_2CN$, $ArCH_2SO_2Ph$, $ArCH_2SO_2CF_3$ decrease from 5·5 to 4·8 to 3·7. This decrease is in line with the decreasing negative charge density on carbon in the corresponding carbanions caused by the progressive increase in electron attraction of the CN, SO_2Ph, and SO_2CF_3 groups. (The pK_a data and a Hammett plot for $ArCH_2SO_2CF_3$ acidities are shown in Figure 3.)

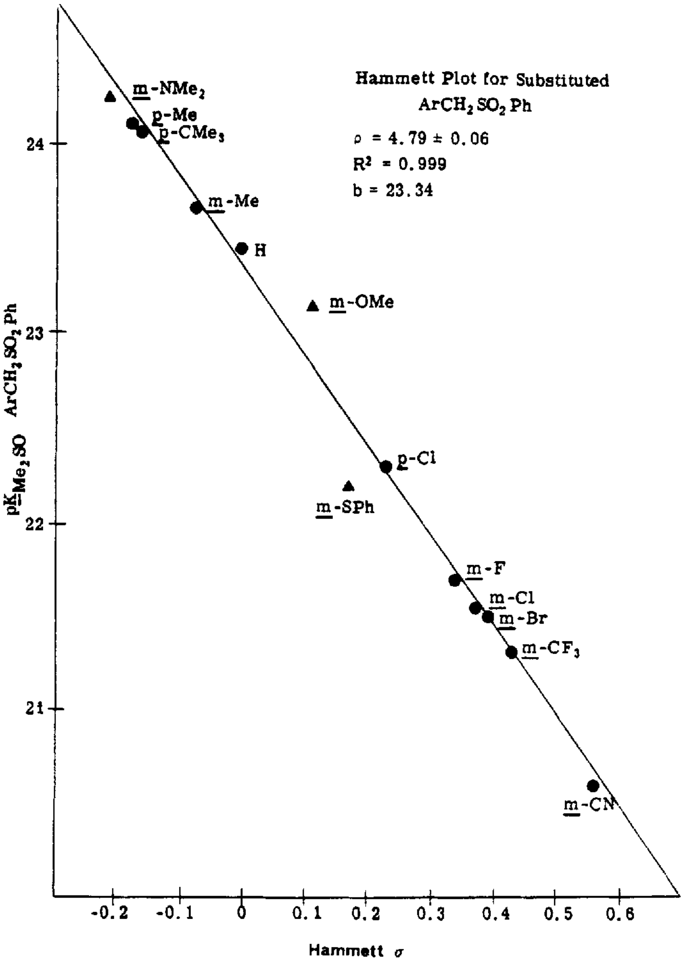


Figure 1. Hammett plot for the equilibrium acidities of benzyl phenyl sulfones in dimethyl sulfoxide solution

Homolytic bond dissociation energies (BDEs) of benzyl phenyl sulfones compared to phenylacetonitriles

The BDEs of benzyl phenyl sulfones and 20 *m*- and *p*-substituted derivatives, and the acidities of the corresponding radical cations are presented in Table 2, together with the oxidation potentials used to estimate these values. The BDEs were estimated using equation (1) and the $pK_{HA^{+\cdot}}$ values were obtained using equation (2).[14]

$$pK_{HA^{+\cdot}} = pK_{HA} + [E_{ox}(A^-) - E_{ox}(HA)]23{\cdot}06/1{\cdot}37 \qquad (2)$$

The BDEs estimated by using equation (1) are believed to be accurate to ±3 kcal/mol, but relative BDEs are probably accurate to ±1 kcal/mol.[9] The 2 kcal/mol higher BDE for the α—C—H bond in $PhCH_2SO_2Ph$ than that in toluene[15] supports the earlier conclusion that an α-SO_2Ph group is bond-strengthening,[11] and radical destabilizing, contrary to the thermolysis results.[5] When G in $GC_6H_4CH_2SO_2Ph$ is *m*-CN, *p*-CN, *m*-CF_3, or 4-CF_3, the BDEs of the

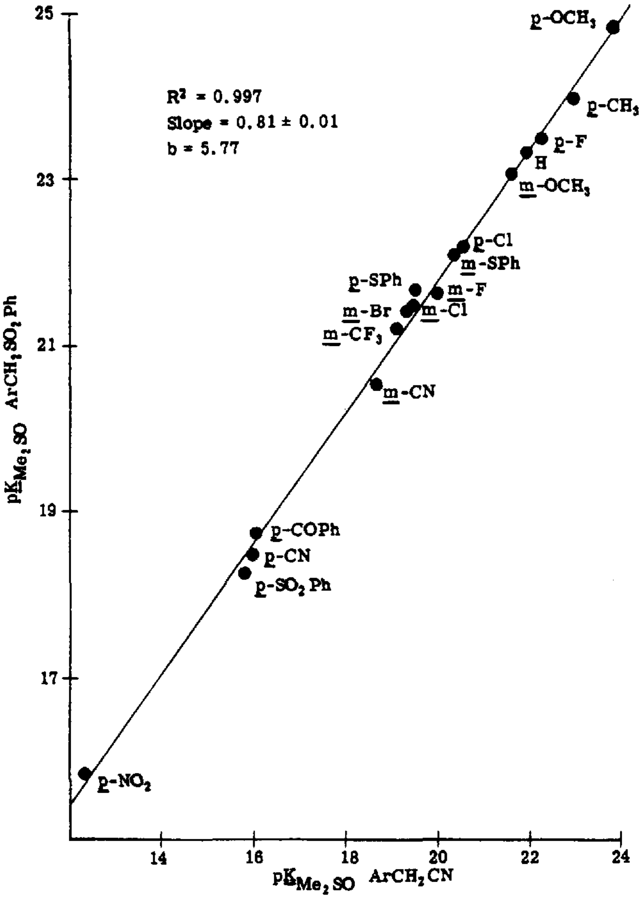
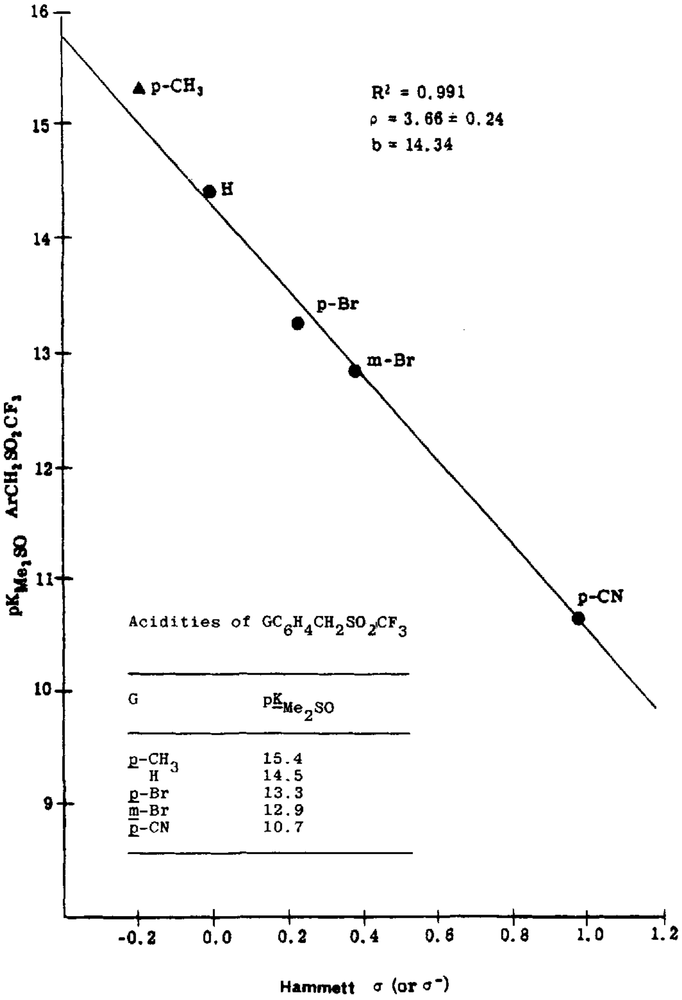


Figure 2. Plot of the equilibrium acidities of benzyl phenyl sulfones vs. those of benzyl cyanides in dimethyl sulfoxide solution

benzylic C—H bonds increase by 1–2 kcal/mol; these effects are similar to, but slightly larger than, those observed in $GC_6H_4CH_2CN$.[10] Weak electron acceptors or donors (*p*-F, *m*-F, *p*-Cl, *p*-Me, *m*-Me, *p*-*t*-Bu, *m*-OMe, *p*-SPh, *m*-SPh) have little or no effect on BDE. (It was surprising to find that *p*-NO_2 also falls in this group. This needs to be checked.) The strong donors, *p*-OMe and *p*-NMe_2, decrease the BDE by 1 and 5 kcal/mol, respectively. These results are comparable to those observed with *p*-$MeOC_6H_4CH_2CN$ and *p*-$Me_2NC_6H_4CH_2CN$.[10]

Acidities of $GC_6H_4CH_2SO_2Ph^{+\cdot}$ compared to $GC_6H_4CH_2CN^{+\cdot}$

According to our estimate, the parent radical cation $PhCH_2SO_2Ph^{+\cdot}$ (G = H), is a super acid ($pK_{HA^{+\cdot}} \simeq -25$), but is nevertheless a weaker acid by 7 units than is the $PhCH_2CN^{+\cdot}$ radical cation ($pK_{HA^{+\cdot}} = -32$).[10] In earlier papers we have shown that the oxidation potential of the acid, $E_{ox}(HA)$, is usually the dominant term in equation (2) that controls the acidity of the radical cation.[14] However, the $E_{ox}(HA)$ value for $PhCH_2CN$ in acetonitrile is only



Acidities of $GC_6H_4CH_2SO_2CF_3$

G	pK_{Me_2SO}
p-CH$_3$	15.4
H	14.5
p-Br	13.3
m-Br	12.9
p-CN	10.7

Figure 3. Hammett plot for the equilibrium acidities of benzyl trifluoromethyl sulfones

1·7 kcal/mol less positive than that of $PhCH_2SO_2Ph$, which is sufficient to account for only a 1·2 pK_{HA^+} unit greater acidity. The major factor leading to the 7 unit higher acidity of $PhCH_2CN^{+\cdot}$ than $PhCH_2SO_2Ph^{+\cdot}$ must lie, therefore, in the much greater stabilizing effect of CN on the radical formed on deprotonation (equation (3)).

$$PhCH_2CN^{+\cdot} + Me_2SO \rightleftarrows PhCHCN^{\cdot} + Me_2SOH^+ \tag{3}$$

The difference in BDEs for the benzylic C—H bonds in $PhCH_2SO_2Ph$ and $PhCH_2CN$ is 8 kcal/mol. If we equate the ΔBDE to the difference in radical stabilization, this effect, together with the 1·7 kcal/mol less positive $E_{ox}(HA)$, will account for the 7 pK_{HA^+} units greater acidity of $PhCH_2CN^{+\cdot}$. The pertinent data are summarized in Scheme 1.

Table 2. Acidity and oxidation potential data for benzyl phenyl sulfones, $GC_6H_4CH_2SO_2Ph$

G	pK_a[a]	$E_{ox}(A^-)$[b]	$E_{ox}(HA)$[c]	BDE[d]	$pK_{HA^{+\cdot}}$[e]
4-NO_2	15·8	+0·531 (50)	3·39 (100)	90	−32
4-CN	18·5	+0·451 (70)	3·35 (120)	92	−30
3-CN	20·7	+0·373 (100)	3·55 (160)	93	−33
4-CF_3	20·2	+0·332 (70)	3·45 (160)	91	−32
3-CF_3	21·3	+0·303 (80)	3·45 (160)	92	−32
4-F	23·6	+0·091 (70)	2·96 (140)	90	−25
3-F	21·7	+0·221 (70)	3·04 (140)	91	−26
4-Cl	22·3	+0·168 (70)	2·92 (140)	90	−24
3-Cl	21·55	+0·215 (70)	3·02 (140)	90	−26
H	23·4	+0·098 (50)	2·95 (100)	90	−25
4-Me	24·1	+0·074 (50)	2·60 (100)	91	−18
3-Me	23·6	+0·070 (60)	2·73 (100)	90	−21
4-*t*-Bu	24·0	+0·037 (50)	2·73 (100)	90	−21
4-MeO	25·1	−0·057 (50)	2·15 (100)	89	−12
3-MeO	$23{\cdot}1_5$	+0·097 (50)	2·23 (100)	90	−12·7
4-PhS	21·7	+0·174 (70)	1·87 (70)	90	−6·8
3-PhS	22·2	+0·210 (70)	1·93 (70)	91	−6·8
3-NMe_2	24·2	+0·042 (70)	1·21 (70)	90	+4·5
4-NMe_2	25·9	−0·266 (50)	1·25 (60)	85	+0·40

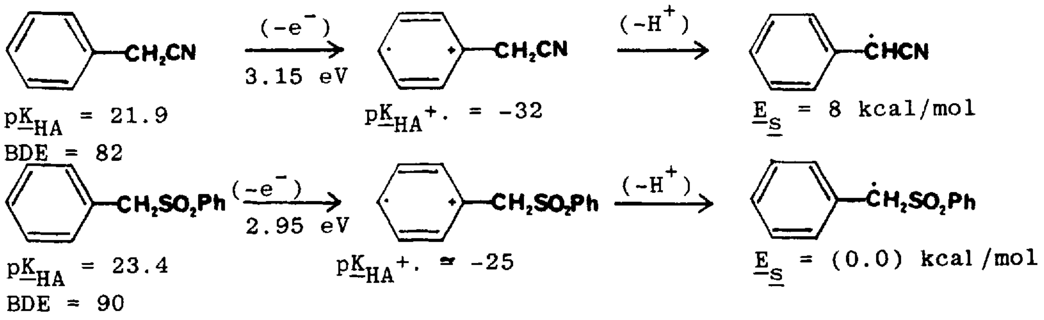
[a] Average of 3-point titrations with two or more indicators; standard deviations ±0·1 or less, unless otherwise noted.

[b] Measured by cyclic voltammetry in Me_2SO vs Ag/Ag/I; referenced to Standard Hydrogen Electrode $(SHE)_{aq}$ by adding −0·125 V.

[c] In MeCN vs $(SHE)_{aq}$ (wave widths in parentheses).

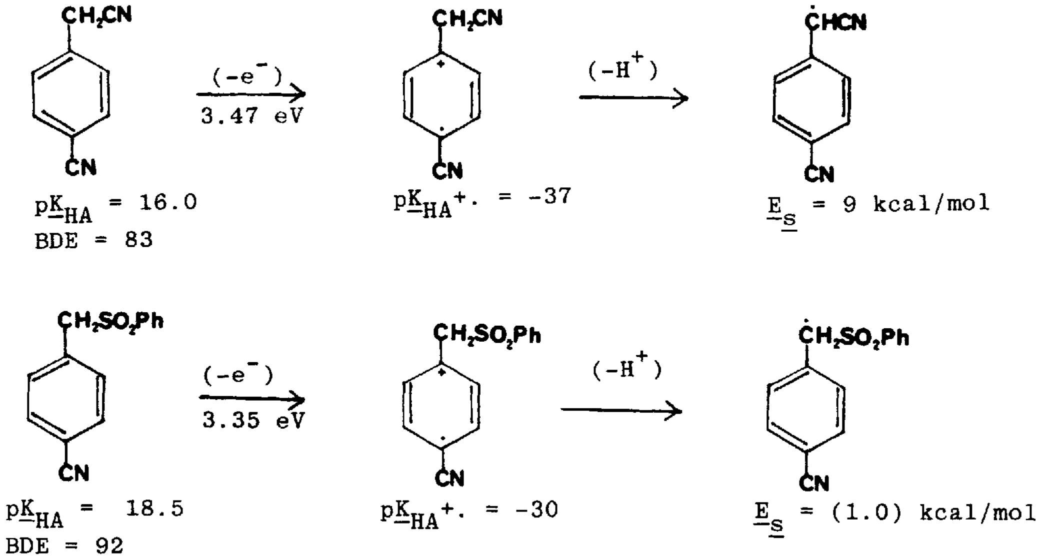
[d] Calculated using equation (1).

[e] Calculated using equation (2).

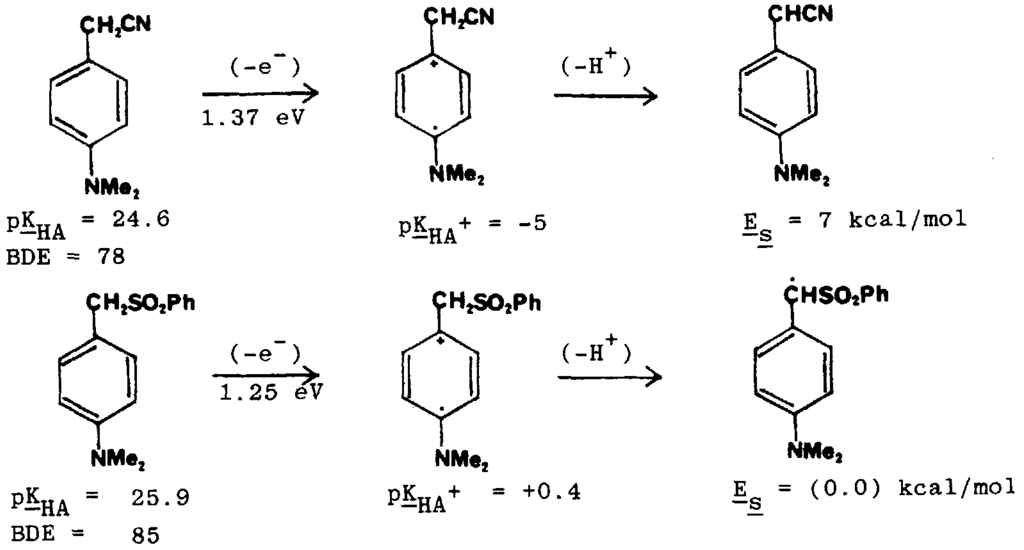


Scheme 1. (E_s = relative radical stabilities)

The effects of remote substituents on p$K_{\mathrm{HA}^{+\cdot}}$ can be rationalized in a similar manner. The strong acceptor substituents (*p*-NO_2, *p*-CN, *m*-CN, *p*-CF_3, and *m*-CF_3) all increase the acidity of the $PhCH_2SO_2Ph^{+\cdot}$ radical cation (by 6–8 p$K_{\mathrm{HA}^{+\cdot}}$ units), but the halogens (*p*-F, *m*-F, *p*-Cl, *m*-Cl) have little or no effect. Donors have acid-weakening effects (in the order, *m*-Me, *p*-*t*-Bu < *p*-Me < *m*-OMe < *p*-OMe < *m*-SPh, *p*-SPh < *m*-NMe_2 < *p*-NMe_2) ranging from 3 to 20 units. The large acid-weakening effects for strong donors attests to their ability to stabilize the positive charge in radical cations by delocalization. Note also, however, that $E_{\mathrm{ox}}(\mathrm{A}^-)$ is more negative for *p*-OMe, *p*-SPh, and *p*-NMe_2 than for the corresponding *meta* isomers, pointing to a greater stabilizing effect of the *para* donor groups on the radical. For *p*-$Me_2NC_6H_4CH_2SO_2Ph$, radical stabilization leads to a 5 kcal/mol lower BDE and a 4 p$K_{\mathrm{HA}^{+\cdot}}$ unit smaller acid-weakening effect than for the *meta* isomer. Some of these comparisons are illustrated in Schemes 2 and 3.



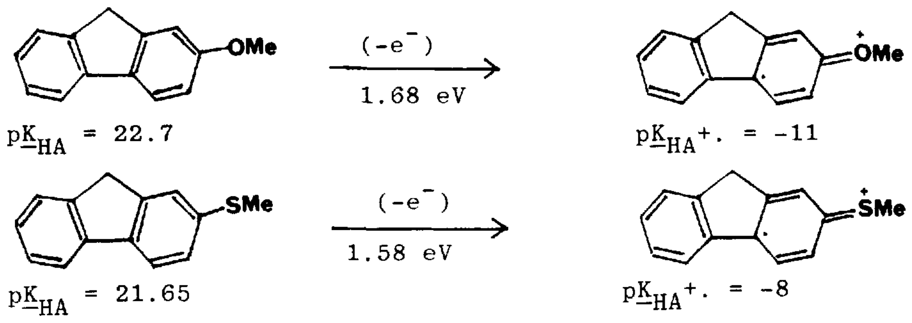
Scheme 2. (E_s = relative radical stabilities)



Scheme 3. (E_s = relative radical stabilities)

Effects of *p*-SPh, *p*-OMe, and *p*-CN on acidities of $GC_6H_4CH_2SO_2Ph^{+\cdot}$

The 5·2 $pK_{HA^{+\cdot}}$ unit larger acid-weakening effect of a *p*-SPh (or *m*-SPh) group than for *p*-OMe is noteworthy since the relative abilities of RS and RO to stabilize an adjacent carbocation have been the subject of some controversy. Gas-phase measurements[16] and *ab initio* calculations[17] indicate that sulfur is the more effective donor, but rates of reactions to form carbocations in hydroxylic solvents generally indicate that oxygen is the better donor,[18] presumably because solvation is more effective in lowering the transition state energy. The 0·285 eV lower oxidation potentials for *p*-$PhSC_6H_4CH_2SO_2Ph$ than for *p*-$MeOC_6H_4CH_2SO_2Ph$ suggests that the *p*-SPh group stabilizes the radical cation by about 6·6 kcal/mol, relative to the effect of the *p*-MeO group. This is consistent with the results obtained with *p*-$PhSC_6H_4CH_2CN$ and *p*-$MeOC_6H_4CH_2CN$, where the difference in E_{ox}(HA) values points to a 7·1 kcal/mol greater stabilization by *p*-SPh.[10] They differ from the results obtained with 2-PhS-FlH and 2-MeO-FlH, however, where the relative oxidation potentials point to a 1·4 kcal/mol greater stabilization by 2-MeO than by 2-PhS.[19] But when the E_{ox}(HA) values for 2-MeO-FlH and 2-MeS-FlH are compared MeS is more stabilizing by about 3·5 kcal/mol.[20] We conclude, therefore, that sulfur is the stronger donor toward radical cations in these quasi-thermodynamic measurements in which solvent effects should not play a major role (Scheme 4).



Scheme 4. (E_s = relative radical stabilities)

Table 3. Effects of aryl and alpha structural changes on acidities, radical cation acidities, and bond dissociation energies

Sulfone	$\mathrm{p}K_{\mathrm{HA}}$[e]	$E_{\mathrm{ox}}(\mathrm{HA})$[f]	$E_{\mathrm{ox}}(\mathrm{A}^-)$[h]	BDE[j]	$\mathrm{p}K_{\mathrm{HA}^{+\cdot}}$[k]
$PhCH_2SO_2Ph$	23·4	2·95 (100)	+0·098 (50)	90	−25
$2\text{-}NpCH_2SO_2Ph$[a]	22·3	2·11 (50)	+0·106[i] (50)	89	−11
$9\text{-}AnCH_2SO_2Ph$	21·6	1·64 (70)	−0·036 (50)	85	−6·6
$9\text{-}AnCH_3$[b]	31·1	1·56 (90)	−0·780 (70)	81	−8·5
$9\text{-}Xn(H)SO_2Tol$	$21{\cdot}0_5$	2·16 (120)	−0·097 (50)	82	−17
XnH_2[c]	30·0	1·88[g] (60)	−0·935 (60)	75	−18
$9\text{-}Fl(H)SO_2Ph$	$11{\cdot}5_5$	2·36 (140)	+0·441[g] (60)	82	−21
$9\text{-}Fl(H)SO_2Me$	12·8	2·28 (90)	0·342[f] (70)	81	−20
$9\text{-}Fl(H)SO_2Et$	12·3	2·20 (100)	+0·346 (50)	81	−19
FlH_2[d]	22·6	2·02 (100)	−0·319 (50)	79·5	−17

[a] 2-Np = 2-Naphthyl.
[b] 9-Methylanthracene.
[c] Xanthene.
[d] Fluorene.
[e] Values previously reported from our laboratory.
[f] In MeCN vs. the aqueous Standard Hydrogen Electrode $(SHE)_{aq}$ unless otherwise noted.
[g] J.-P. Cheng, Ph.D. Dissertation, Northwestern University, 1987.
[h] In Me_2SO vs. $(SHE)_{aq}$.
[i] 0·083 in MeCN.
[j] Calculated using equation (1).
[k] Calculated using equation (2); estimated to be accurate to ±3 units.

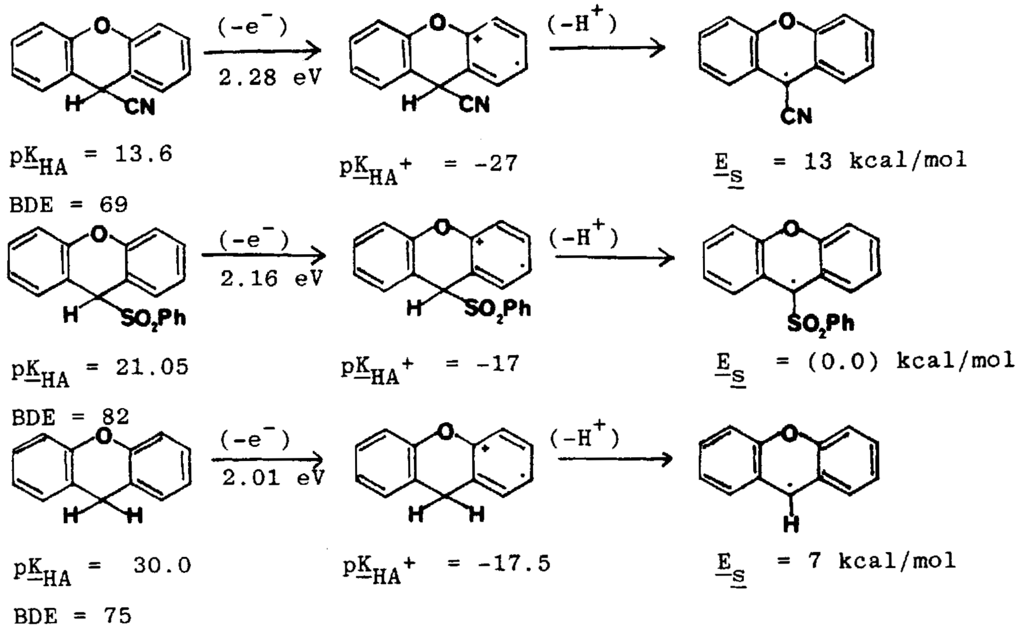
The effect of the *p*-cyano function is also worthy of special note since CN has been shown to provide resonance stabilization to adjacent carbocations.[21] Examination of Table 2 reveals a slightly lower $E_{\mathrm{ox}}(\mathrm{HA})$ value for *p*-CN than *p*-NO_2 or *p*-CF_3, but it is clear that the dominant effect of *p*-CN on the radical cation is one of destabilization. A comparison of $E_{\mathrm{ox}}(\mathrm{HA})$ values for phenylacetonitriles bearing *p*-CN, *p*-COPh and *p*-CF_3 groups leads to a similar conclusion.[10] The phenyl ring in the SO_2Ph moiety is a possible source of an electron when benzyl phenyl sulfones are oxidized electrochemically. It is an unlikely source inasmuch as the benzylsulfonyl group is strongly electron withdrawing and radical destabilizing. Indeed, a measurement of E_{ox}(HA) for CH_3SO_2Ph gave a potential of 3·72 V, which is more positive than any of the values in Tables 2 or 3.

Effects of aryl structural changes in $ArCH_2SO_2Ph$ on pK_a, BDE, and $pK_{HA^{+\cdot}}$

As shown in Table 3, structural changes in the aryl group along the series $PhCH_2SO_2Ph$, 2-$NpCH_2SO_2Ph$, 9-$AnCH_2SO_2Ph$, 9-$PhSO_2XnH$, 9-$PhSO_2FlH$ cause progressive decreases in pK_as (23·4, 22·3, 21·6, 21·0$_5$, 11·5$_5$) and in BDEs (90·2, 88·9, 84·6, 82·4, 81·9). The small decreases in pK_a caused by 2-naphthyl and 9-anthryl groups, relative to phenyl, can be associated with the extent to which delocalization of the negative charge in the anion increases with increased aryl size. The 9-Xn(H)SO_2Tol^- ion is stabilized by the field effect of oxygen and the 9-Fl(H)SO_2Ph^- ion is strongly stabilized by an aromaticity factor. The small decrease in BDEs for the α—C—H bonds 2-$NpCH_2SO_2Ph$ and 9-$AnCH_2SO_2Ph$, relative to $PhCH_2SO_2Ph$, which parallel the pK_a decreases, can be associated with the abilities of the larger aryl groups to delocalize the incipient radical. The slightly larger effect for 9-Xn(H)SO_2Tol can be associated with the ability of oxygen to delocalize the incipient radical. For Fl(H)SO_2Ph, the much larger effect on pK_a than on BDE is consistent with the aromaticity of the HFl^- ion and the lack thereof in the $HFl^{\cdot}$ radical. These effects are similar to those observed for $ArCH_2CN$.[10]

The effects of these structural changes on radical cation acidities are much larger than those on pK_as and BDEs. The estimated acidities of $PhCH_2SO_2Ph^{+\cdot}$, 2-$NpCH_2SO_2Ph^{+\cdot}$, and 9-$AnCH_2SO_2Ph^{+\cdot}$ calculated from equation (2) are −25, −11, and −6.6, respectively (Table 3). The progressive decreases in acidity can be associated with the increased possibilities for delocalization of the positive charge and odd electron in the (high energy) radical cation with increased aryl size. The Xn(H)$SO_2Tol^{+\cdot}$ radical cation has an acidity 8 $pK_{HA^{+\cdot}}$ units lower than that of $PhCH_2SO_2Ph^{+\cdot}$ due in part to the greater ability of the xanthyl moiety to stabilize the radical formed on deprotonation ($\Delta BDE \simeq 8$ kcal/mol) and in part to a greater ability of the xanthyl moiety to stabilize the positive charge in the radical cation. The fluorenyl moiety exhibits similar effects on the acidities of the Fl(H)$SO_2R^{+\cdot}$ radical cations. (The spread in $pK_{HA^{+\cdot}}$ values for Fl(H)$SO_2R^{+\cdot}$ radical cations is probably a consequence of the difficulty in obtaining reliable measures of the oxidation potential of the uncharged acids (note the broad CV waves). The average value of -20 ± 3 is within the experimental error of the measurements.)

In the preceding paper a comparison of the effect on $pK_{HA^{+\cdot}}$ of introducing an α-cyano group into the hydrocarbon was shown to cause an increase in acidity for 9-methylanthracene, fluorene, and xanthene of 4·5, 8, and 9 units, respectively.[10] Examination of Table 3 shows the effect of introducing an α-$ArSO_2$ group is a 1·9 unit decrease for 9-$AnCH_3$, no change for xanthene, and a 3 unit increase for FlH_2 (see above). For 9-$AnCH_3$, the acidity decrease can be associated with the 3·2 kcal/mol decrease in radical stability indicated by the increase in BDE. For XnH_2, there is an even larger increase in BDE (7 kcal/mol), but this is offset by a nearly equal positive shift in E_{ox}(HA). For FlH_2, the increase in BDE is smaller (1·8 kcal/mol) and is overshadowed by the increase in E_{ox}(HA). As brought out previously,[10] the introduction of an α-cyano group increases the acidity of the radical cation in two ways, (a) by stabilizing the radical formed on deprotonation, and (b) by destabilizing the radical cation through its field effect (σ_F), which causes a positive shift in E_{ox}(HA) (Scheme 5). The field effect of an α-SO_2Ph group is probably acid-strengthening to about a similar degree (smallest in $AnCH_3$ and largest in XnH_2), but is counteracted by the destabilizing effect it has on the radical formed on deprotonation, which is acid weakening.



Scheme 5. (E_s = relative radical stabilities)

SUMMARY AND CONCLUSIONS

The linearity of a plot of pK_a values for $GC_6H_4CH_2SO_2Ph$ vs. those for $GC_6H_4CH_2CN$ shows that the electronic effects of the $PhSO_2$ and CN groups on the heterolytic dissociation of the α—C—H bond are essentially identical, as are the substituent solvation assisted resonance (SSAR) effects of *para* electron acceptors. On the other hand, the electronic effects of CN and $PhSO_2$ on the homolytic dissociation of an α—C—H bond are opposite in nature, the CN groups in $PhCH_2CN$ being bond weakening and the $PhSO_2$ group in $PhCH_2SO_2Ph$ being bond strengthening. The effects of the remote G substituents are similar for the two substrates; strong electron acceptors cause small BDE increases and donors cause BDE decreases. The $PhCH_2SO_2Ph^{+\cdot}$ radical cation is less acidic than the $PhCH_2CN^{+\cdot}$ radical cation by 10 kcal/mol. The difference is attributed to the ability of the CN group to stabilize the radical formed on deprotonation of the radical cation, whereas the effect of $PhSO_2$ on the radical is destabilizing. Remote G electron acceptor substituents cause large acidity increases by destabilizing the radical cations, whereas donors decrease the acidity by stabilizing the radical cations. In each instance the effect of 4-SPh is larger than that of 4-OMe, indicating a greater donor ability of S than O for an adjacent carbocation.

EXPERIMENTAL SECTION

Materials and syntheses

Melting points and ^{1}H-NMR data for the substituted benzyl phenyl sulfones appear in Table 4. NMR were recorded on a Varian EM-390 spectrometer and reported in parts per million relative to tetramethylsilane as the internal standard. Melting points were recorded on a Thomas–Hoover melting point apparatus and are uncorrected. NMR and mps for 4-Cl, 3-Cl, 4-CN, 3-CN, and 4-NO_2 were consistent with those reported by Jarvis and Saukaitis.[22]

Table 4. Melting points and ^{1}H-NMR of G-$C_6H_4CH_2SO_2Ph$ compounds

Compound	mp, °C[a]	lit mp, °C	^{1}H-NMR
4-NMe_2	148–148·5	---	2·8 (6H, s), 4·28 (2H, s), 6·5–7·75 (9H, m)
4-OMe[c]	139·5–140·5	---	3·8 (3H, s), 4·15 (2H, s), 6·7–7·8 (9H, m)
4-Me	151–151·5	145–146[d]	2·3 (3H, s), 4·2 (2H, s), 6·7–7·8 (9H, m)
4-*t*-Bu	161–162	---	1·3 (9H, s), 4·3 (2H, s), 6·9–7·8 (9H, m)
3-Me_2N	114–115	---	2·9 (6H, s), 4·2 (2H, s), 6·25–7·7 (9H, m)
3-Me	122–124	104–105[e]	2·3 (3H, s), 4·2 (2H, s), 6·7–7·8 (9H, m)
H	147–147·5	146–146·5[f]	4·3 (2H, s), 7·05–7·75 (9H, m)
4-F	155·5–156	---	4·3 (2H, s), 6·7–7·8 (9H, m)
3-OMe[c]	111–112	---	3·7 (3H, s), 4·3 (2H, s), 6·5–7·8 (9H, m)
3-SPh	93–94·5	---	4·3 (2H, s), 6·8–7·6 (14H, m)
3-F	129·5–130·5	---	4·3 (2H, s), 6·6–8·0 (9H, m)
4-SPh	121–121·5	---	4·3 (2H, s), 7·05–7·75 (14H, m)
3-COPh	156–157	---	4·35 (2H, s), 7·25–7·85 (14H, m)
3-Br	121–123	129[g]	4·3 (2H, s), 7·0–7·8 (9H, m)
3-CF_3	108–109	---	4·35 (2H, s), 7·1–7·9 (9H, m)
4-CF_3	237·5–239	---	4·35 (2H, s), 7·25–7·65 (9H, m)
4-S(O)Ph	187–188	---	4·3 (2H, s), 7·1–7·8 (14H, m)
4-(COPh)	166–167	---	4·37 (2H, s), 7·05–7·8 (14H, m)
4-SO_2Ph	213–214	---	4·5 (2H, s), 7·2–8·1 (14H, m)
3-$NMe_3^+OTs^-$	153–153·5	---	2·25 (3H, s), 3·45 (9H, s), 4·7 (2H, s), 7·0–8·0 (14H, m)
4-$NMe_3^+Br^-$	~140 (dec)	---	3·65 (9H, s), 4·8 (2H, s), 7·3–8·3 (m, 9H)
4-$NMe_3^+OTs^-$[c]	179–180	---	2·25 (3H, s), 3·6 (9H, s), 6·9–8·0 (14H, m)

[a] Uncorrected.
[b] In $CDCl_3$ with δ reported relative to $Me_4Si = 0$.
[c] Prepared by G. J. McCollum, these laboratories.
[d] C. M. M. DaSilva-Correa, A. S. Lindsay and W. A. Waters, *J. Chem. Soc. (C)* 1872–1874 (1968).
[e] R. S. Asthana and G. S. Mistra, *J. Ind. Chem. Soc.* **31**, 459–460 (1954).
[f] R. L. Shriner, H. C. Struck and W. J. Jorison, *J. Am. Chem. Soc.* **52,** 2060–2069 (1930).
[g] M. Simalty-Siemiatycki, J. Carretto and F. Malbec, *Bull. Soc. Chim. France* 125–128 (1962).

In general, the sulfones that were not commercially available were prepared by heating the appropriate benzyl halide with sodium benzenesulfinate (2 equiv.) in a saturated solution of ethanol and water, the composition of which was varied to produce homogeneity. After an hour of the steam bath crystallization was induced by cooling, and the product was recrystallized from 95% ethanol or ethanol/$CHCl_3$.

m- and *p*-(Dimethylamino)benzyl phenyl sulfones were prepared by reductive methylation of the amine with aq. HCHO and hydrogen over 10% Pd/C in EtOH at 35 psi for 4 h.

The benzyl trifluoromethyl sulfones were a gift from P. L. Skipper.

4-Methoxybenzyl phenyl sulfone was obtained by reaction of 4-methoxybenzyl alcohol with sodium benzenesulfinate (2 equiv.) in boiling ethanol:water (1:1) at pH = 2 for 24 h.

3-Methoxybenzyl phenyl sulfone was prepared by reacting the sulfide with two equiv. of *m*-chloroperoxybenzoic acid (MCPBA) in $CHCl_3$.

4-(Phenylsulfonyl)benzyl sulfone was prepared by reaction of two equiv. of MCPBA with 4-phenylthiobenzyl phenyl sulfone in chloroform.

The tosylate salts of 3-(trimethylammonio)benzyl phenyl sulfone and 4-(trimethylammonio) benzyl phenyl sulfone were obtained by treating the corresponding dimethylamino compounds with excess methyl tosylate in dry acetonitrile at room temperature. Addition of ether induced crystallization and the products were recrystallized from CH_3CN/ether. The bromide salt of 4-(trimethylammonio)benzyl phenyl sulfone was prepared by refluxing a solution of acetonitrile and the dimethylamino compound under a methyl bromide atmosphere for 4 h. Upon cooling, the product precipitated as fine white needles.

2-(Phenylsulfonylmethyl)naphthalene[23] and 9-(phenylsulfonylmethyl)anthracene[24] were prepared by the general method except that DMF was used as the solvent. 2-(Phenylsulfonylmethyl)naphthalene: mp = 189·5–190 °C, lit[25] mp = 186–7 °C, ^{1}H-NMR: δ 4·8 (2H, s), 7·0–7·9 (12 H, m). 9-(Phenylsulfonylmethyl)anthracene: mp = 205–205·5 °C, ^{1}H-NMR: δ 5·4 (2H, s), 7·3–8·5 (14H, m).

9-(*p*-Methylphenylsulfonyl)xanthene[26] was prepared by the method of Balfe, Kenyon, and Thain.[27] 9-Methylsulfonyl- and 9-ethylsulfonylfluorene were prepared in a manner analogous to that described for 9-phenylsulfonylfluorene.[2]

pK_a Measurements in Me_2SO were carried out as described earlier.[2]

Cyclic voltammetry was carried out in the manner previously described.[14]

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REFERENCES

1. (a) J. Hine, *Structural Effects on Equilibria in Organic Chemistry*, Wiley, New York (1975). (b) The σ_F values (formerly σ_I) are from R. W. Taft and R. D. Topsum, *Prog. Phys. Org. Chem.* **16**, 1–83 (see p. 16) (1987).
2. W. S. Matthews, *et al. J. Am. Chem. Soc.*, **97**, 7006–7014 (1975).
3. E. L. Eliel and D. Kanasamy, *J. Org. Chem.*, **41**, 3899–3904 (1976).
4. C. Walling, *Free Radicals in Solution*, Wiley, New York, (1957) pp. 120–121. C. C. Price and J. Zomlefer, *J. Am. Chem. Soc.* **72**, 14–17 (1950).
5. A. E. Luedtke and J. W. Timberlake, *J. Org. Chem.* **50**, 268–270 (1985).
6. D. D. M. Wagner and D. R. Arnold, *Can. J. Chem.* **62**, 1164–1168 (1984).
7. R. A. Kaba and K. U. Ingold, *J. Am. Chem. Soc.* **98**, 523–526 (1976).
8. P. M. Carton *et al. J. Chem. Soc. Perk. Trans. 2*, 1245–1249 (1975).
9. F. G. Bordwell, J.-P. Cheng and J. A. Harrelson Jr., *J. Am. Chem. Soc.* **110**, 1229–1231 (1988).
10. F. G. Bordwell, J.-P. Cheng, M. J. Bausch and J. E. Bares, *Journal of Physical Organic Chemistry*, **1**, 209–223 (1988).
11. F. G. Bordwell and M. J. Bausch, *J. Am. Chem. Soc.* **108**, 1979–1985 (1986).
12. F. G. Bordwell and F. J. Cornforth, *J. Org. Chem.* **43**, 1763–1768 (1978).
13. (a) M. Fujio, R. T. McIver, Jr. and R. W. Taft, *J. Am. Chem. Soc.* **103**, 4017–4029 (1981). (b) M. Mishima, *et al. J. Am. Chem. Soc.* **106**, 2717–2718 (1984). (c) R. W. Taft and R. D. Topsom, *Prog. Phys. Org. Chem.* **16**, 59–64 (1987). (d) F. G. Bordwell and D. J. Algrim, *J. Am. Chem. Soc.* **110**, in press (1988).

14. F. G. Bordwell and M. J. Bausch, *J. Am. Chem. Soc.* **108**, 2473–2474 (1986). F. G. Bordwell, J.-P. Cheng and M. J. Bausch, *J. Am. Chem. Soc.* **110** (2 papers accepted) (1988).
15. D. I. McMillen and G. M. Golden, *Ann. Rev. Phys. Chem.* **37**, 493–533 (1982).
16. R. W. Taft, R. H. Martin and F. W. Lampe, *J. Am. Chem. Soc.* **87**, 2490–2492 (1965). J. K. Pau, M. B. Ruggera, J. K. Kim and M. C. Caseiro, *J. Am. Chem. Soc.* **100**, 4242–4248 (1978).
17. F. Bernardi, *et al. J. Am. Chem. Soc.* **99**, 7465–7470 (1977). Y. Apeloig and M. Karni, *J. Chem. Soc. Perk. Trans. 2*, in press.
18. H. Böhme, *Chem. Ber.* **74**, 248–256 (1941). F. G. Bordwell, G. D. Cooper and H. Morita, *J. Am. Chem. Soc.*, **79**, 376–378 (1957). G. Modena, G. Scorrano and P. Venturello, *J. Chem. Soc. Perk. Trans. 2*, 1–6 (1979). L. J. Santry and R. A. McClelland, *J. Am. Chem. Soc.* **105**, 3167–3172 (1983).
19. F. G. Bordwell, J.-P. Cheng and M. J. Bausch, *J. Am. Chem. Soc.* **110** in press (1988).
20. J. A. Harrelson, Jr., unpublished results.
21. P. G. Gassman and T. T. Tidwell, *Acc. Chem. Res.* **16**, 279–285 (1983).
22. B. B. Jarvis and J. C. Saukaitis, *J. Am. Chem. Soc.* **95**, 7708–7715 (1973).
23. G. J. McCollum, Ph.D. Dissertation, Northwestern University, 1977.
24. Prepared by A. V. Satish, these laboratories.
25. A. H. Lamberton and J. E. Thorpe, *J. Chem. Soc. (C)* 2571–2574 (1967).
26. D. L. Hughes, Ph.D. Dissertation, Northwestern University, 1981.
27. M. P. Balfe, J. Kenyon and E. M. Thain, *J. Chem. Soc.* 790–6 (1952).