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Polarizability Effects of Alkyl Groups in RCH_2, R, RS, RSO_2, RO, and R_2N Moieties in Families of Weak Acids on the Stabilities of Adjacent Anions and Radicals in DMSO Solution

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Abstract: The homolytic bond dissociation energies (BDEs) of the acidic C–H bonds in the following families wherein R is changed along the series Me, Et, *i*-Pr, and *t*-Bu have been estimated: (a) 9-alkylfluorenes (9-RFlH), (b) 9-RCH_2-FlH, (c) 9-RSFlH, (d) 9-RSO_2FlH, (e) $(RSO_2)_2CH_2$, (f) $RSCH_2CN$, (g) 9-ROFlH, (h) $PhCOCH_2XR$ (X = O or S), (i) $RSCH_2CO_2Et$, (j) 9-R_2NFlH, and (k) 9-piperidinylfluorenes. For the 9-RFlH family there is a progressive decrease in acidities from 9-MeFlH to 9-*t*-BuFlH caused by steric hindrance to solvation, and the BDEs show a progressive increase along the series. On the other hand, for the 9-RCH_2FlH family there is a progressive *increase* in acidities from 9-$MeCH_2$FlH to 9-*t*-$BuCH_2$FlH and the BDEs remain *essentially* constant. The acidity increases for this family and for the families c–k are believed to be caused by progressive increases in anion stabilizing polarizability effects of the R group in RCH_2, RS, RSO_2, RO, and R_2N with increasing alkyl size. The pattern of behavior observed wherein the acidities increase but BDEs remain constant is dictated by the ability of polarizability effects to stabilize anions, but not analogous radicals. Similar behavior, but with much larger polarizability stabilizing effects, has been observed previously for the Ph_3P^+ group in $Ph_3P^+CH^-G$ ylides.

Introduction

Polarizability effects are known to be pervasive in the gas phase but are difficult to identify in solution because they are often masked by solvation effects. For example, the acidities of alcohols in the gas phase increase along the series MeOH, EtOH, *i*-PrOH, and *t*-BuOH because of a progressive increase in polarizability of the alkyl groups with increasing size along the series of corresponding anions, MeO^-, EtO^-, *i*-PrO^-, and *t*-BuO^-, which causes a progressive increase in alkoxide ion stabilities.[1] On the other hand, in DMSO solution there is a progressive *decrease* in alcohol activities along the series MeOH, EtOH, *i*-PrOH, and *t*-BuOH because the corresponding alkoxide ions become progressively more destabilized by steric inhibition of solvation.[2] In other words, in DMSO the stabilizing effects of the alkyl groups on alkoxides in this series are overshadowed by the destabilizing effects of steric inhibition of solvation. Steric inhibition of solvation also dictates a progressive decrease in acidities of 9-alkylfluorenes in DMSO along the series 9-Me-, 9-Et-, 9-*i*-Pr-, and 9-*t*-BuFlH over 2 pK_{HA} units (2.8 kcal/mol). (Henceforth kcal/mol will be abbreviated as kcal.) But when these alkyl groups are separated from the acidic sites in the fluorenide ions by a CH_2, S, or SO_2 moiety, their steric effects on solvation of the anions are decreased and a reversal of the acidity order occurs. Now the acidities of the 9-RX-fluorenes in the series 9-MeX-, 9-EtX-, 9-*i*-PrX-, and 9-*t*-BuXFlH progressively increase, rather than decrease. When X = CH_2 or S the increase from Me to *t*-Bu amounts to 2.1 pK_{HA} units, and for X = SO_2 the increase amounts to 2.2 units. These progressive increases in acidities have been ascribed to increasing polarizabilities of the alkyl groups that stabilize the anions.[3] The effects are dependent on chain length since for X = CH_2 or SO_2 they were found to disappear when one additional methylene group was inserted.[3b] The acidities in the series $MeSCH_2CN$, $EtSCH_2CN$, *i*-$PrSCH_2CN$, *t*-$BuSCH_2CN$, and $PhSCH_2CN$ also were observed to increase over a range of 3.4 pK_{HA} units (4.7 kcal). These effects were also attributed to polarizability of the RS groups.[3]

In earlier studies of the effects on acidities in DMSO, replacing an acidic hydrogen atom in CH_3EWG parent carbon acids by a PhS group was observed to cause acidity increases ranging from 5.6 to 10.7 pK_{HA} units, depending on the nature of EWG (CN > $PhSO_2$ > MeCO > SO_2CF_3 > PhCO > NO_2). The acidifying effects of α-Ph groups on these substrates were similar to those of α-PhS groups, but the effects of α-PhS groups were appreciably larger than those of α-Ph groups on sulfone substrates (8.9 vs 5.8 pK_{HA} units for the CH_3SO_2Ph substrate and 8.0 vs 4.4 pK_{HA} units for the SO_2CF_3 substrate). Also, in more crowded substrates Ph acidifying effects were subject to steric inhibition of resonance whereas PhS effects were not.[4]

Separation of polar and resonance acidifying effects of the PhS groups was attempted by using the Me_3N^+ group as a model for the polar effect. The results were interpreted to mean that strong conjugative interactions existed between the PhS group and the adjacent carbanion (presumably involving overlap of p–d orbitals). Comparison of acidities of 2-phenyl-1,3-dithiane and 4-methyl-2,6,7-trithiabicyclo[2.2.2]octane with those of open-chain analogues failed to reveal any sizable stereoelectronic requirements, however, for these presumed conjugative interactions.[4] Theoretical calculations have, for many years, discounted the importance of conjugation involving d orbitals and have ascribed the acidifying effects of PhS and RS groups to charge transfer or polarizability effects.[5]

In more recent work we have found that the acidifying effects of Ph_3P^+ groups on adjacent C–H bonds are much greater than those of Me_3N^+ groups.[7] Furthermore, definitive experimental

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Table 1. Equilibrium Acidities and Homolytic Bond Dissociation Energies of the Acidic C–H Bonds in 9-Substituted Fluorenes (9-RFlH)

compd	pK_{HA}[a]	$E_{\mathrm{ox}}(\mathrm{A}^-)$[b]	BDE[c]
fluorene	22.6	−1.069	79.5
9-MeFlH	22.3	−1.230	75.4
9-EtFlH	22.7	−1.221	76.2
9-*i*-PrFlH	23.2	−1.203	77.3
9-*t*-BuFlH	24.35	−1.159	79.9

[a] Equilibrium acidities measured in DMSO.[3a] [b] Oxidation potentials of the conjugate anions measured by cyclic voltametric instrument and referenced to the ferrocene/ferrocenium couple. [c] Estimated by eq 1. Since eq 1 is empirical and the oxidation potentials are irreversible, the BDEs are subject to experimental errors of as much as ±2 kcal/mol. The relative BDEs are much more accurate, however, as is apparent from the consistency of the trends for the equilibrium acidities and the constancy of the BDEs observed in Tables 2–9.

and theoretical studies of the structures of the $Ph_3P^+CH^-G$ ylides, where G is an electron-withdrawing group, have shown that the negative charge on the carbanion moiety in these ylides is localized on carbon rather than delocalized into d orbitals on phosphorus.[6] Although the Ph_3P^+ groups in these $Ph_3P^+CH^-G$ ylides were found to have large stabilizing effects on the carbanions, as judged by the high acidities of the precursor salts, the Ph_3P^+ groups in the salts were found to exert little or no effect on the homolytic bond dissociation energies (BDEs) of the acidic C–H bonds. Evidently d-orbital overlap with phosphorus is ineffective at stabilizing either an adjacent carbanion or an adjacent carbon-centered radical![7] The failure to stabilize an adjacent odd electron is consistent with ESR evidence indicating that the odd electron in the radical cation $Ph_3P^+CH^{\bullet}CO_2R$ is not delocalized into an adjacent phosphonium group.[8]

The observation of large increases in acidities on substitution of a Ph_3P^+ group for an acidic hydrogen atom in members of a family of CH_3G substrates, accompanied by little or no change in the BDEs of the acidic H–A bonds present, appears to be characteristic of polarizability effects of the phosphorus atoms in $[Ph_3PCH_2G]^+$ cations. In this paper the acidity increases observed on substrates bearing RCH_2, RS, RSO_2, RO, or R_2N moieties at the acidic site as the size of R is increased along the series Me, Et, *i*-Pr, and *t*-Bu are also attributed to increases in polarizability. Here too the BDEs of the acidic C–H bonds remain essentially constant.

Results and Discussion

We first will examine BDE effects of compounds in the series 9-MeFlH, 9-EtFlH, 9-*i*-Pr-FlH, and 9-*t*-BuFlH where acidities *decrease* along the series (Table 1) because the polarizability effects are overshadowed by progressive increases in steric inhibition of solvation.

In Table 1 we see that substitution of a methyl group in fluorene for one of the acidic hydrogen atoms decreased the BDE by about 5 kcal. This is typical of the effect on the BDE of replacing a hydrogen atom in a hydrocarbon by a methyl group. For example, the BDE of $MeCH_2$–H is about 7 kcal lower than that of CH_3–H, an effect attributable to hyperconjugation.[9] Similarly, the decrease in BDE of the acidic C–H bond in fluorene on methyl substitution can be attributed to stabilization of the fluorenyl radical by hyperconjugation. The BDEs increase progressively as the hydrogen atoms in the methyl group of 9-methylfluorene are successively replaced by methyl groups (Table 1). Finally, with 9-*t*-BuFlH, the BDE comes back to that of fluorene itself.

Table 2. Equilibrium Acidities and Homolytic Bond Dissociation Energies of the Acidic C–H Bonds in 9-RCH$_2$FlH

compd	pK_{HA}[a]	$E_{\mathrm{ox}}(\mathrm{A}^-)$[b]	BDE[c]
9-MeCH$_2$FlH	22.7	−1.221	76.2
9-EtCH$_2$FlH	22.2	−1.197	76.1
9-*i*-PrCH$_2$FlH	21.6	−1.202	75.1
9-*t*-BuCH$_2$FlH	20.3	−1.193	73.6
9-PhC(Me)$_2$CH$_2$FlH	20.3	−1.183	73.8
9-PhCH$_2$FlH	21.35	−1.152	75.9

[a] Equilibrium acidities measured in DMSO.[3a] [b] Oxidation potentials of the conjugate anions measured in DMSO solution and referenced to the ferrocene/ferrocenium couple. [c] Estimated by eq 1.

Table 3. Equilibrium Acidities and Homolytic Bond Dissociation Energies of the Acidic C–H Bonds in 9-RSFlH

compd	pK_{HA}[a]	$E_{\mathrm{ox}}(\mathrm{A}^-)$[b]	BDE[c]
9-MeSFlH	18.0	−1.011	74.6
9-EtSFlH	17.5	−0.993	74.3
9-*i*-PrSFlH	16.9	−0.960	74.3
9-*t*-BuSFlH	15.9	−0.879	74.8
9-PhSFlH	15.4	−0.849	74.8

[a] Equilibrium acidities measured in DMSO solution.[3a] [b] Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1979–1985 and referenced to the ferrocene/ferrocenium couple. [c] Estimated by eq 1.

Next, let us look at the BDEs in families b–k where separation of the R groups in this series from the fluorene ring by a CH_2, S, or SO_2 moiety causes a reversal in the order of these acidities. The effects on acidities and BDEs obtained when a CH_2 moiety is interspersed between the R groups and the fluorene ring are shown in Table 2.

Examination of Table 2 shows that there is a progressive increase in acidities from 9-MeCH$_2$FlH to 9-*t*-BuCH$_2$FlH, the range of acidities being 2.4 pK_{HA} units (3.3 kcal). This family is unusal with respect to the families we will consider later, however, in that the acidifying effect of the 9-*t*-Bu group is greater than that of the Ph group. The BDE for 9-*t*-BuCH$_2$FlH and 9-PhC(Me)$_2$CH$_2$FlH are also out of line. We have commented in an earlier paper that the acidifying effect of 9-*t*-BuCH$_2$FlH may be augmented by relief of steric strain in forming the planar anion.[10] If the pK_{HA} is lowered by this effect, the BDE would also be lowered since the BDEs are estimated by eq 1.[11]

$$\mathrm{BDE} = 1.37\mathrm{p}K_{\mathrm{HA}} + 23.1E_{\mathrm{ox}}(\mathrm{A}^-) + 73.3 \tag{1}$$

The average of the BDEs in Table 2, omitting those of 9-*t*-BuCH$_2$FlH and 9-PhC(Me)$_2$CH$_2$FlH, is 75.8 ± 0.4. These results, which reveal increases in acidities of family members accompanied by near constancy of BDEs, follow, on the whole, the characteristic pattern for polarizability effects established by the $[Ph_3PCH_2G]^+$ cation model.[7]

The same general pattern of behavior was observed also for the 9-RSFlH family in which a sulfur atom has been interspersed between the R groups, Me, Et, *i*-Pr, *t*-Bu, and Ph, and the fluorene ring (Table 3).

Examination of Table 3 shows that the acidities increase progressively from a pK_{HA} value of 18 for 9-MeSFlH to 15.4 for 9-PhSFlH. The range covered is 2.6 pK_{HA} units (3.6 kcal) and the average BDE is 74.6 ± 0.3 kcal.

The corresponding sulfone family also follows the same pattern (Table 4).

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Table 4. Equilibrium Acidities and Homolytic Bond Dissociation Energies of the Acidic C–H Bonds in 9-RSO_2FlH

compd	pK_{HA}[a]	$E_{\mathrm{ox}}(\mathrm{A}^-)$[b]	BDE[c]
9-$MeSO_2FlH$	12.76	–0.375	82.1
9-$EtSO_2FlH$	12.30	–0.377	81.4
9-*i*-$PrSO_2FlH$	11.69	–0.357	81.1
9-*t*-$BuSO_2FlH$	10.55		
9-$PhSO_2FlH$	11.55	–0.308	82.0
9-(*p*-BrPh)SO_2FlH	11.0	–0.276	82.0

[a] Equilibrium acidities measured in DMSO.[3a] [b] Oxidation potentials of the conjugate anions measured in DMSO solution and referenced to the ferrocene/ferrocenium couple. [c] Estimated by eq 1.

Table 5. Equilibrium Acidities and Homolytic Bond Dissociation Energies of The Acidic C–H Bonds in $(RSO_2)_2CH_2$

compd	pK_{HA}[a]	$E_{\mathrm{ox}}(\mathrm{A}^-)$[b]	BDE[c]
$(MeSO_2)_2CH_2$	15.01	0.325	101.4
$(EtSO_2)_2CH_2$	14.42	0.359	101.3
(*i*-$PrSO_2)_2CH_2$	14.10	0.323	100.1
(*t*-$BuSO_2)_2CH_2$	13.70	0.331	99.7
$(PhSO_2)_2CH_2$	12.25	0.343	98.0

[a] Equilibrium acidities measured in DMSO.[3a] [b] Oxidation potentials of the conjugate anions measured in DMSO solution and referenced to the ferrocene/ferrocenium couple. [c] Estimated by eq 1.

Table 6. Equilibrium Acidities and Homolytic Bond Dissociation Energies of the Acidic C–H Bonds in $RSCH_2CN$

compd	pK_{HA}[a]	$E_{\mathrm{ox}}(\mathrm{A}^-)$[b]	BDE[c]
$MeSCH_2CN$	24.26	–0.885	86.0
$EtSCH_2CN$	23.96	–0.858	86.2
i-$PrSCH_2CN$	23.6	–0.845	86.1
t-$BuSCH_2CN$	22.86	–0.810	85.9
$PhSCH_2CN$	20.84	–0.700	85.7

[a] Equilibrium acidities measured in DMSO.[3a] [b] Oxidation potentials of the conjugate anions measured in DMSO solution and referenced to the ferrocene/ferrocenium couple. [c] Estimated by eq 1.

In this family the pK_{HA} range from 9-$MeSO_2FlH$ to 9-$PhSO_2FlH$ is smaller (1.2 pK_{HA} units; 1.7 kcal), perhaps, in part, because the polarizability of tetravalent sulfur is smaller than that of divalent sulfur. Here the average BDE is 81.7 ± 0.3 kcal.

The bis(alkylsulfone) family, $(RSO_2)_2CH_2$, also shows the same pattern of behavior (Table 5).

In this family the pK_{HA} range is from 15.01 for $(MeSO_2)_2CH_2$ to 12.25 for $(PhSO_2)_2CH_2$ (2.3 pK_{HA} units or 3.8 kcal). The average BDE is 100 ± 2. Once again the data support the idea of increasing stabilization of the anion by polarizability effects of the alkyl groups that increase with increasing alkyl size, and are accompanied by constancy of the BDE values.

BDEs have also been determined for the $RSCH_2CN$ family, for which polarizability effects were postulated earlier[3a] to account for the acidity increase as the size of R increases (Table 6).

Examination of Table 6 shows that the acidity increase from a pK_{HA} of 24.26 for $MeSCH_2CN$ to 20.84 for $PhCH_2CN$ (3.5 pK_{HA} units or 4.7 kcal) is accompanied by essentially constant BDEs, which averge 86.0 ± 0.2 kcal.

We have seen that the polarizability effects for 9-RS groups in fluorenes (Table 3; 3.6 kcal from MeS to PhS) are appreciably larger than those for 9-RCH_2 groups (Table 2; 1.9 kcal from RCH_2 to $PhCH_2$). Note also that the RS polarizability effects in $RSCH_2CN$ from MeS to PhS are increased by 4.7 kcal (Table 6). The polarizability effects of second-row elements are known to be much greater than those for first-row elements, the dipolar polarizabilities (in atomic units) being P (24.5), S (19.6), N (7.4), and O (5.4).[12a] We would expect, therefore, that RO moieties would have smaller polarizability effects than RS moieties. Examination of Table 7 shows that the spread in acidities from 9-MeOFlH to 9-PhOFl is indeed somewhat smaller (2.2 pK_{HA} units or 3 kcal). The BDE average in this family is 73.6 ± 0.7 kcal.

Table 7. Equilibrium Acidities and Homolytic Bond Dissociation Energies of the Acidic C–H Bonds in 9-ROFlH

compd	pK_{HA}[a]	$E_{\mathrm{ox}}(\mathrm{A}^-)$[b]	BDE[c]
9-MeOFlH	22.1	–1.324	73.0
9-EtOFlH	22.0	–1.322	72.9
9-*i*-PrOFlH	21.4	–1.297	72.7
9-*t*-BuOFlH	21.3	–1.233	74.0
9-PhOFlH	19.9	–1.135	74.3

[a] Equilibrium acidities measured in DMSO.[14] [b] Oxidation potentials of the conjugate anions measured in DMSO solution and referenced to the ferrocene/ferrocenium coupled. [c] Estimated by eq 1.

Table 8. Equilibrium Acidities and Homolytic Bond Dissociation Energies of the Acidic C–H Bonds in Other Families

compd	pK_{HA}[a]	$E_{\mathrm{ox}}(\mathrm{A}^-)$[e]	BDE[f]
$PhCOCH_2OCH_3$	22.9[b]	–1.050	80.4
$PhCOCH_2OCH_2CH_3$	22.9[b]	–1.042	80.6
$PhCOCH_2OPh$	21.1[c]	–0.935	80.6
$PhCOCH_2S(CH_2)_2CH_3$	19.78[d]	–0.854	80.7
$PhCOCH_2SCH_2Ph$	19.0[d]	–0.787	81.1
$PhCOCH_2SPh$	17.1[d]	–0.669	81.3
$EtSCH_2CO_2Et$	24.27[d]	–0.842	87.0
$PhSCH_2CO_2Et$	21.17[d]	–0.715	85.8

[a] Equilibrium acidities measured in DMSO. [b] Reference 12b. [c] Reference 14. [d] Reference 15. [e] Oxidation potentials of the conjugate anions measured in DMSO solution and referenced to the ferrocene/ferrocenium couple. [f] Estimated by eq 1.

In Table 8 we have combined a $PhCOCH_2OR$ family (R = Me, Et, and Ph) with a $PhCOCH_2SR$ family (R = Pr, CH_2Ph, and Ph). The total acidity range from $PhCOCH_2OMe$ to $PhCOCH_2SPh$ is 5.8 pK_{HA} units (8 kcal) and the average BDE is 80.8 ± 0.5 kcal.

A truncated $RSCH_2CO_2Et$ family with only two members (R = Et and Ph) is also shown in Table 8. The acidity span of 3.1 pK_{HA} units (4.2 kcal) is close to that for the $RSCH_2COPh$ family with R = Pr and Ph (2.7 pK_{HA} units; 3.98 kcal); the 1.2-kcal span in BDEs is, however, twice that for the $PrSCH_2COPh$ vs $PhSCH_2COPh$ ΔBDE.

Finally, we present in Table 9 results in two (dialkylamino)-fluorene families where the size of the alkyl portion of the molecule is increased progressively.

In the top half of Table 9 R in the R_2N moiety of 9-R_2N-FlH molecules is changed from Me to Et or *i*-Pr causing an increase in acidity of 1.7 pK_{HA} units (2.3 kcal).[12b] The corresponding BDEs show no trend, although they are known to be subject to large stereoelectronic effects.[10] The average BDE is 71.7 ± 1.2 kcal.

In the bottom half of Table 9, 1, 2, and 4 methyl groups have been introduced into the 2 and/or 6 positions of the 9-piperidinyl moiety of 9-piperidinylfluorene causing the acidity to increase by 4.3 pK_{HA} units (5.9 kcal). It was suggested earlier that these acidity increases were caused by polarizability effects.[10] The average BDE for these four fluorenes is 71.6 ± 0.6 kcal.

Summary and Conclusions

In Tables 2–9 of the present paper we have presented numerous examples where the acidities of carbon acids are increased progressively with increasing size of hydrocarbon groups, Me < Et < *i*-Pr < *t*-Bu < Ph, that are present at a position removed from the acidic site by an intervening atom or groups of atoms. The effects are small, the largest (3–4 kcal) being observed when the effects are augmented by the presence of a divalent sulfur atom as the intervening atom. Within these families the size of the BDEs of the acidic C–H bonds remain essentially constant. These two results are consistent with the observations obtained with triphenylphosphonium cations of the type $[Ph_3PCH_2G]^+$, where G is CN, CO_2Et, COPh, $COCH_3$, and the like.[7] Here the

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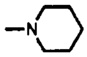
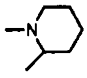
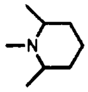
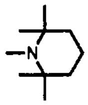
Table 9. Acidities and Homolytic Bond Dissociation Energies of the Acidic C–H Bonds in 9-(Dialkylamino)fluorenes (9-R_1R_2NFlH)

compd no.	substituted amino (R_1R_2N)	pK_{HA}[a]	$E_{ox}(A^-)$[b]	BDE[c]
1	$R_1 = R_2 = Me$	22.5	−1.418	71.5
2	$R_1 = R_2 = Et$	21.4	−1.388	70.5
3	$R_1 = R_2 = i\text{-}Pr$	20.8	−1.242	73
4		22.5	−1.382	72
5		21.4	−1.348	71.5
6		19.4	−1.198	72
7		18.2	−1.166	71

[a] Equilibrium acidities measured in DMSO.[10,12] [b] Oxidation potentials of the conjugate anions measured in DMSO solution and referenced to the ferrocene/ferrocenium couple. [c] Estimated by eq 1.

effects on acidities are much larger (25–35 kcal) but the BDEs also remain essentially constant.[7] These two studies indicate that neither the stabilities of the ylides nor those of the corresponding radicals are affected by $(p\text{–}d)_\pi$ overlap. It now appears that there is both experimental and theoretical reason to believe that the increases in acidities of C–H bonds in families caused by adjacent Ph_3P^+, R, or RS groups are caused entirely by field/inductive and polarizability effects but that BDEs of the C–H bonds or the stabilities of the corresponding radicals are not affected by polarizability effects. In retrospect, we now believe that the effects of PhS groups on acidities discussed earlier[3] are also due entirely to field/inductive and polarizability effects. The appreciability larger effects by α-PhS than α-Ph groups on the acidities of CH_3SO_2Ph and $CH_3SO_2CF_3$ substrates,[3] which are particularly subject to polarizability effects, supports this conclusion, as does the relative insensitivity of the effects of PhS groups to saturation and steric effects. The polarizability effects of adjacent R_2S^+ groups are expected to be much larger than those of RS groups.

Experimental Section

Materials. Most of the samples are commercial. The syntheses for the other compounds were described in earlier papers (referenced in the tables). The purity and identity of each sample were confirmed by spectral analysis and melting point.

The equilibrium acidities in DMSO solution were determined by the indicator overlapping titration as described previously.[13] The oxidation potentials of the conjugate anions were measured by conventional cyclic voltammetric instruments.[11] The working electrode (BAS) consists 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 or cleaned with an ultrasonic instrument and rinsed with ethanol and dried before each run. The counter electrode was platinum wire (BAS). The reference electrode was Ag/AgI, and the reported oxidation potentials were referenced to the ferrocenium/ferrocene couple ($E_{1/2} = 0.875$ V vs the Ag/AgI couple in our instrument). Tetraethylammonium tetrafluoroborate was used as the supporting electrolyte. All electrochemical experiments were carried out under an argon atmosphere.

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