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Acidities and Homolytic Bond Dissociation Energies (BDEs) of Benzyl-Type C–H Bonds in Sterically Congested Substrates

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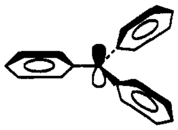
Equilibrium acidities in DMSO and BDEs for the benzylic C–H bonds are reported for 19 triphenylmethanes, three 9,10-dihydroanthracenes, and nine xanthenes. The phenyl groups in triphenylmethane, 9-phenyl-9,10-dihydroanthracene, and 9-phenylxanthene are shown to be constrained in their ability to delocalize either the negative charges in the anions formed by loss of a proton or the odd electrons released by loss of hydrogen atom. Analysis of the pK_{HA} values showed, however, that strong solvation of para electron-withdrawing substituents in a phenyl ring of each of these substrates caused the corresponding anion to adopt a conformation where effective conjugative overlap occurred between the substituent and the carbanion via the phenyl ring. In other words, a conformational change was induced via a substituent solvation assisted resonance (SSAR) effect. In sharp contrast to these large solvation-induced substituent effects on anion stabilities, remote substituent effects on radical stabilities in these congested species were found to be negligible. Substitution of either a *p*-toluenesulfonyl or CN group into the 9-position of xanthene caused a large increase in acidity, but the *p*-$CH_3C_6H_4SO_2$ group caused an increase in the BDE of the acidic C–H bond, whereas the CN group caused a small decrease.

Introduction

Both anions and radicals are known to be strongly stabilized by adjacent phenyl groups in the absence of steric effects. For example, the acidity of toluene is estimated to be greater than that of methane by about 35 kcal/mol in the gas phase,[1] due primarily to delocalization of the negative charge on the corresponding anion into the phenyl ring, and the BDE of the benzylic C–H bond in toluene is decreased by 17 kcal/mol, relative to that in methane, due to delocalization of the odd electron in the corresponding benzyl radical into the phenyl ring. (Henceforth kcal/mol will be abbreviated as kcal.) These large phenyl effects on acidities and BDEs are both strongly attenuated by saturation (leveling) and steric effects when successive substitutions of Ph groups are made into methane. Thus, the gas-phase acidities (in kcal) are: CH_4 (408); $PhCH_3$ (373); Ph_2CH_2 (358); Ph_3CH (352).[1] The gas-phase BDE values (in kcal) are CH_3–H (105);[2] $PhCH_2$–H (88);[2] Ph_2CH–H (82);[2] Ph_3CH (81).[3] The relative BDEs are not likely to be much different in solution because recent studies have shown that ΔBDEs of N–H, C–H, O–H, and S–H bonds in the gas phase, in aqueous solution, and in DMSO are remarkably similar.[4]

There is an enormous increase in acidity on changing from the gas phase to solution caused by the strong solvation of the anions. For example, the acidity of Ph_2CH_2 is about 300 kcal stronger in DMSO than in the gas phase. The acidities in DMSO (in kcal) in the above series are: CH_4 (~77); $PhCH_3$ (~59); Ph_2CH_2 (44); Ph_3CH (42).[5] The attenuation in acidities on Ph substitution is sometimes greater in DMSO than in the gas phase because it may be caused by both steric inhibition of solvation *and* steric hindrance of charge delocalization. The congestion caused by introducing a phenyl group into diphenylmethane leads to only about a 2 kcal increase in acidity in DMSO. Introduction of a *p*-$PhSO_2$ group into one of the phenyl rings of triphenylmethane causes a 9.6 kcal increase in acidity.[6] This is a surprisingly large effect because introducing a *p*-$PhSO_2$ group into the phenyl ring of $PhCH_2CN$, an uncongested but weaker acid, causes an 8.4 kcal increase, i.e., a 1.2 kcal *smaller* effect on acidity. A large effect on acidity was also observed on introduction of a *p*-$PhSO_2$ group into the phenyl ring of 9-phenylxanthene, another congested molecule. These unexpectedly large effects on acidities in DMSO on introducing a para electron-withdrawing group led us to conclude that a conformational change in these congested systems was occurring on deprotonation in order to provide maximum solvation of the anion, e.g. 1 → 2.[6]



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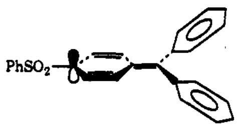
Molecular propeller



2

Comparisons of gas phase acidities with either aqueous or DMSO solution acidities of phenols have revealed good linear correlations when substituents are in meta positions, but para substituents capable of charge delocalization deviated from the lines. The deviations are larger in DMSO than in water because of stronger solvation of the basic oxide site by hydrogen bonding in the aqueous phase and consequent smaller solvation at the substituent site.[7] These correlations indicate that the conformational changes occur, at least partly, because of substituent solvation assisted resonance (SSAR) effects in the anion. Recently, a similar conformational change has been demonstrated by ^{13}C NMR spectral analysis and AM1 calculations when a *p*-CN group was introduced into the 9-phenyl ring of the 9-phenyl-9,10-dihydroanthracenide ion.[8] Here too, a large acidifying effect in DMSO for the introduction of a *p*-electron-withdrawing group into a congested system was observed.

In the present paper we report additional data concerning the effects on the heterolytic bond dissociation energies (i.e., acidities) of triphenylmethanes, 9-phenyl-

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(1) From *The Gas-Phase Acidity Scale*, available by writing to Prof. John E. Bartmess, Jr., Department of Chemistry, University of Tennessee, Knoxville, TN 37996.

(2) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 492–532 and references cited therein.

(3) Bordwell, F. G.; Cheng, J.-P.; Ji, G.-Z.; Satish, A. V.; Zhang, X.-M. *J. Am. Chem. Soc.* **1991**, *113*, 9790–9795.

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(5) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456–463. The acidities of CH_4 and $PhCH_3$, which are too weakly acidic to measure in DMSO, were estimated by extrapolation.

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0022-3263/92/1957-6542$03.00/0

Table I. Effects on Acidities and Homolytic Bond Dissociation Energies of Meta and Para Substituents in Triphenylmethanes and 9-Phenyl-9,10-dihydroanthracene

acid	pK_{HA}[a]	$E_{ox}(A^-)$[c]	BDE[d]
4-$FC_6H_4CHPh_2$	30.8		
triphenylmethane	30.6	−1.486	80.95
4-*t*-$BuOC_6H_4CHPh_2$	31.4	−1.537	80.9
4-$ClC_6H_4CHPh_2$	29.6	−1.477	79.8
4-$PhC_6H_4CHPh_2$	29.4	−1.430	80.6
3-$ClC_6H_4CHPh_2$	28.6	−1.433	79.4
4-$PhSC_6H_4CHPh_2$	28.3	−1.352	80.9
3-$F_3CC_6H_4CHPh_2$	28.4	−1.337	81.4
3-$Me_3N^+C_6H_4CHPh_2$ TsO^-	27.1	−1.290	80.5
4-$Me_3N^+C_6H_4CHPh_2$ TsO^-	27.0		
4-$NO_2C_6H_4CHPh_2$	16.8	−0.682	80.6
(4-$NO_2C_6H_4)_2CHPh$	14.4		
(4-$NO_2C_6H_4)_3CH$	12.7	−0.492	79.3
(4-$ClC_6H_4)_3CH$	27.0		
4-$PhSO_2C_6H_4CHPh_2$	23.6	−1.078	80.8
4-$PhCOC_6H_4CHPh_2$	22.4	−1.067	79.4
4-$NO_2C_6H_4CH$(2,4-$diMeC_6H_3)_2$	~19[b]	−0.661	~84[e]
4-$NO_2C_6H_4CH$(2,4-$diMeOC_6H_3)_2$	~19[b]	−0.742	~82[e]
4-$NO_2C_6H_4CH$(2,4,6-triMeO)$_2$	~19.5[b]	−0.940	~78[e]
9,10-dihydroanthracene	30.1	−1.575	78
9-phenyl-9,10-dihydroanthracene	28.8	−1.459	79.1
(p-cyanophenyl)-9,10-dihydroanthracene	23.5	−1.170	78.5

[a] Measured in DMSO against two or more indicators unless otherwise noted. [b] Estimated (see text). [c] Measured by cyclic voltammetry in DMSO by the method described in earlier papers and referenced to the ferrocene–ferrocenium couple; the $E_{1/2}$ for the Fc/Fc^+ couple is 0.875 V vs Ag/AgI in DMSO. Our earlier $E_{ox}(A^-)$ values, relative to the standard hydrogen electrode (SHE), are 0.750 V more positive, and the $E_{ox}(A^-)$ values, relative to the Ag/AgI electrode, are 0.875 V more positive than those in this paper. [d] Calculated by eq 1. [e] There is some uncertainty in this value because the pK_{HA} is an estimated value.

xanthenes, and 9-phenyl-9,10-dihydroanthracenes on introducing electron-withdrawing groups into the para positions of the phenyl rings. These effects are then compared with the substituent effects on the homolytic bond dissociation energies (BDEs) of the acidic C–H bonds in these molecules.

Results and Discussion

Acidities of Substituted Triphenylmethanes and Related Hydrocarbons in DMSO. The pK_{HA} values for 19 triphenylmethanes are given in Table I.

A Hammett plot for the triphenylmethane parent and the derivatives: 4-F, 4-Cl, 3-Cl, 3-CF_3, 3-Me_3N^+, and 4-Me_3N^+ was linear and gave $\rho = 5.5$ ($R^2 = 0.98$). This ρ value is remarkably close to those for anilines (5.7),[9] arylacetonitriles (5.7),[10] and 3-substituted fluorenes (5.9).[11] A plot of pK_{HA} values for anilines vs arylacetonitriles has revealed that not only is the plot linear with a slope near unity but also the points for resonance-enhanced electron-withdrawing groups (4-CN, 4-$PhSO_2$, 4-PhCO, and 4-NO_2) fall on or close to the line. The plot of pK_{HA} values for triphenylmethanes vs arylacetonitriles is also linear with a slope near unity (Figure 1), but the points for the resonance-enhanced electron-withdrawing groups, 4-$PhSO_2$, 4-PhCO, and 4-NO_2, deviate substantially from the line. Examination of Figure 1 shows that these deviations all occur because the ΔpK_{HA} values for 4-$PhSO_2$, 4-PhCO, and 4-NO_2 are *larger* for substituted triphenylmethanes than for like-substituted arylacetonitriles by 1.23, 3.15, and 5.75 kcal, respectively. These data provide strong support for the existence of the triphenylmethide ions bearing para electron-withdrawing groups in a conformation such as 2 where the p-orbital of the carbanion can overlap with those of the aryl ring and the para substituents.

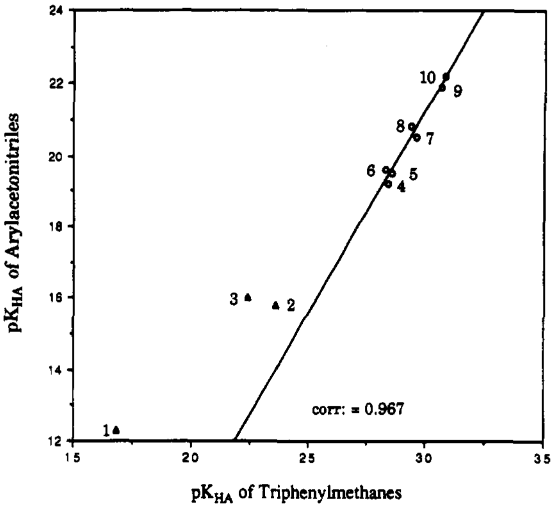

Figure 1. Plot of pK_{HA} values for triphenylmethanes, $GC_6H_4CHPh_2$, versus pK_{HA} values for arylacetonitriles in DMSO: 4 (3-CF_3), 5 (3-Cl), 6 (4-PhS), 7 (4-Cl), 8 (4-Ph), 9 (H), 10 (4-F). The points for 1 (4-NO_2), 2 (4-$PhSO_2$), and 3 (4-PhCO) (triangles) were not included in the correlation.

The introduction of a nitro group into the para position of one of the phenyl rings of triphenylmethane increases the acidity by 18.9 kcal, but the effect of a like substitution into a second phenyl ring causes only a 3.29 kcal further increase in acidity, and introduction of a nitro group into a para position of the remaining ring cause only a 2.33 kcal further increase. The dramatic attenuation of the successive substitutions of *p*-NO_2 groups into triphenylmethane provides an unusual example of the power of saturation and steric effects. Since the first *p*-NO_2 group has already stabilized the carbanion by 18.9 kcal, primarily through charge delocalization, the negative charge on the methide carbon atom has been markedly decreased, which should produce a sizable saturation effect. Furthermore, the ring holding the second nitro group is severely twisted relative to the plane holding the first *p*-NO_2 phenyl ring. Although solvation of the second *p*-NO_2 group will no doubt occur, along with an SSAR effect, the overlap of the carbanion with the second ring will remain relatively weak. In other words, both saturation *and* steric inhibition of the SSAR effect will reduce the effect of the second *p*-nitro substituent. The saturation and steric effects will be even more severe for the third *p*-nitro substitution.

Ordinarily, equilibrations between carbon acids and indicators (or standard acids) in DMSO are very rapid. For example, the reaction of (*p*-nitrophenyl)diphenylmethane with CH_3SOCH_2K, where the difference in pK_{HA} values is 26 kcal in DMSO, is very fast, as expected, but equilibration of *p*-$NO_2C_6H_4CHPh_2$ (pK_{HA} = 16.8) with indicators (or standard acids) with similar pK_{HA}s such as 9-PhSFlH, pK_{HA} = 15.8, 9-*i*-PrSFlH, pK_{HA} = 16.9, or PhC(=S)NH_2, pK_{HA} = 16.16 (a standard acid), are *very* slow (hours). Fortunately, the 4-$NO_2C_6H_4CPh_2^-$ anion was found to be very stable, and reproducible pK_{HA} values were obtained from titrations lasting over *several days*. The same was true for pK_{HA} determinations with (4-$NO_2C_6H_4)_2CHPh$ and (4-$NO_2C_6H_4)_3CH$. These slow equilibrations are exaggerated versions of those that we have observed with aliphatic nitro compounds, the slowness of which has been attributed to the extensive structural and solvent reorg-

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Table II. Acidities and Homolytic Bond Dissociation Energies of Xanthenes

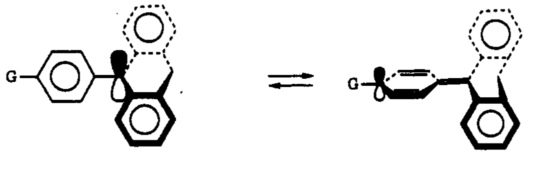
acid	pK_{HA}[a]	$E_{ox}(A^-)$[b]	BDE[c]
xanthene	30.0	−1.685	75.5
9-phenylxanthene	27.9	−1.531	76.2
9-(4-methoxyphenyl)xanthene	28.43	−1.573	76.0
9-[4-(methylthio)phenyl]xanthene	27.55	−1.539	75.5
9-[4-(phenylthio)phenyl]xanthene	26.8	−1.486	75.7
9-[3-(chlorophenyl)phenyl]xanthene	26.6	−1.474	75.7
9-[4-(phenylsulfonyl)phenyl]xanthene	23.1	−1.261	75.9
9-cyanoxanthene	13.6	−0.993	69.0
9-(*p*-toluenesulfonyl)xanthene	21.05	−0.847	82.6

[a] Measured in DMSO against two or more indicators. [b] Measured by cyclic voltammetry in DMSO by the method described in earlier papers and referenced to the ferrocene–ferrocenium couple; the $E_{1/2}$ for the Fc/Fc$^+$ couple is 0.875 V vs Ag/AgI in DMSO. Our earlier $E_{ox}(A^-)$ values, relative to the standard hydrogen electrode (SHE), are 0.750 V more positive, and the $E_{ox}(A^-)$ values, relative to the Ag/AgI electrode, are 0.875 V more positive than those in this paper. [c] Calculated by eq 1.

anization required to convert the nitroalkane to its conjugate base and vice versa. Equilibrations of bis(2,4-dimethylphenyl)-, bis(2,4-dimethoxyphenyl)-, and bis-(2,4,6-trimethoxyphenyl)(4-nitrophenyl)methanes are even slower, but reasonable estimates of the pK_{HA} values may be made by assuming that acid-weakening effects (based on model analogues) are about 1 and 1.2 pK_{HA} units for 4-Me and 4-MeO groups, respectively, and about 0.5 unit for 2-Me and 2-MeO groups.

The steric congestion in 9-phenyl-9,10-dihydroanthracene must be about the same as that in triphenylmethane since the introduction of the 9-phenyl group into the methylene group of 9,10-dihydroanthracene causes a small (2.6 kcal) increase in acidity that is comparable to that produced by introduction of a phenyl group into the methylene group of diphenylmethane (2 kcal).

The conformations of 9-phenyl-9,10-dihydroanthracenide ion (**3**) and its *p*-cyanophenyl derivative (**4**) deduced from C-13 NMR spectra and AM1 calculations,[8] show that in **3** the plane of the ring bearing the *p*-G substituent is nearly orthogonal to the carbanion p-orbital ("perpendicular conformation") whereas the *p*-CN derivative adopts a "planar conformation" (**4**), where the ring is nearly coplanar with the carbanion p-orbital. This representation is strongly supported by the pK_{HA} data, which show that the cyano group has increased the acidity by 7.3 kcal (Table I). This shift in the preferred conformation of the anion caused by introduction of a para electron-withdrawing group is analogous to the effects of para electron-withdrawing effects observed in trityl anions and is again a consequence of an SSAR effect.



3 ("perpendicular" favored for G = H)

4 ("parallel" favored for G = CN)

9-Phenylxanthene can be considered to be a derivative of 9-phenyl-9,10-dihydroanthracene in which an oxygen atom has replaced one of the methylene groups. (Both are triphenylmethane analogues.) The corresponding anion can exist in conformations analogous to **3** and **4**. The acidity of 9-phenylxanthene is only 3.3 kcal greater than that of the parent, xanthene. This suggests slightly less congestion than in triphenylmethane or 9-phenyl-9,10-dihydroanthracene and points to a "perpendicular conformation" for its conjugate base, analogous to that in **3**. Introduction of a *p*-$PhSO_2$ group into the phenyl ring causes a 6.7 kcal increase in acidity (Table II), which again suggests a shift in conformation of the anion to the "planar conformation," analogous to **4**.[6]

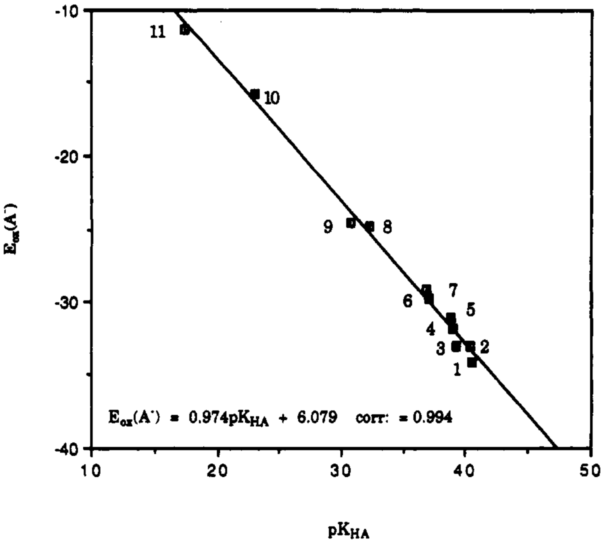


Figure 2. Plot of oxidation potentials of substituted triphenylmethide anions versus pK_{HA} of triphenylmethanes (in kcal/mol): 1 (4-Cl), 2 (4-Ph), 3 (3-Ph), 4 (3-CF_3), 5 (4-PhS), 6 (3-Me_3N^+), 7 tris-(4-Cl), 8 (4-$PhSO_2$), 9 (4-PhCO), 10 (4-NO_2), 11 tris-(4-NO_2).

Homolytic Bond Dissociation Energies (BDEs) for Substituted Triphenylmethanes and Related Hydrocarbons. Recently, we have shown that BDE values estimated for acidic C–H bonds in weak carbon acids by the semiempirical eq 1 gave agreement to ±2 kcal, or better,

$$\mathrm{BDE(kcal/mol)} = 1.37pK_{HA} + 23.06E_{ox}(A^-) + 73.3 \quad (1)$$

with the best gas-phase literature values for 11 of the 12 compounds examined.[3] The lone exception was Ph_3C–H, where our value of 81 ± 1 was 6 kcal higher than the literature value. Reasons for favoring our value were given. Perhaps the best argument given is that presented in Table I, where BDE values for the acidic C–H bonds in 10 meta- and para-substituted triphenylmethanes of the type $GC_6H_4CHPh_2$ estimated by eq 1 are listed. The average BDE for these 10 triphenylmethanes is 80.4 ± 1 kcal. The constancy of these BDEs and of the apparent radical stabilization energies (RSEs) of the corresponding trityl radicals is truly remarkable when one considers that the anions from which the radicals are derived have energies that vary over 14 pK_{HA} units (19.2 kcal). Additional support for the higher value has come recently from H$^\bullet$ atom abstraction data for trityl radicals reacting with metal hydrides.[12]

In terms of eq 1 the constancy of the BDEs for the benzylic C–H bonds in $GC_6H_4CHPh_2$ is achieved because the bond-weakening changes caused by pK_{HA} decreases are balanced by the bond-strengthening changes brought about in the incipient radicals being formed that are reflected in the $E_{ox}(A^-)$ values. In other words, there is a linear correlation between pK_{HA} and $E_{ox}(A^-)$ with a slope near unity (Figure 2).

Similar linear plots of $E_{ox}(A^-)$ vs pK_{HA} with slopes near unity have been observed previously for 2-substituted and 2,7-disubstituted fluorenes, where the partial meta and partial para character of the 2- and 7-positions in fluorene lead to offsetting stabilizing and destabilizing effects on

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[12] Eisenberg, D. C.; Lawrie, C. J. C.; Moody, A. E.; Norton, J. R. *J. Am. Chem. Soc.* **1991**, *113*, 4888–4895.

the radical being formed,[13] and for 3-aryl-1,1,5,5-tetraphenyl-1,4-pentadienes, $p\text{-GC}_6H_4CH(CH{=}CPh_2)_2$, where steric hindrance to effective orbital overlap damps out the radical-stabilizing effects of remote substituents on BDEs.[14]

Recent work has shown that the C–Br bonds in 4-F, 4-Br, 4-CF_3, and 4-CN benzyl bromides are weakened by 0.52, 1.9, 2.8, and 5.5 kcal, respectively, relative to the parent benzyl bromide, and that a 4-Me group strengthens the bond by about 0.3 kcal.[15] The authors point out that the effects of donors and acceptors on these C–Br bond BDEs are opposite to the remote substituent effects on the benzylic C–H bonds of toluene and suggest that in this instance the effects of the substituents on BDEs are dictated by dipolar effects that raise or lower the ground-state energies of the benzyl bromides, rather than by the effects of the substituents on the radical stabilization energies (RSEs) of the benzyl radicals being formed. It should be noted that the donor and acceptor effects observed on BDEs of C–Br bonds are also opposite to those we have observed for remote substituents on H–A bonds in 3-substituted fluorenes,[13] arylacetonitriles,[10] phenols,[16] anilines,[17] and thiophenols.[17] It is possible, as the authors and others have pointed out,[15] that ground-state effects need also to be taken into account in estimating the effects of substituents on BDEs (and RSEs) for other weak acids where the H–A bond is polar, such as the O–H bonds in phenols, but for acids where the acidic bonds are relatively nonpolar, such as C–H bonds, we believe that BDEs in unstrained molecules should give reasonable estimates of RSEs. The interpretation is complicated further, however, by the small size of remote substituent effects and their dual nature, as will be brought out further in the section on proximate substituent effects.

If ground-state effects were important in dictating the substituent effects on the benzylic C–H bonds in $GC_6H_4CHPh_2$ molecules, one would expect, from the dipolar model,[15] that the substituent dipole would interact with the small $C^{\delta-}–H^{\delta+}$ dipole. (The electronegativities of C and H are 2.5 and 2.1–2.2, respectively, according to the Pauling or Allred–Rochow electronegativity scales.) An electron-withdrawing group, such as 4-NO_2, should then stabilize the dipole, lower the ground-state energy, and strengthen the bond according to the pattern set by the substituted benzyl bromides. The BDEs shown for the triphenylmethanes in Table I give no indications of the presence of such an effect. Even in $(4\text{-}NO_2C_6H_4)_3C–H$, where more than one NO_2 dipole can be brought to bear, the BDE appears to be slightly *less*, rather than more, than that of the parent, although the value is within experimental error of the method. Our conclusion is that remote substituent effects on BDEs (and RSEs) of the acidic C–H bonds are small in triphenylmethanes because of steric and saturation effects and because substituent solvation effects on radical sites are too weak to enforce the conformational change necessary for effective overlap stabilization, as occurs in the anions.

Substituent effects fail to alter the BDEs in the 9,10-dihydroanthracene system for similar reasons. Introduction of a phenyl group into the 9-position causes a 1 kcal *increase* in BDE of the acid C–H bond, and introduction of a *p*-CN group into this phenyl ring causes essentially no change in BDE (Table I).

Introduction of a phenyl group into the methylene group of xanthene has about the same effect on the BDE of the acidic C–H bond as does the comparable substitution into a methylene group of 9,10-dihydroanthracene, i.e., about a 1 kcal *increase*. Here too the phenyl group in the 9-phenylxanthyl radical must be essentially orthogonal to the xanthyl moiety, and this interpretation is supported by the failure of the para donors MeO, MeS, or PhS to lower the BDE. As a consequence, the average BDE estimated for the acidic H–C bond in 9-phenylxanthene and its five para-substituted derivatives shown in Table II is 75.8 ± 0.4 kcal.

Proximate Effects of Cyano and Arenesulfonyl Functions on BDEs. The introduction of a cyano group directly into the methylene group of xanthene causes a 6 kcal decrease in the BDE of the acidic C–H bond.[18] This effect is appreciably larger than the effect of a (remote) para cyano effect. (Note the negligible bond weakening effect in 9-(*p*-cyanophenyl)-9,10-dihydroanthracene in Table I.) It is comparable to the bond-weakening effect of introducing a cyano group at the acidic site of toluene (6 kcal),[18] or fluorene (5 kcal),[13] but is much smaller than the effect on introducing a cyano group into methane (10–12 kcal).[2] As pointed out previously,[12] introduction of a *p*-toluenesulfonyl group at the acidic site of xanthene causes a 7 kcal *bond-strengthening* effect (Table II). A 2 kcal bond-strengthening effect had been observed earlier for 9-(benzenesulfonyl)fluorene,[13] and similar bond strengthening effects of 1–5 kcal were observed for 9-(methanesulfonyl)- and 9-(ethanesulfonyl)fluorenes, α-(benzenesulfonyl)toluene, and α-(benzenesulfonyl)-9-methylanthracene.[18] At the time these results were published, we were uncertain as to the origin of these bond-strengthening effects and of the apparent bond-strengthening effect of the *p*-cyano group in (*p*-cyanophenyl)-acetonitrile.[10] Later work revealed an apparent bond-strengthening effect of a *p*-cyano group in *p*-cyanophenol[16] and an apparent 6 kcal bond *weakening* effect in the acidic H–C bond of methyl phenyl sulfone, relative to the H–C bond in methane.[19] These observations led to the postulate that proximate and remote substituents play a dual role in affecting radicals, stabilizing by virtue of their ability to delocalize the odd electron and destabilizing by virtue of their electron-attracting ability. This dual role had previously been observed in the effect of fluorine atoms on the BDEs of the H–C bonds in methane where the single fluorine atom in CH_3F weakens the C–H BDE by 3 kcal by virtue of its delocalizing effect in the corresponding radical, but the three fluorine atoms in CHF_3 exert a net 2 kcal bond-strengthening ability by virtue of their electron-withdrawing ability[2] and their lowering of the ground-state energy. (Radicals are electron deficient and are destabilized by electron withdrawal.) The dual nature of the destabilizing–stabilizing effects of substituents on radicals does not appear to have been generally recognized, although it has also been brought out by the calculations of Pasto.[20] The large steric bulk of alkane- and arenesulfonyl groups[21] impedes their already modest odd-electron delocalizing ability, which is no doubt subject

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to stereoelectronic control,[22] and their strong destabilizing electron-withdrawing ability often takes over. The effects of α-Me_3N^+ and α-$C_5H_5N^+$ (α-pyridinium) groups on the BDE of the acidic H–C bonds in $Me_3N^+CH_2COPh$ and $C_5H_5N^+CH_2COPh$ provide a good example. The Me_3N^+ group has no delocalizing ability and is purely bond strengthening, but the $C_5H_5N^+$ group has both destabilizing electron-withdrawing and stabilizing delocalizing ability. The net effect is bond weakening.[23]

Experimental Section

General. NMR spectra were recorded on a Varian EM-390 or XLA-400 spectrometer using $CDCl_3$ as solvent and Me_4Si as internal standard. Melting points were determined on a Thomas Hoover capillary melting point apparatus and are uncorrected. All known compounds were identified by comparison of their mp and NMR with literature data. The procedure for electrochemical measurement has been described earlier.[3] All potentials are reported with reference to the formal potential ($E_{1/2}$) of ferrocene/ferrocenium couple (see the footnotes under the tables).

Materials. Commercial samples of triphenylmethane, 9,10-dihydroanthracene, xanthene, and thioxanthene were purified by crystallization. We thank Prof. P. W. Rabideau for the sample of 9-(4-cyanophenyl)-9,10-dihydroanthracene.[8]

(*p*-Nitrophenyl)diphenylmethane,[24] (*p*-chlorophenyl)diphenylmethane,[25] (*p*-benzoylphenyl)diphenylmethane,[26] and 9-phenyl-9,10-dihydroanthracene[27] were prepared by literature procedures.

[*m*-(Trifluoromethyl)phenyl]diphenylmethane. To the Grignard reagent obtained from magnesium metal (2.07 g, 85.0 mmol) and bromobenzene (13.35 g, 85.0 mmol) in anhydrous THF was added ethyl *m*-(trifluoromethyl)benzoate (7.42 g, 34.0 mmol). The reaction mixture was stirred for additional 1 h and quenched with aqueous NH_4Cl. Upon workup the organic layer was dried over anhydrous $MgSO_4$. The crude carbinol obtained as an oil (3.3 g) on solvent removal from the organic layer was reduced by the literature[28] procedure. The crude product obtained as an oil upon reduction was treated with hot hexane to afford white crystals: mp 38–39 °C; NMR δ 5.56 (s, 1 H), 6.56–7.46 (m, 14 H).

General Procedure for the Preparation of (Diaryl)(*p*-nitrophenyl)methanes. (Diaryl)(*p*-nitrophenyl)methanes were prepared by reacting 4-nitrobenzaldehyde with the appropriate aromatic compound in the presence of concentrated sulfuric acid as described by Baeyer.[24]

Bis(2,4-dimethylphenyl)(*p*-nitrophenyl)methane: yield[17] 80%; mp 142–144 °C; NMR δ 2.13 (s, 6 H), 2.31 (s, 6 H), 5.69 (s, 1 H), 6.5–7.23 (m, 8 H), 8.13 (d, 2 H).

Bis(2,4-dimethoxyphenyl)(*p*-nitrophenyl)methane: yield[17] 80%; purification by preparative TLC gave a semisolid; NMR δ 3.66 (s, 6 H), 3.80 (s, 6 H), 6.06 (s, 1 H), 6.3–6.7 (m, 6 H), 7.22 (d 2 H), 8.10 (d, 2 H).

Bis(2,4,6-trimethoxyphenyl)(*p*-nitrophenyl)methane: yield 36%; mp 149–149.5 °C; NMR δ 3.53 (s, 12 H), 3.80 (s, 6 H), 6.11 (s, 4 H), 6.27 (s, 1 H), 7.17 (d, 2 H), 8.02 (d, 2 H).

The preparation of substituted xanthenes has already been described in an earlier[6] paper.

[*p*-(Phenylthio)phenyl]diphenylmethane. To a mixture of diphenyl sulfide (15.87 g, 85.2 mmol) and benzhydryl chloride (5.76 g, 28.4 mmol) was added $AlCl_3$ (0.60 g, 4.5 mmol) in portions. The thick brown paste obtained after mixing was allowed to stand for 1 h, treated with water, and extracted with ether. The combined ether layer was washed with water and dried over $MgSO_4$. The crude product obtained after solvent removal under reduced pressure was recrystallized from hexane: white crystals; mp 122–124 °C (lit.[29] mp 121–123 °C).

[*p*-(Phenylsulfonyl)phenyl]diphenylmethane. [*p*-(Phenylthio)phenyl]diphenylmethane (4.0 g, 11.3 mmol) was dissolved in CH_2Cl_2 and cooled to 0 °C. To this cooled solution was slowly added *m*-chloroperbenzoic acid (5.33 g, 28.4 mmol), and the mixture was stirred overnight at room temperature. The precipitated *m*-chlorobenzoic acid was separated by filtration. The CH_2Cl_2 layer was washed with $NaHSO_3$ solution (10%) and $NaHCO_3$ (satd.) and dried over anhydrous $MgSO_4$. The crude product obtained after solvent removal under reduced pressure was recrystallized from ethanol: white flakes; mp 130–136 °C (lit.[29] mp, 136–143 °C).

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Registry No. *p*-$FC_6H_4CHPh_2$, 437-23-0; Ph_3CH, 519-73-3; *p*-*tert*-$BuOC_6H_4CHPh_2$, 10357-72-9; *p*-$ClC_6H_4CHPh_2$, 69361-54-2; *p*-$PhC_6H_4CHPh_2$, 745-36-8; *m*-$ClC_6H_4CHPh_2$, 85554-26-3; *p*-$PhSC_6H_4CHPh_2$, 85554-39-8; *m*-$CF_3C_6H_4CHPh_2$, 13865-59-3; $Ph_2CHC_6H_4$-*m*-NMe_3^+ TsO^-, 144018-61-1; $Ph_2CHC_6H_4$-*p*-NMe_3^+ TsO^-, 144018-63-3; *p*-$NO_2C_6H_4CHPh_2$, 2945-12-2; (*p*-$NO_2C_6H_4)_2CHPh$, 21112-02-7; (*p*-$NO_2C_6H_4)_3CHPh$, 603-49-6; (*p*-$ClC_6H_4)_3CH$, 27575-78-6; *p*-$PhSO_2C_6H_4CHPh_2$, 85554-27-4; *p*-$PhCOC_6H_4CHPh_2$, 7375-38-4; *p*-$NO_2C_6H_4CH(2,4\text{-}Me_2C_6H_3)_2$, 98293-92-6; *p*-$NO_2C_6H_4CH(2,4\text{-}(MeO)_2C_6H_3)_2$, 143959-23-3; *p*-$NO_2C_6H_4CH(2,4,6\text{-}(MeO)_3C_6H_2)_2$, 54921-80-1; PhBr, 108-86-1; *m*-$CF_3C_6H_4CO_2Et$, 76783-59-0; *p*-$NO_2C_6H_4CHO$, 555-16-8; Ph_2S, 139-66-2; Ph_2CHCl, 90-99-3; 9,10-dihydroanthracene, 613-31-0; 9-phenyl-9,10-dihydroanthracene, 13577-28-1; 9-(*p*-cyanophenyl)-9,10-dihydroanthracene, 144018-64-4; xanthene, 92-83-1; 9-phenylxanthene, 3246-80-8; 9-(4-methoxyphenyl)xanthene, 19234-05-0; 9-[4-(methylthio)phenyl]xanthene, 144018-65-5; 9-[4-(phenylthio)phenyl]xanthene, 144018-66-6; 9-[4-(3-chlorophenyl)phenyl]xanthene, 144041-62-3; 9-[4-(phenylsulfonyl)phenyl]xanthene, 85554-25-2; 9-cyanoxanthene, 85554-24-1; 9-(*p*-toluenesulfonyl)xanthene, 42503-30-0.

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