Table IV. Calculated and Experimental Coupling Constants for the D Ring of I in $CDCl_3$ and DMSO

	$^3J_{expt}{}^a$	$^3J_{expt}{}^b$	$^3J_{calc}{}^c$
14α–15α	5.8	5.8	5.4
14α–15β	12.4	12.4	11.8
15α–16α	9.0	9.1	11.1
15α–16β	0.9	1.1	1.1
15β–16α	9.1	9.2	7.6
15β–16β	8.9	9.1	11.0

[a] DMSO solution. [b] $CDCl_3$ solution. [c] Calculated using 3JMM2.[23]

represented in the parameterizing data-set of Haasnoot et al.[23] may explain this. The most important 2α–3β coupling is, however, well-reproduced. This is consistent with a predominance (>90%) of the twist-boat conformation in $CDCl_3$.

The remaining coupling constants for the B and C rings are generally in good agreement with the calculated values, with the exception of those to the 8β and 14α protons (data not shown). As these protons are attached to tertiary centers it is possible that additional strain effects, which the Karplus equation does not consider, are coming into play. There is nothing to suggest that the B and C rings deviate from chair conformations. The D ring couplings have been compared to those determined by Schneider et al.[14] for 5α*H*-androstan-17-one. The values are almost identical, indicating that the substituents on the A and D rings do not appear to interact in a way which disrupts the individual conformational equilibria. In Table IV the observed and calculated coupling constants are compared for both solvents. On the basis of these data, and the energy profile for rotation about the C15–C16 bond, it is possible to speculate that there is some interconversion between half-chair and envelope conformations.[14]

The 200-MHz ^1H spectrum of I in $CDCl_3$ (and in mixed $CDCl_3$/DMSO) was also studied from −20 to 50 °C and showed no evidence of any dynamic effects.

Conclusions

In this study we have shown that the ^1H NMR spectra of steroids are amenable to analysis using high-field (600 MHz) instruments, together with 2D experiments to aid with assignment. More importantly, this has allowed the examination of conformational problems.

The solvent-dependent nature of the conformation of I indicates that while steroids offer a rigid stereochemical skeleton upon which to base drug molecules, the conformational changes resulting from the incorporation of certain substituents may have a profound effect on properties. In the case of I it is clearly shown that the molecule assumes a twist-boat ring A in a hydrophobic medium such as $CDCl_3$; in effect the polar group charges are masked via a hydrogen bond. In the much more polar DMSO solution the A ring of the steroid is a chair with the morpholino and hydroxy groups trans-diaxial. The polar groups in this case may be solvated by intermolecular hydrogen bonds with solvent molecules. This is a specific atom–atom solvation effect as opposed to the more general reaction field where solvation is mediated by the solvent dielectric.[19] In future work we will apply molecular dynamics methods to the question of the individual contributions of steric strain and hydrogen bonding to the conformational equilibria.

The medium-dependent behavior of I also has important implications for drug design in that conformational changes in the steroid may facilitate the passage of the molecule through membranes, while a different conformation, and hence different spatial arrangement of substituents, will be assumed at the more polar receptor site.

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Registry No. I, 52-72-2.

Bond Dissociation Energies in DMSO Related to the Gas Phase

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Abstract: Estimates have been made of the homolytic bond dissociation energies (BDEs) for (a) the benzylic or allylic H–C bonds in 14 hydrocarbons, (b) the acidic H–C bonds in 12 hydrocarbons containing one or more heteroatoms, and (c) the H–N bonds in five nitrogen acids as well as thiophenol and phenol. For the 18 compounds where literature gas-phase values were available, agreement to within ±2 kcal/mol was observed for all but three (Ph_3CH, $PhNH_2$, and PhOH). For Ph_3CH and $PhNH_2$, the literature values were shown to be in error. For the BDEs of the acidic H–A bonds in 17 compounds, error limits of ±2 kcal/mol, or better, were established from BDE estimates made for three or more derivatives in which remote substituents were placed on the benzene ring of the parent compound. In all, the BDEs of the acidic H–A bonds of 32 compounds have been established to ±2 kcal/mol or better.

Quantitative measurements in the gas phase by a variety of methods have yielded estimates of homolytic bond dissociation energies (BDEs) that have generally been considered to provide the best measures of relative radical stabilization energies obtained to date.[1] In our laboratory we have developed a method of

$$\Delta\text{BDE(kcal/mol)} = 1.37\Delta \text{p}K_{\text{HA}} + 23.06\Delta E_{\text{OX}}(\text{A}^-) \quad (1)$$

estimating relative BDEs, e.g. eq 1, for families of acids, HA, by combining equilibrium acidity constants, $\text{p}K_{\text{HA}}$, with the oxidation potentials of their conjugate bases, A^-, both measured in DMSO.[2] The method is based on a thermodynamic cycle and is the solution counterpart of one devised by Brauman to estimate BDEs from gas-phase acidities, electron affinities, and ionization potentials.[3]

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(1) McMillen, D. F.; Golden, D. M. *Ann. Rev. Phys. Chem.* **1982**, *33*, 493–532 and references cited therein.

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

(3) Janousek, B. K.; Reed, K. T.; Brauman, J. I. *J. Am. Chem. Soc.* **1980**, *102*, 3125–3129.

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Table I. Homolytic Bond Dissociation Energies (BDEs) for the H–C Bonds in Benzylic-Type Hydrocarbons

hydrocarbon	$\mathrm{p}K_{\mathrm{HA}}$[a]	$E_{\mathrm{ox}}(\mathrm{A}^-)$,[b] kcal/mol	BDE,[c] kcal/mol	BDE (lit.), kcal/mol	ref (lit.)
fluorene	22.6	−1.069	80 ± 1	80.1	10a
9-phenylfluorene	17.9	−1.028	74 ± 1		
1,2-benzofluorene	19.7	−0.957	78.7		
2,3-benzofluorene	23.1	−1.164	78.4	78.8	10a
indene	20.1	−0.952	78.9		
2-phenylindene	19.35	−0.865	80 ± 1		
1,3-cyclopentadiene	18.0	−0.778	81	81.2	10c
1,4-diphenylcyclopentadiene	14.3	−1.175	75 ± 1		
1,1,3,5,5-pentaphenyl-1,4-pentadiene	23.4	−1.309	75.1 ± 0.1		
9-methylanthracene	31.1	−1.489	81.5 ± 0.1	81.8 ± 1.5	1
9,10-dihydroanthracene	30.1	−1.575	78	76	10a
9-phenyl-9,10-dihydroanthracene	28.8	−1.459	79		
triphenylmethane	30.6	−1.486	81 ± 1	75	10d
diphenylmethane	32.2	−1.54	82 ± 1	81.4 ± 1	10e

[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 $E_{\mathrm{ox}}(\mathrm{A}^-)$ values, relative to the standard hydrogen electrode (SHE), are 0.750 V more positive, and the $E_{\mathrm{ox}}(\mathrm{A}^-)$ values, relative to the Ag/AgI electrode are 0.875 V more positive than those in this paper. [c] Calculated by eq 2; where error limits are given, the value shown is an average of the BDE of the parent and several remotely substituted derivatives (see the text for details).

The term $1.37\Delta\mathrm{p}K_{\mathrm{HA}}$ in eq 1 is the equilibrium acidity of the weak acid in DMSO, expressed in kilocalories per mole (henceforth denoted as kcal), relative to that of the parent in a family of weak acids, such as the phenol family.[4] The term $23.06\Delta E_{\mathrm{OX}}(\mathrm{A}^-)$ is the oxidation potential of the conjugate base, A$^-$, of the acid in DMSO, expressed in kcal, relative to the parent. The $\Delta\mathrm{p}K_{\mathrm{HA}}$ values are usually accurate to ±0.2 kcal or better. Most of the CV waves formed in measuring the anion oxidation potentials are irreversible but are reproducible to within ±20 mV (0.5 kcal), or better, for a series of runs made by a single investigator. We believe, therefore, that within a family the ΔBDEs are accurate to ±1 kcal. This view is supported by the fact that the ΔBDE = 5.6 ± 0.3 kcal for the O–H bond in *p*-methoxyphenol vs that in phenol as obtained by eq 1 together with four other methods including gas-phase kinetic studies and photoacoustic calometric measurements in a variety of media.[4]

It was desirable to modify eq 1 in order to estimate BDEs that would allow comparisons to be made between compounds belonging to different families and with gas-phase values. In 1983, Friedrich suggested that eq 2 might be used to obtain BDEs in solution. Aqueous literature values for $E_{\mathrm{OX}}(\mathrm{A}^-)$ were used for

$$\mathrm{BDE(kcal)} = 1.37\mathrm{p}K_{\mathrm{HA}} + 23.06E_{\mathrm{OX}}(\mathrm{A}^-) + C \qquad (2)$$

p-HOC$_6$H$_4$O$^-$, *p*-$^-$OC$_6$H$_4$O$^-$, and C$_6$H$_5$O$^-$ referenced to the aqueous standard hydrogen electrode (SHE) and *C* was taken as the sum of the free energy of the hydrogen atom (48.6 kcal) and an 8.2-kcal $T\Delta S°$ term.[5] In 1988, we evaluated *C* as 55.4–55.9;[6a] more recently a value of 56 has been used. The BDEs estimated in this way were found to agree remarkably well with most gas-phase values. In retrospect, this was surprising because (a) most of the cyclic voltammetric (CV) waves used to evaluate the oxidation potentials were irreversible, (b) the potentials were referenced to SHE, but there is no truly thermodynamic way to accomplish this, and (c) several of the other constants used to obtain *C* are not well-established.[6b] We concluded that the good agreement between our BDEs estimated from data in DMSO and literature BDEs determined in the gas phase was fortuitous and that our comparisons with gas-phase values must be considered to be empirical.

In view of the empirical nature of the constant *C*, comparison with gas-phase values is essential to establishing the meaningfulness of the BDEs obtained. Fortunately, our values agree with the best gas-phase values to within ±2 kcal/mol for almost every compound for which literature values are available, as will be amply demonstrated in this paper. (The BDE of the H–O bond in phenol may prove to be the lone exception.)

The use of irreversible oxidation potentials ($E_{\mathrm{OX}}(\mathrm{A}^-)$) has since been justified in a number of instances by the studies of Arnett and his students, which have shown that, for several series of anions, plots of $E_{1/2}$(reversible) and $E_{\mathrm{OX}}(\mathrm{A}^-)$ (irreversible) are linear.[7] Furthermore, reversible oxidation potentials obtained by high-speed voltammetry (200–10 000 V/s) have been found to agree with oxidation potentials obtained from irreversible CVs to within 50 mV for most of the 20 anions tried to date.[8]

Recently, Parker has obtained a value of *C* (relative to F$_c$/F$_c$$^+$) similar to our empirical value by using an isodesmic scheme together with an independently derived BDE.[9] This method emphasizes the advantages of referring the oxidation potentials to that of the ferrocene–ferrocenium couple in the solvent being used. In this and subsequent papers, our $E_{\mathrm{OX}}(\mathrm{A}^-)$ values will be referenced to the F$_c$/F$_c$$^+$ couple in DMSO, and a value of *C* = 73.3 kcal (equivalent to 56 kcal when referenced to SHE) will be used in estimating BDEs. It must be kept in mind, however, that the BDEs estimated in this way are empirically derived gas-phase BDEs, *not DMSO solution BDEs*.

In our original paper,[6a] we pointed out that for five compounds (9-methylanthracene, diphenylmethane, cyclopentadiene, fluorene, and acetone) our estimates in DMSO using eq 2 were within ±2 kcal of the BDEs chosen as best by McMillen and Golden (MG) in their much-quoted review of the gas-phase literature.[1] For five other compounds, triphenylmethane (−6), indene (+5), thiophenol (+5), phenol (−4), and aniline (−4), the MG values differed from ours by the values (in kcal) shown in parentheses. In the present paper we show that our estimates for the BDEs of the acidic H–A bonds in four of these compounds, triphenylmethane, indene, thiophenol, and aniline, are more reasonable than the MG values. We also present estimates of the BDEs for the acidic H–A bonds in 26 other weak acids, which we believe to be accurate to ±2 kcal or better. These BDEs usually agree with estimates made from gas-phase measurements to within ±2 kcal.

Results and Discussion

A. BDEs of Weak Carbon Acids Bearing Remote Substituents.

In Table I, the $\mathrm{p}K_{\mathrm{HA}}$ and $E_{\mathrm{OX}}(\mathrm{A}^-)$ data for 14 hydrocarbons are summarized, together with the estimated BDEs from measurements in DMSO and the gas phase.

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(4) Bordwell, F. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 1736–1743.

(5) Friedrich, L. E. *J. Org. Chem.* **1983**, *48*, 3851–3852.

(6) (a) Bordwell, F. G.; Cheng, J.-P.; Harrelson, J. A., Jr. *J. Am. Chem. Soc.* **1988**, *110*, 1229–1231. (b) Bordwell, F. G.; Harrelson, J. A.; Satish, A. V. *J. Org. Chem.* **1989**, *54*, 3101–3105. (c) Bordwell, F. G.; Harrelson, J. A., Jr. *Can. J. Chem.* **1990**, *68*, 1714–1718.

(7) (a) Arnett, E. M.; Amarnath, K.; Harvey, N. G.; Cheng, J.-P.; *J. Am. Chem. Soc.* **1990**, *112*, 344–355. (b) Arnett, E. M.; Harvey, N. G.; Amarnath, K.; Venimadhavan, S. *J. Am. Chem. Soc.* **1990**, *112*, 7346–7353. (c) Venimadhavan, S.; Amarnath, K.; Harvey, N. G.; Arnett, E. M. *J. Am. Chem. Soc.*, in press. We thank Prof. Arnett for sending us a preprint of his paper.

(8) Hupp, J. T.; Satish, A. V.; Jones, L.; Zion, D. A. Unpublished results.

(9) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711–6717. Parker, V. D.; Handoo, K. L.; Roness, F.; Tilset, M. *J. Am. Chem. Soc.*, in press. We thank Prof. V. D. Parker for sending us a preprint of this paper prior to publication.

Fluorene and Derivatives of Fluorene. For 2-substituted and 2,7-disubstituted fluorenes, a plot of the oxidation potentials of their conjugate bases vs their pK_{HA} values is linear with a slope near unity.[2] For 11 of these fluorenes, the ΔBDE calculated from eq 1 is within ±0.25 kcal of that of the parent compound, which suggests that these substituents have little or no radical-stabilizing ability. The small size of these effects is due, in part, to the nature of the 2- and 7-positions in the fluorene ring. Although they are formally meta positions, they have some para character in that the odd electron can be delocalized to the 2- and 7-positions by resonance through the second benzene ring.[2] Radical-stabilizing para effects therefore tend to cancel radical-destabilizing meta effects. Advantage can be taken of these unusually small effects to obtain a good estimate of the BDE for the acidic H–C bond in fluorene itself. The average of the BDE values calculated for 11 substituents using eq 2 is 79.8 ± 0.3 kcal, which we report in Table I as 80 ± 1 kcal. This value agrees with a value of 80.1 kcal estimated by Stein and Brown.[10a]

The BDE for the acidic H–C bond in 9-phenylfluorene has been estimated to be 74.0 kcal,[10b] and those for 9-(*p*-methylphenyl)- and 9-(*m*-chlorophenyl)fluorene have been estimated to be 73.6 and 74.6 kcal, respectively.[10b] (Recently we have obtained a BDE = 74.5 kcal for 9-phenylfluorene under conditions where $E_{OX}(A^-)$ for its anion has been made reversible by fast scan.[8]) These estimates allow us to assign a BDE of 74 ± 1 kcal for 9-phenylfluorene with confidence.

The difference in BDEs for the acidic H–C bond in fluorene and 9-phenylfluorene of ~6 kcal is small compared to the difference in the phenyl effects of 17 kcal between $H{-}CH_3$ and $PhCH_2{-}H$[1] or that of 11 kcal between the acidic H–C bond in CH_3COPh and $PhCH_2COPh$.[6c] Part of the smaller effect is no doubt caused by "saturation" (or leveling) since the BDE of the H–C bond in fluorene is 25 kcal lower than that of methane and 13 kcal lower than that of acetophenone. The small effect of Ph in 9-phenylfluorene must be due in part to a steric effect, however, because the BDEs of the acidic H–C bonds in 9-(dialkylamino)- and 9-(cyclic dialkylamino)fluorenes have been shown to be subject to strong steric attenuation,[11] and this should also be true for the (bulky) phenyl group. By contrast, the effects of benzo fusions in 1,2-benzo- and 2,3-benzofluorenes (Table I) are much smaller (about 1.5 kcal), as expected for remote substituent effects in the fluorene system. (For example, the (remote) 3-MeO group lowers the BDE of the 9-H–C bond by ~1 kcal compared to ~7 kcal for the proximate 9-MeO substituent.[2])

Indene and Indene Derivatives. The BDE estimated for the acidic H–C bond for indene is 79 kcal. This has not yet been checked by making measurements on meta and para indene derivatives. The estimated BDE for the acidic H–C bond in 2-phenylindene from eq 2 of 79.9 kcal has been supported by measurements on 2-phenylindenes with *p*-Me (80), *p*-MeS (79), and 4-MeO (80.5) groups present in the phenyl ring. The average of the BDEs for these derivatives is 80.0 ± 1 kcal and is given in Table I. Previously we reported a value of 78.8.[6a] The 2-position in the indenyl radical is expected to have a low electron density, so a 1 kcal higher BDE for 2-phenylindene than indene is not unreasonable. Examination of the literature shows that the value of 84.3 kcal given by McMillen and Golden for the H–C bond in indene[1] is actually a value estimated by Stein for the benzylic H–C bond in *indan*.[12]

1,3-Cyclopentadiene and Phenylcyclopentadienes. The BDE estimated for the acidic H–C bond in 1,3-cyclopentadiene of 81 kcal[6a] is within 1 kcal of the gas-phase estimate.[1] The small size (1–2 kcal) of the decrease in BDE caused by one and two benzo fusions across the double bonds of 1,3-cyclopentadiene to give indene and fluorene, respectively, indicates that delocalization of the odd electron in the latter two molecules is confined largely to the cyclopentadienyl ring. These effects are comparable in size to those caused by benzo fusions onto the 1,2- and 2,3-positions of fluorene (Table I).

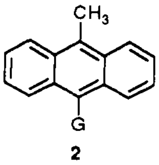
Substitution of phenyl groups at the 1- and 4-positions of 1,3-cyclopentadiene decreases the pK_{HA} by 5 kcal and the BDE of the acidic H–C bond by 6 kcal. The presence of a 4-Me or a 4-MeO substituent on the 1-phenyl ring causes the acidity to decrease by 0.68 and 1.2 kcal, respectively; 4-Cl and 3-MeO substituents cause *increases* in acidity of 1.1 and 0.27 kcal, respectively. The BDEs of the acidic H–C bonds in these four derivatives average 75.0 ± 0.6 kcal (reported as 75 ± 1 kcal for the acidic H–C bond of 1,4-diphenyl-1,3-cyclopentadiene in Table I).[10b] 1,2,3,4-Tetraphenyl- and 1,2,3,4,5-pentaphenylcyclopentadienes have been shown to have pK_{HA} values of 13.2 and 12.5 and to have BDEs for the acidic H–C bonds of 76.5 and 77.9 kcal, respectively.[10b]

B. Remote Substituent Effects in Sterically Hindered Hydrocarbons. 3-Aryl-1,1,5,5-tetraphenyl-2,4-pentadienes. As mentioned earlier, a linear plot between pK_{HA} and $E_{OX}(A^-)$ with a slope near unity was obtained for 2- and 2,7-substituted fluorenes because of a cancellation of destabilizing and stabilizing substituent effects. Similar linear plots are also observed for a number of families where steric hindrance minimizes substituent effects on radical stabilities. For example, the average of the BDEs for the acidic H–C bonds in 3-aryl-1,1,5,5-tetraphenyl-2,4-pentadienes (**1**) is 75.1 ± 0.1 kcal.[10b] Neither the presence of the powerful donor, $4\text{-}Me_2N$, nor the powerful acceptor, $3\text{-}NO_2$, on the 3-aryl ring has any observable effect on the radical stability. The pK_{HA} values increase with substitution over a range of 5.9 kcal, and the $E_{OX}(A^-)$ values become increasingly more negative over a range of 5.9 kcal. Examination of molecular models shows that the steric restraints imposed by the four phenyl groups at C-1 and C-5 force the 3-aryl group to be essentially orthogonal to the π bond.

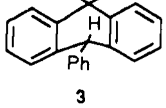
10-Substituted 9-Methylanthracenes. Even in the absence of steric constraints there appear to be two opposing factors that contribute to the stabilizing and destabilizing influence of remote substituents: (1) their capacity to delocalize an odd electron (stabilizing +*R* effect) and (2) their field/inductive capacity for electron withdrawal (destabilizing *F* effect). In arylacetonitryl radicals ($GC_6H_4\dot{C}HCN$)[13] and phenoxyl radicals ($GC_6H_4O^\bullet$),[4] the *F* effect overshadows the *R* effect for 4-PhCO, 4-CN, and $4\text{-}NO_2$ acceptors, and for proximate radicals of the type $C_5H_5N^+\dot{C}HG$, where G = PhCO, CN, or CO_2Et, the *R* effect of the pyridinium function overshadows its *F* effect.[14] In 10-substituted 9-methylanthracenes (**2**), one might anticipate larger substituent effects than in arylacetonitriles because the effects are not attentuated by the stabilizing effect of the CN. In fact, however, the effects are small.[15] The BDEs for G = H, Me, and MeO are 81.5 ± 0.1 kcal. If the BDEs for G = Ph, Cl, PhS, PhO, CN, and CHO are also included, BDE = 81.8 ± 0.8 kcal.

$(Ph_2C{=}CH)_2CHAr$

1



2



3

Examination of molecular models shows that the methyl group fits snugly between the C-1 and C-9 peri hydrogen atoms, but only the linear Cl and CN of those groups examined would fit between the C-4 and C-6 peri hydrogen atoms. The MeO group fails to lower the BDE significantly, and the CN group causes

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[10] (a) Stein, S. E.; Brown, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 787–793. (b) Bordwell, F. G.; Cheng, J.-P.; Bausch, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 2867–2872. (c) Furugama, S.; Golden, D. M.; Benson, S. W. *Int. J. Chem. Kinet.* **1971**, *3*, 237–248. Lossing, F. P.; Traeger, J. C. *J. Am. Chem. Soc.* **1975**, *97*, 1579–1580. DeFrees, D. J.; McIver, R. T.; Hehre, J. *J. Am. Chem. Soc.* **1980**, *102*, 3334–3338. (d) Swarc, M. *Proc. R. Soc. London Ser. A* **1951**, *207*, 5–13. (e) Rossi, M. J.; McMillen, D. F.; Golden, D. M. *J. Phys. Chem.* **1984**, *88*, 5031–5039.

[11] Bordwell, F. G.; Cheng, J.-P.; Seyedrezai, S. E.; Wilson, C. A. *J. Am. Chem. Soc.* **1988**, *110*, 8178–8183.

[12] Stein, S. E. In *New Approaches in Coal Chemistry*; ACS Symposium Series 169; American Chemical Society: Washington, D.C., 1981; pp 97–129.

[13] Bordwell, F. G.; Cheng, J.-P.; Bausch, M. J.; Bares, J. E. *J. Phys. Org. Chem.* **1988**, *1*, 209–223.

[14] Bordwell, F. G.; Zhang, X. *J. Org. Chem.* **1990**, *55*, 6078–6079.

[15] Cheng, J.-P. Ph.D. Dissertation, Northwestern University, Evanston, IL, 1987.

Table II. Homolytic Bond Dissociation Energies (BDEs) for Acidic H–C Bonds in Hydrocarbons Bearing One or More Heteroatoms

hydrocarbon	pK_{HA}[a]	$E_{ox}(A^-)$,[b] kcal/mol	BDE,[c] kcal/mol	BDE (lit.), kcal/mol	ref (lit.)
xanthene	30.0	−1.685	75.5	74	10a
9-phenylxanthene	27.9	−1.531	75.8 ± 0.4		
$PhCH_2SO_2Ph$	23.4	−0.652	90.2 ± 0.6		
$PhCH_2CN$	21.9	−0.923	81.9 ± 0.3		
$PhCH(CN)_2$	4.2		77 ± 1[d]		
$CH_2(CN)_2$	11.0	0.063	90		
CH_3COCH_3	26.5	−0.674	94	92 ± 1.5	23
CH_3CO-*t*-Bu	27.7	−0.750	94		
CH_3COPh	24.7	−0.607	93 ± 1		
2-benzylpyridine	28.2	−1.294	82	82.3	10e
3-benzylpyridine	30.1	−1.336	84		
4-benzylpyridine	26.7	−1.162	83	82.3	10e

[a] Measured in DMSO against two or more indicators. [b] See footnote b in Table I. [c] Calculated by eq 2; where error limits are given, the value shown is an average of the BDE of the parent and several remotely substituted derivatives (see the text for details). [d] Average of the values for *p*-$ClC_6H_4CH(CN)_2$ (77.1), *p*-$MeC_6H_4CH(CN)_2$ (76.2), and *m*-$ClC_6H_4CH(CN)_2$ (79.0).

a slight lowering of the BDE. On the other hand, the NO_2 and PhCO groups, which must assume an orthogonal orientation to the π system because of their bulk, cannot delocalize the odd electron and, as a consequence, destabilize the radical about 1 kcal by reason of their *F* effect.

9-Phenyl-9,10-dihydroanthracene (3). In 9,10-dihydroanthrancene the 9- and 10-carbon atoms are forced out of the plane of the two benzene rings, but sufficient delocalization of the odd electron of the radical into the benzene rings occurs to make the BDE 4 kcal lower than that of diphenylmethane (78 vs 82 kcal). Substitution of a phenyl group at the 9-position introduces additional steric hindrance, however, and the BDE *increases* by 1 kcal.

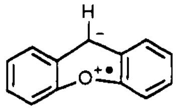
Triphenylmethanes and Diphenylmethanes. The oxidation potentials of triphenylmethide ions bearing a substituent are reversible, and that of the parent is partially reversible. Neither donors (*p*-*t*-BuO, *p*-Ph, *p*-PhS) nor acceptors (*m*-CF_3, *p*-$PhSO_2$, *p*-NO_2) have any appreciable effect on the BDEs (average 80.9 ± 0.6 kcal), although the estimates for the *p*-Cl and *p*-PhCO derivatives fall outside this range (1.0 and 1.5 kcal lower, respectively). The pK_{HA} values vary over a range of 20 kcal, and the $E_{OX}(A^-)$ values vary over a range of 19.7 kcal. Here too, as with the 3-aryl-1,1,5,5-tetraphenyl-2,4-pentadienes and 10-substituted 9-methylanthracenes, steric factors have led to a linear relationship between $E_{OX}(A^-)$ and pK_{HA}, with a slope near unity. As pointed out earlier,[16] the value of 81 kcal[6a] for the BDE of Ph_3C–H provides a new value for the standard BDE to be used in Breslow's method of estimating pK_{HA}s from the algebraic sum of the differences in BDEs of hydrocarbons and the differences in the oxidation potentials of their conjugate bases.[17] Using this method and a standard BDE of 75 kcal for Ph_3C–H, Breslow estimated the pK_{HA} of 1,3-cyclopentadiene to be 22. The pK_{HA} estimate becomes 6/1.37 = 4.4 pK_{HA} units lower, i.e., 17.6, when the value of 81 kcal is used for the BDE of Ph_3C–H. This value is in good agreement with the pK_{HA} of 18 measured in DMSO.[16]

The estimate of 82.0 for the acidic H–C bond in diphenylmethane is within 1 kcal of the literature value (Table I). The BDEs estimated for *p*-$CNC_6H_4CH_2Ph$ and (*p*-$NO_2C_6H_4)_2CH_2$ are 81.8 and 81.1, respectively, which are consistent with the assignment of a BDE of 82 ± 1 for diphenylmethane. We see that in the series CH_3–H (105), $PhCH_2$–H (88), Ph_2C–H (82), and Ph_3C–H (81) the phenyl effects on the BDE decrease from 17 to 6 to 1 kcal due to a combination of saturation and steric effects.

C. BDEs of the Acidic H–C Bonds in Hydrocarbons Bearing One or More Heteroatoms.

Xanthene and Xanthene Derivatives. Our estimate for the BDE of xanthene of 75.5 kcal agrees well with the literature value of 74 kcal (Table II).

Steric effects in xanthenes are severe, as has been brought out by studies of their acidities and the reactivities of their conjugate bases with alkyl halides in S_N2 reactions.[18] The two benzene rings form the sides of a boat in a manner comparable to that of 9,10-dihydroanthracene. Xanthene and **2** have the same pK_{HA} values, but xanthene has a 6 kcal lower BDE, which indicates that the oxygen atom can stabilize the corresponding radical as in **4**.



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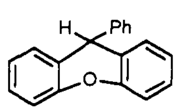

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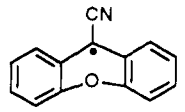

6

9-Phenylxanthene (**5**) is ~3 kcal more acidic than xanthene, suggesting that the phenyl group can stabilize the negative charge, despite being constrained in a position where its π bonds appear to be essentially orthogonal to the two benzene rings in the xanthene framework. The BDE for 9-phenylxanthene is, however, about the same as that of xanthene, and the BDE for 9-phenyl-9,10-dihydroanthracene is 1 kcal higher than that of 9,10-dihydroanthracene, pointing to a greater sensitivity of the radical than the anion to steric effects. Substitution of *p*-MeO, *p*-MeS, *p*-PhS, *m*-Cl, and *p*-$PhSO_2$ groups onto the phenyl group of 9-phenylxanthene increases the acidity by 2–9 kcal, but the BDEs remain essentially constant, the average being 75.8 ± 0.4 kcal.[15]

The powerful attenuation of BDEs caused by steric effects is brought out by comparing the effects of introducing Ph and CN substituents into methane and xanthene on H–C BDEs. For $PhCH_2$–H vs CH_3–H, ΔBDE = 17 kcal, and for $CNCH_2$–H vs CH_3–H, ΔBDE = 12 kcal.[1] For 9-phenylxanthene vs xanthene, ΔBDE = −1 kcal, and for 9-cyanoxanthene vs xanthene, ΔBDE = 6.5 kcal.[13] We see that substitution of a Ph group for a hydrogen in methane, where the steric effect in the corresponding $PhCH_2^\bullet$ radical is minimal, weakens the C–H bond by 5 kcal more than does substitution of a CN group. But for substitution of Ph and CN onto xanthene where steric effects in the corresponding radicals are large, Ph destabilizes the radical (**5**) by 1 kcal, whereas the (linear) CN group, which has minimal steric demands, stabilizes the radical (**6**) by 6.5 kcal.

Benzyl Phenyl Sulfone, Phenylacetonitrile, and Phenylmalononitrile. The BDE estimated for benzyl phenyl sulfone is 90.3 kcal, and the average value for the parent plus its 4-F, 3-F, 4-Cl, 3-Cl, 4-Me, 3-Me, 4-*t*-Bu, 4-MeO, 3-MeO, 4-PhS, 3-PhS, and 3-NMe_2 derivatives is 90.2 ± 0.6 kcal.[19a] The 3-CF_3 and 3-CN derivatives have the highest BDEs (92.2 and 92.9 kcal, respectively). The slightly smaller BDEs for 4-CF_3, 4-CN, and 4-NO_2 (91.3, 91.7, and 89.9 kcal, respectively) can probably be rationalized by the presence of a delocalizing factor in these three substituents that is being overshadowed by its field/inductive effect.[4]

The BDE estimated for phenylacetonitrile from eq 2 is 81.9 kcal. The average BDE of the parent and its 4-F, 4-MeO, 4-Cl, 3-Me, and 3-F derivatives is 81.9 ± 0.3 kcal. The BDE of

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(16) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456–462.

(17) Juan, B.; Schwarz, J.; Breslow, R. *J. Am. Chem. Soc.* **1980**, *102*, 5741–5748.

(18) Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1983**, *48*, 2216–2222.

(19) Bordwell, F. G.; Bausch, M. J.; Branca, J. C.; Harrelson, J. H., Jr. *J. Phys. Org. Chem.* **1988**, *1*, 225–241. Bordwell, F. G.; Lynch, T.-Y. *J. Am. Chem. Soc.* **1989**, *111*, 7558–7562.

malononitrile has been calculated by LeRoy to be 81 kcal.[20] Our value of 90 kcal estimated from eq 2 has been checked by a measurement using a fast-scan technique.[8] The reversible oxidation potential obtained in this way was within 50 mV of that we obtained earlier. This value was given further support from an estimate of the BDE of $PhCH(CN)_2$ (Table II). The ΔBDE of 13 kcal for the acidic H–C bonds between $CH_2(CN)_2$ and $PhCH(CN)_2$ is consistent with the ΔBDE of 11 kcal between CH_3CN and $PhCH_2CN$, whereas the ΔBDE of 4 kcal using a value of 81 kcal for $CH_2(CN)_2$ is not.

Acetone, *tert*-Butyl Methyl Ketone, and Acetophenone. In the 1960s a value of 92.3 ± 3 kcal was obtained for the H–C bond in acetone by measuring the activation energy for the rate of hydrogen atom abstraction by $F_2N^{\bullet}$ radicals.[21] In 1970 a determination of the BDE from the rate of bromine atom abstraction and the heat of formation of the acetonyl radical gave a value of 98.3 ± 1.8 kcal,[22] which led to the conclusion that the acetonyl radical has zero stabilizing energy relative to the ethyl radical. This value was accepted as best by McMillen and Golden,[1] but in 1984 a corrected value for the heat of formation of the acetonyl radical brought the value back to 92 ± 1.5 kcal.[23] Estimates made from eq 2 give values of 94 kcal for acetone and also for $t\text{-BuCOCH}_2\text{–H}$.[6c] The estimate of 93 ± 1 kcal for acetophenone is an average of that for the parent and nine of its meta- and para-substituted derivatives.[6c]

2-, 3-, and 4-Benzylpyridines. The BDEs for the acidic H–C bonds in 2- and 4-benzylpyridines have been determined to be 82.3 kcal by very low pressure pyrolysis.[24] Our estimates of the BDEs in kcal, using eq 2, are 83.0 for 4-benzylpyridine, 82.0 for 2-benzylpyridine, and 83.6 for 3-benzylpyridine. The DMSO acidity order (pK_{HA} values in parentheses) is 4- (26.7) > 2- (28.2) > 3- (30.1),[25] which also gives the order of relative anion stabilities. The lower acidity of 2- than 4-benzylpyridine is presumably caused by lone pair–lone pair repulsions that destabilize the 2-benzylpyridinide anion. The relative order of radical stabilities (BDEs in kcal in parentheses) appears to be 2- (82) > 4- (83) > 3- (84), but the differences are small. The 3-benzylpyridinide anion has the most negative $E_{OX}(A^-)$ value of the three, which contributes to bond weakening, but the higher pK_{HA} value overshadows this effect on the BDE as estimated by eq 2, and the net result is the highest BDE of the three.

D. Heteroatom-Centered Radicals. Nitrogen-Centered Radicals. The most common nitrogen-centered radicals are those derived from amines. The H–N bond in ammonia has a BDE in the range of 107 to 109 kcal; the most recent value is 109.2 kcal.[26] McMillen and Golden give the following BDEs (kcal): H_2N–H, 107.4 ± 1.1; MeNH–H, 100.0 ± 2.5; Me_2N–H, 91.5; PhNH–H, 88.0 ± 2; PhN(Me)H, 87.5. Alkylamines are too weakly acidic for a pK_{HA} to be measured, in DMSO, but the acidities of the H–N bond in aniline, its meta- and para-substituted derivatives, and those in a number of other families such as pyrroles, indoles, carbazoles, imidazoles and like azoles are measurable. The BDEs of the N–H bonds estimated for some of these are given and compared with literature values in Table III.

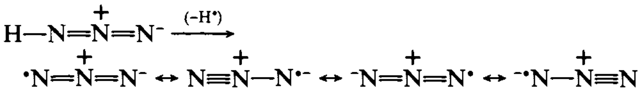
Aniline and Diphenylamine. According to McMillen and Golden,[1] the best BDE for the N–H bond in aniline is 88 ± 2 kcal, which was determined by Colussi and Benson.[27a] This value is not consistent, however, with the recent value of 87.3 reported for diphenylamine,[27b] because a sizable decrease in BDE would be expected on the introduction of a second Ph group. Our estimate of BDE = 92 ± 1 kcal for aniline is based on an average (92.4 ± 0.4 kcal) of the BDEs of aniline (92.3)[6a] and its *p*-Me (92.0), *p*-Cl (92.5), *m*-Cl (92.6), and *p*-Br (92.4) derivatives. Our average value obtained for Ph_2NH (87.5) and its 4-Me (86.9), 3-Me (87.6), 4,4′-diBr (87.8) derivatives plus iminodibenzyl (87.0) is 87.4 ± 0.5 kcal. The 5-kcal difference in the average values for PhNH–H and Ph_2N–H agrees well with the 6-kcal difference between $PhCH_2$–H (88) and Ph_2CH–H (82).[1]

Table III. Homolytic Bond Dissociation Energies (BDEs) of a Variety of H–N, H–S, and H–O Bonds

weak acid	pK_{HA}[a]	$E_{ox}(A^-)$,[b] kcal/mol	BDE,[c] kcal/mol	BDE (lit.), kcal/mol	ref (lit.)
PhNH–H	30.6	–0.992	92 ± 1	88 ± 2	1
PhN(Me)–H	29.5	–1.054	89	87.5 ± 2	1
Ph_2NH	24.95	–0.865	87.5 ± 1	87.3	27b
pyrrole	23.05	–0.355	97	99 ± 6	28
hydrazoic acid	7.9[b]	0.415	94	92 ± 5	31
PhS–H	10.3	–0.360	79 ± 1	78, 78.5	33, 7c
PhO–H	18.0	–0.325	90 ± 1	85–88[d]	

[a] Measured in DMSO against two or more indicators. [b] See footnote b in Table I. [c] Calculated by eq 2; where error limits are given, the value shown is an average of the BDE of the parent and several remotely substituted derivatives (see the text for details). [d] See text for details.

Pyrrole and Hydrazoic Acid. The BDE of the H–N bond in pyrrole has been estimated to be 99 ± 6 kcal from photodetachment and electron affinity experiments.[28] The observation of a higher BDE than for the H–N bond in an aliphatic secondary amine, Me_2NH (91.5 kcal), was rationalized on the basis that the nitrogen atom in pyrrole may be approximately trigonal, whereas that in Me_2NH is approximately tetrahedral. Our estimate for the BDE of the H–N bond in pyrrole from eq 2 of 97 kcal is in reasonable agreement with the gas-phase value. We also have evidence to indicate that oxidation of the carbazolide ion may involve formation of a σ radical,[29] which is consistent with Brauman's postulate that a σ-pyrrolyl radical is formed from the pyrrolide ion.[28] A much higher BDE (118 kcal) has been estimated recently, however, for the H–N bond attached to the sp^2-hybridized nitrogen atom in $Ph_2C{=}NH$.[30] At first sight one might expect the BDE of the H—N= bond in hydrazoic acid to have a BDE in the same region, but Pellerite, Jackson, and Brauman have reported a value of 92 ± 5 kcal, estimated from the proton affinity of the azide ion using ion cyclotron resonance.[31] Our estimate of 94 kcal using eq 2 is consistent with this value. The lower than expected value can be rationalized by the delocalization of the odd electron in the azidyl radical.



$$\mathrm{H{-}N{=}\overset{+}{N}{=}N^{-}} \xrightarrow{(-\mathrm{H}^{\bullet})}$$

$$\mathrm{{}^{\bullet}N{=}\overset{+}{N}{=}N^{-}} \leftrightarrow \mathrm{N{\equiv}\overset{+}{N}{-}N^{\bullet -}} \leftrightarrow \mathrm{{}^{-}N{=}\overset{+}{N}{=}N^{\bullet}} \leftrightarrow \mathrm{{}^{-\bullet}N{-}\overset{+}{N}{\equiv}N}$$

Thiophenol and Phenol. The 79 ± 1 kcal value for the thiophenol given in Table III for our estimate is an average of the values for the parent, 78.5,[6a] and its 3-Me, 4-Me, 3-Cl, 4-Cl, and 4-Br derivatives. Earlier literature values are 75[32] and 83.3 ± 2 kcal.[27] Our value is within 1 kcal of a recent value (78 kcal) measured by photoacoustic calorimetry.[33] Arnett has recently reported a value of 78.5 from an oxidation obtained under reversible conditions.[7c]

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(20) LeRoy, G.; Peeters, D.; Sana, M.; Wilante, C. In *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janousek, Z., Merênyi, R., Eds.; NATO ASI Series; D. Reidel Publishing Co.: Boston, 1986; pp 1–47.

(21) Grzechowiak, J.; Kerr, J. A.; Trotman-Dickenson, A. F. *J. Chem. Soc.* **1965**, 5080–5082.

(22) King, K. D.; Golden, D. M.; Benson, S. W. *J. Am. Chem. Soc.* **1970**, *92*, 5541–5546.

(23) Holmes, J. L.; Lossing, F. P.; Terlouw, J. K. *J. Am. Chem. Soc.* **1984**, *108*, 1086–1087.

(24) Rossi, M. J.; McMillen, D. F.; Golden, D. M. *J. Phys. Chem.* **1984**, *88*, 5031–5039.

(25) Van Der Puy, M. Unpublished results.

(26) Hack, W.; Rouvelirolles, P.; Wagner, H. C. *J. Phys. Chem.* **1986**, *90*, 2505–2511.

(27) (a) Colussi, A. J.; Benson, S. W. *Int. J. Chem. Kinet.* **1978**, *10*, 1139–1149. (b) Varlamov, V. T.; Denisov, E. T. *Dokl. Akad. Nauk USSR* **1987**, *293(1)*, 126–128; *Chem. Abstr.* **1988**, *108*, 130931p.

(28) Richardson, J. H.; Stephenson, L. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1975**, *97*, 1160–1162.

(29) Bordwell, F. G.; Zhang, X.; Cheng, J.-P. *J. Org. Chem.* **1991**, *56*, 3216–3219.

(30) Bordwell, F. G.; Ji, G.-Z. *J. Am. Chem. Soc.*, in press.

(31) Pellerite, M. J.; Jackson, R. L.; Brauman, J. I. *J. Phys. Chem.* **1981**, *85*, 1625–1626.

(32) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465–500.

(33) Alnajjar, M. A. Unpublished results privately communicated.

The BDE of the H–O bond in phenol has been determined over the years by a number of different methods in several different laboratories: (a) 88 ± 5 in 1971,[34] (b) 86.5 ± 2 in 1978,[27a] (c) 86.5 ± 2 in 1980,[35] (d) 85 ± 1 by photoacoustic calorimetry,[36] and (e) 88 kcal in 1990 by combining the reduction potential of the phenoxyl radical with the pK_a in aqueous solution.[37] Our estimate of 90 ± 1 from eq 2 is an average for the parent and its 3-Me, 3,5-diMe, 3-MeO, 4-Cl, and 4-Br derivatives.[4]

Summary and Conclusions. Estimates of BDEs made using eq 2 have been found to agree with gas-phase literature values to ±2 kcal/mol or better for 15 compounds. For 10 other compounds where gas-phase values do not appear to be available, BDEs with error limits of ±2 kcal/mol, or better, were obtained. For the remaining eight compounds, the BDEs obtained are believed to be reliable to ±2 kcal/mol or better.

In highly sterically congested systems such as 3-aryl-1,1,5,5-tetraphenyl-2,4-pentadienes, 10-substituted 9-methylanthracenes, triphenylmethanes, and 9-phenylxanthenes, remote substituents subjected to steric attenuation are able to stabilize an anionic center much more effectively than they can stabilize a radical at that center.

A few literature BDE values have been found to be in error. That given for indene is too high because the value is actually one estimated for the benzylic H–C bond in indan. Evidence is presented to show that the best BDE for Ph_3C–H is 81 rather than 75 kcal/mol. Our estimate of 92 ± 1 kcal/mol for the acidic H–N bond in aniline is consistent with the BDE values obtained for *N*-methylaniline and diphenylamine, whereas the literature value is not.

Experimental Section

The parent compounds in Table I were commercial samples that were carefully purified, if necessary, before use. Details concerning the sources and measurements for substituted fluorenes,[2] acetophenones,[18] phenols,[4] and diphenylamines[23] have been published; those for substituted 9-methylanthracenes, diphenylmethanes, triphenylmethanes, indenes, anilines, and thiophenols will be published separately.

BDE Estimates. Since the method of estimating BDEs that we have developed is empirical, it is important to understand the accuracies and possible errors in the three terms of eq 2. The pK_{HA} measurements in DMSO can be made accurately over a range from about pK_{HA} 2 to pK_{HA} 30, with errors of ±0.1 unit or less. These values present no problem, but it should be noted that the use of *C*, which refers everything to the gas phase, has removed these pK_{HA} values from their usual standard state in DMSO.

The referencing of the oxidation potentials to either the ferrocene–ferrocenium couple (F_c/F_c^+) or the aqueous standard hydrogen electrode (SHE_{aq}) introduces some uncertainties. In our laboratory an $E_{1/2}$ of 0.875 V was observed for F_c/F_c^+ using Ag/AgI_{DMSO} as the reference electrode and platinum as the working and auxiliary electrodes with 0.1 M Et_4NBF_4 as the electrolyte. A BAS CV27 voltammeter was used for recording the CV. The $E_{1/2}$ of F_c/F_c^+ relative to the Ag/AgI_{DMSO} electrode was checked before each experiment. The corrections (usually ±20 mV) required to adjust this potential to 0.875 V were added to the oxidation potentials observed in that experiment. The oxidation potentials thus measured were referenced to SHE_{aq} by adding –0.125 V.[6b] The resulting $E_{1/2}$ of 0.750 V for F_c/F_c^+, relative to SHE_{aq}, is in good agreement with the value of 0.732 V reported by earlier workers[38] and cited by Kolthoff and Chantooni.[39] With another voltammeter we observed a smaller $E_{1/2}$ (0.805 V) for F_c/F_c^+ relative to Ag/AgI_{DMSO}. To maintain consistency we corrected the measurement made with the second instrument by adding 0.70 V. Parker[9] reports a much smaller $E_{1/2}$ (0.537) for F_c/F_c^+ relative to SHE_{aq}. Thus, it is possible that the oxidation potentials measured in different laboratories will vary by up to 0.1 V, depending upon the instrument and the electrochemical setup used, and larger differences could result depending on how the measurements are referenced to SHE_{aq}. The constant $C = 73.3$ kcal consists of the earlier constant $C = 56$ kcal (when $E_{OX}(A^-)$ values were referenced to SHE_{aq}) and a correction of 17.3 kcal for referencing the $E_{OX}(A^-)$ values to F_c/F_c^+. After realizing the ambiguities in some of the terms leading to a value of $C = 56$ kcal,[6b] the constant was termed empirical. The internal consistency of our BDEs and the success of the comparisons with gas-phase values for the 15 compounds presented in this paper provide the best evidence that our BDEs are meaningful.

Acknowledgment. We are grateful to the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. 3, 13577-28-1; **5**, 3246-80-8; $PhCH_2SO_2Ph$, 3112-88-7; $PhCH_2CN$, 140-29-4; $PhCH(CN)_2$, 3041-40-5; $CH_2(CN)_2$, 109-77-3; CH_3COCH_3, 67-64-1; CH_3CO-*t*-Bu, 75-97-8; CH_3COPh, 98-86-2; PhNH-H, 62-53-3; PhN(Me)-H, 3913-67-5; Ph_2NH, 122-39-4; PhS-H, 108-98-5; PhO-H, 108-95-2; fluorene, 86-73-7; 9-phenylfluorene, 789-24-2; 1,2-benzofluorene, 238-84-6; 2,3-benzofluorene, 243-17-4; indene, 95-13-6; 2-phenylindene, 4505-48-0; 1,3-cyclopentadiene, 542-92-7; 1,4-diphenylcyclopentadiene, 4982-34-7; 1,1,3,5,5-pentaphenyl-1,4-pentadiene, 6240-48-8; 9-methylanthracene, 779-02-2; 9,10-dihydroanthracene, 613-31-0; triphenylmethane, 519-73-3; diphenylmethane, 101-81-5; xanthene, 92-83-1; 2-benzylpyridine, 620-95-1; 4-benzylpyridine, 2116-65-6; pyrrole, 109-97-7; hydrazoic acid, 7782-79-8.

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(34) Carson, A. S.; Fine, D. H.; Gray, P.; Laye, P. G. *J. Chem. Soc. B* **1971**, 1611–1615.

(35) DeFrees, D. J.; McIver, R. T., Jr.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 3334–3338.

(36) Mulder, P.; Saastand, O. W.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 4090–4091.

(37) Lind, J.; Shen, X.; Eriksen, T. E.; Merényi, G. *J. Am. Chem. Soc.* **1990**, *112*, 479–482.

(38) Le Démézet, M. *Bull. Soc. Chim. Fr.* **1970**, 4550–4554. Courtot-Coupez, J.; Laouenan, A.; Le Démézet, M. *C. R. Acad. Sci. Ser. C* **1968**, *267*, 1475–1478.

(39) Kolthoff, I. M.; Chantooni, M. K., Jr. *J. Phys. Chem.* **1972**, *76*, 2024–2034.