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# Acidities and Homolytic Bond Dissociation Energies of the Acidic C–H Bonds in Radical Cations

Xianman Zhang and F. G. Bordwell*

*Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113*

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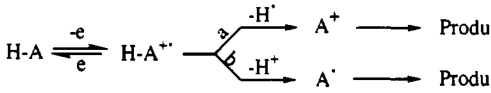
The homolytic bond dissociation energies ($\mathrm{BDE_{HA^{+\bullet}}}$) of the acidic C–H bonds in radical cations of the type $\mathrm{HA^{+\bullet}}$ have been estimated by using the equation $\mathrm{BDE_{HA^{+\bullet}}} = \mathrm{BDE_{HA}} + 23.1[E_{ox}(\mathrm{A^{\bullet}}) - E_{ox}(\mathrm{HA})]$. The $\mathrm{BDE_{HA}}$ values of the acidic H–A bonds in neutral molecules were estimated from $\mathrm{p}K_{\mathrm{HA}}$ and $\mathrm{E_{ox}(A^-)}$ values in DMSO. Most $E_{ox}(\mathrm{A^-})$ and $E_{ox}(\mathrm{A^{\bullet}})$ values were obtained from the reversible oxidation potentials of the conjugate bases of HA, and most $E_{ox}(\mathrm{HA})$ values were obtained from the irreversible oxidation potentials of the neutrals by cyclic voltammetric measurements. The method has been applied to obtain $\mathrm{BDE_{HA^{+\bullet}}}$ values for thirteen 9-(dialkylamino)fluorenes, two 2-benzoyl-*N,N'*-dialkylperhydropyrimidines, two $\alpha,\alpha$-bis(alkylamino)acetophenones, three triphenylmethanes, two diphenylmethanes, 9,10-dihydroanthracene, four xanthenes, toluene, four fluorenes, and three arylacetonitriles. (The acidities of the corresponding radical cations have also been estimated.) For most of the carbon-centered radical cations stabilized by one or two adjacent dialkylamino groups, the $\mathrm{BDE_{HA^{+\bullet}}}$ values were estimated to be in the 22–40 kcal/mol range; i.e., they are 30–50 kcal/mol lower than the corresponding $\mathrm{BDE_{HA}}$ values in the neutral parents. These relatively low $\mathrm{BDE_{HA^{+\bullet}}}$ values were correlated with the stabilities of the cations formed in reactions of the type $\mathrm{HA^{+\bullet} \rightarrow H^{\bullet} + A^+}$. On the other hand, the $\mathrm{BDE_{HA^{+\bullet}}}$ values for substituted aromatic hydrocarbons were found to be controlled primarily by the stabilities of the radical cations, $\mathrm{HA^{+\bullet}}$, rather than by the stabilities of the product cations. Aromatic hydrocarbons containing two or more aryl groups usually gave radical cations with $\mathrm{BDE_{HA^{+\bullet}}}$ values in the 30–40 kcal/mol range whereas those with only one aryl group gave $\mathrm{BDE_{HA^{+\bullet}}}$ values in the 40–50 kcal/mol range.

## Introduction

The loss of an electron from a neutral molecule, HA, to form a radical cation, $\mathrm{HA^{+\bullet}}$, is the initial step for numerous oxidative degradations of organic molecules. The radical cations formed can react further by either losing a proton or a hydrogen atom, as outlined in Scheme I.

**Scheme I**



In solution, loss of a proton is ordinarily expected to be the favored pathway for compounds where the proton is attached to a *carbon* atom because these radical cations are often superacids with large negative $\mathrm{p}K_{\mathrm{HA^{+\bullet}}}$ values.[1,2] The high acidity of hydrocarbon radical cations can be moderated appreciably by suitable substitution, however. For example, the 9-C–H bond in the radical cation derived from fluorene, $\mathrm{FlH_2^{+\bullet}}$, is estimated to have a $\mathrm{p}K_{\mathrm{HA^{+\bullet}}}$ value of ca. −17 in DMSO, but introduction of a 2-$\mathrm{Me_2N}$ group increases the $\mathrm{p}K_{\mathrm{HA^{+\bullet}}}$ to +1, and the value becomes +6.9 for the 9-C–H bond in 2,7-$\mathrm{(Me_2N)_2FlH_2^{+\bullet}}$.[3] Radical cations where the acidic hydrogen atom is attached to *nitrogen* are not superacids, e.g., $\mathrm{p}K_{\mathrm{HA^{+\bullet}}}$ for the N–H bonds in the radical cations derived from phenothiazine and aniline are 4.3 and 7, respectively, in DMSO. Loss of a hydrogen atom (to a suitable acceptor) could conceivably be competitive with loss of a proton, for less acidic radical cations such as these. Indeed, Nelsen and Ippoliti have argued that amine radical cations of the type $\mathrm{R_3N^{+\bullet}}$ may have low enough C–H homolytic bond dissociation energies to allow paths a and b in Scheme I to be competitive.[4] They estimated from eq 1 that the bond dissociation en-

$$\mathrm{BDE_{HA^{+\bullet}}} = \mathrm{BDE_{HA}} + 23.1[E_{ox}(\mathrm{A^{\bullet}}) - E_{ox}(\mathrm{HA})] \quad (1)$$

ergy value for the acidic C–H bond in the radical cation derived from 9-(2-adamantyl)-9-azabicyclo[3.3.1]nonane may be as low as 18 kcal/mol on the basis of an estimated BDE for the acidic C–H bond in the neutral. (Henceforth, kcal/mol will be abbreviated as kcal.) This value is no doubt too low because the estimated $\mathrm{p}K_{\mathrm{HA^{+\bullet}}}$ value is too high,[3,5] but Dinnocenzo and Banach have shown that $\mathrm{(4\text{-}MeOC_6H_4)_2NCH_3^{+\bullet}}$ has a $\mathrm{p}K_{\mathrm{HA^{+\bullet}}}$ of about 10 in $\mathrm{CH_3CN}$ and estimate the $\mathrm{BDE_{HA^{+\bullet}}}$ of the acidic C–H bond to be about 47 kcal, as an upper limit.[5] Also, the $\mathrm{BDE_{HA^{+\bullet}}}$ value for the C–H bond in the $\mathrm{(CH_3)_2NCH_2\text{-}H^{+\bullet}}$ radical cation has recently been estimated by eq 1 to be 34 kcal, compared to 84 kcal for the parent $\mathrm{(CH_3)_2NCH_2\text{-}H}$ molecule.[6] In any event, the strengths of H–A bonds in radical cations are of interest for gas-phase and theoretical chemistry.

Examination of eq 1 shows that this method of estimating the homolytic bond dissociation energies of the H–A bonds in radical cations of the type $\mathrm{H\text{-}A^{+\bullet}}$ requires a knowledge of $\mathrm{BDE_{HA}}$ values and the determination of the oxidation potentials of HA and of the corresponding radical $\mathrm{A^{\bullet}}$. In our laboratory we have developed a simple method of estimating $\mathrm{BDE_{HA}}$ values (eq 2) and have ap-

$$\mathrm{BDE_{HA}(kcal)} = 1.37\mathrm{p}K_{\mathrm{HA}} + 23.1E_{ox}(\mathrm{A^-}) + C \quad (2)$$

plied it to obtain estimates of BDEs of several hundred weak acids containing H–C, H–N, H–O, and H–S bonds. Comparisons with gas-phase BDEs have usually shown agreement to ±2 kcal, or better.[7] The oxidation potentials of most anions, $\mathrm{A^-}$, as obtained in DMSO by cyclic voltammetric measurements under the usual conditions (scan rates of 100 mV/s) are irreversible but generally agree to within 2 kcal, or better, with the reversible values obtained

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(1) Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 2473–2474.

(2) (a) Bordwell, F. G.; Cheng, J.-P.; Bausch, M. J. *J. Am. Chem. Soc.* **1988**, *110*, 2867–2872; 2872–2877. (b) Cheng, J.-P. Ph.D. Dissertation, Northwestern University, Evanston, IL, 1987.

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

(4) Nelsen, S. F.; Ippoliti, J. T. *J. Am. Chem. Soc.* **1986**, *108*, 4879–4881.

(5) Dinnocenzo, J. P.; Banach, T. E. *J. Am. Chem. Soc.* **1989**, *111*, 8646–8653.

(6) Griller, D.; Simoes, J. A. M.; Mulder, P.; Sim, B. A.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1989**, *111*, 7872–7876.

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

0022-3263/92/1957-4163$03.00/0

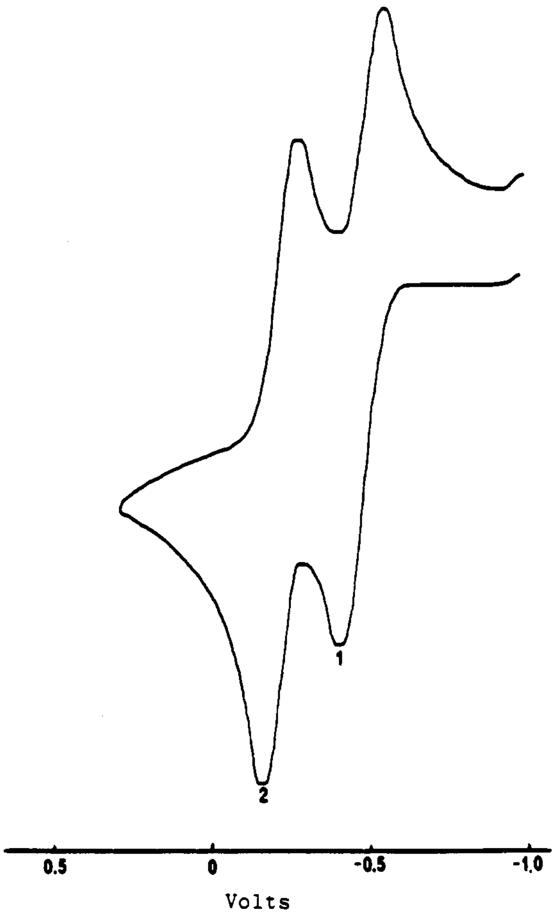
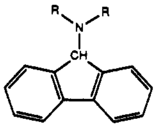
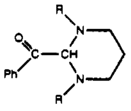


**Figure 1.** Reversible cyclic voltammetric waves for the oxidation of a [PhCOC(morpholino)$_2$]$^-$ anion (A$^-$) in DMSO. Peak 1 represents the oxidation of A$^-$ to A$^\bullet$, and peak 2 the oxidation of A$^\bullet$ to A$^+$. The upper peaks represent the corresponding reduction potentials of A$^+$ and A$^\bullet$, respectively.

under fast scan conditions.[8] We have found that the oxidation potentials of the anions derived from 9-(dialkylamino)fluorenes **1**[3] and 2-benzoyl-*N*,*N'*-dialkylperhydropyrimidines **2**[9] are reversible under the usual conditions. These radicals must persist for some time on the electrode, presumably because a sizable fraction of the spin density is located on the nitrogen atom, which helps to inhibit dimerization or hydrogen atom abstraction. Furthermore, we have now found that the radicals derived by the oxidation of anions of **1**, **2**, and $\alpha,\alpha$-bis(cycloalkylamino)acetophenones **3** can be further oxidized reversibly in DMSO on the electrode to give the corresponding cations. This means that from a single cyclic voltammetric (CV) measurement one can obtain $E_{1/2}$ values for both $E_{ox}(A^-)$ and $E_{ox}(A^\bullet)$ as shown in Figure 1.

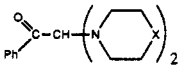


**1**



R = Me or Et

**2**



X = CH$_2$ or O

**3**

In this paper we will shown how these data can be used to estimate the BDEs of the acidic C–H bonds in the radical cations derived from **1**, **2**, and **3** and will then extend the study to C–H bonds in other HA$^{+\bullet}$-type radical cations.

**Scheme II**

$$\begin{array}{lcll}
\text{H-A}^{+\bullet} + e^- & \rightleftharpoons & \text{H-A} & -E_{ox}(\text{HA}) \\
\text{H-A} & \rightleftharpoons & \text{H}^+ + \text{A}^- & \text{p}K_{\text{HA}} \\
\text{A}^- & \rightleftharpoons & \text{A}^\bullet + e^- & E_{ox}(\text{A}^-) \\
\text{A}^\bullet & \rightleftharpoons & \text{A}^+ + e^- & E_{ox}(\text{A}^\bullet) \\
\text{H}^+ + e^- & \rightleftharpoons & \text{H}^\bullet & C \\
\hline
\text{H-A}^{+\bullet} & \rightleftharpoons & \text{H}^\bullet + \text{A}^+ & \text{BDE}_{\text{HA}^{+\bullet}}
\end{array}$$

## Results and Discussion

**Thermodynamic Cycles for Estimating Acidities and Homolytic Bond Dissociation Energies of the Acidic H–C Bonds in HA$^{+\bullet}$-Type Radical Cations.** A thermodynamic cycle from which a method of estimating radical cation acidities was derived (eq 3) has been presented earlier in a paper from this laboratory.[1]

$$\text{p}K_{\text{HA}^{+\bullet}} = \text{p}K_{\text{HA}} + 16.8[E_{ox}(\text{A}^-) - E_{ox}(\text{HA})] \quad (3)$$

A similar thermodynamic cycle for estimating the homolytic bond dissociation energies of the acidic H–C bonds in radical cations is presented in Scheme II.

The summation of the terms in Scheme II, expressed in kcal, gives the homolytic bond dissociation energies of the acidic H–A bonds in HA$^{+\bullet}$-type radical cations (eq 4).

$$\text{BDE}_{\text{HA}^{+\bullet}} = 1.37\text{p}K_{\text{HA}} + 23.1E_{ox}(\text{A}^-) + C + 23.1[E_{ox}(\text{A}^\bullet) - E_{ox}(\text{HA})] \quad (4)$$

The first three terms on the right side of eq 4 are identical with those in eq 2, which means that eq 4 can be rewritten as eq 1. In other words, for these weak acids we now have simple methods for estimating *both* BDE$_{\text{HA}}$ and BDE$_{\text{HA}^{+\bullet}}$, as well as p$K_{\text{HA}^{+\bullet}}$, through measurements of p$K_{\text{HA}}$ and relevant electrochemical data.

**Homolytic Bond Dissociation Energies of HA$^{+\bullet}$-Type Radical Cations Derived from 9-(Dialkylamino)fluorenes.** BDE$_{\text{HA}}$ values for the acidic H–C bonds in eight 9-(dialkylamino)fluorenes, and the p$K_{\text{HA}^{+\bullet}}$ values for the corresponding radical cations, were reported and discussed in 1988.[3] All of the oxidation potentials of the 9-(dialkylamino)fluorenide ions studied were reversible and all but one of the radicals formed have now been found to be further oxidized reversibly to the corresponding cations (e.g., see Figure 1). The $E_{1/2}$ for the second oxidation wave provides the value for $E_{ox}(\text{A}^\bullet)$ needed in eq 1 or eq 4, along with BDE$_{\text{HA}}$ and $E_{ox}(\text{HA})$, to estimate BDE$_{\text{HA}^{+\bullet}}$ values for the acidic C–H bonds in the radical cations derived from these 9-(dialkylamino)fluorenes. Table I summarizes the p$K_{\text{HA}}$, $E_{ox}(\text{A}^-)$, $E_{ox}(\text{A}^\bullet)$, $E_{ox}(\text{HA})$, p$K_{\text{HA}^{+\bullet}}$, and BDE$_{\text{HA}}$ data together with the estimated BDE$_{\text{HA}^{+\bullet}}$ values for thirteen 9-(dialkylamino)fluorenes.

In these oxidations there is strong evidence to indicate that the electron is removed from the nitrogen atom in the dialkylamino group rather than from the $\pi$ system of the fluorene ring.[3] This conclusion is supported by the observations (a) that the oxidation potential of fluorene itself, where the electron *is* removed from the fluorene $\pi$ system, is 0.65 V ($\sim$15 kcal) more positive than the most positive value for the oxidation potentials of the 9-(dialkylamino)fluorenes in Table I and (b) that the presence of 2-methoxy or 2,7-dimethoxy groups on 9-(dialkylamino)fluorenes has relatively little effect on p$K_{\text{HA}^{+\bullet}}$, whereas when these methoxy groups are introduced into fluorene itself, they decrease the radical cation acidity by as much as 11 p$K_{\text{HA}^{+\bullet}}$ units.[3]

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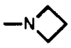
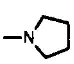
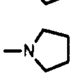
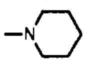
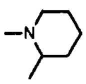
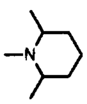
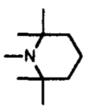
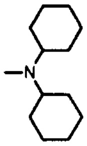
[8] (a) Bausch, M. J.; Gostowski, R. J. *J. Org. Chem.* **1991**, *56*, 6260–6262. (b) Satish, A. V.; Zion, D. A.; Hupp, J. T. Unpublished results.

[9] Bordwell, F. G.; Vanier, N. R.; Zhang, X. *J. Am. Chem. Soc.* **1991**, *113*, 9856–9857.

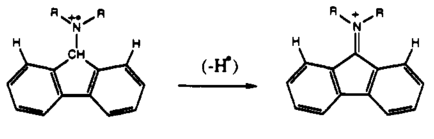
**Table I. Acidities and Homolytic Bond Dissociation Energies of 9-(Dialkylamino)fluorenes (9-$R_1R_2NFlH$) and of the Corresponding Radical Cations**

| no. | compound | p$K_{HA}$[b] | $E_{ox}(A^-)$[e] | $E_{ox}(HA)$[g] | $E_{ox}(A^\bullet)$[h] | p$K_{HA^{+\bullet}}$[j] | $BDE_{HA}$[k] | $BDE_{HA^{+\bullet}}$[l] |
|---|---|---|---|---|---|---|---|---|
| 1 | $R_1 = R_2 = Me$ | 22.5 | -1.418 | 0.575 | -0.928 | -11 | 71.5 | 37 |
| 2 | $R_1 = R_2 = Et$ | 21.4 | -1.388 | 0.555 | -0.919 | -11.5 | 70.5 | 36.5 |
| 3 | $R_1 = R_2 = i\text{-}Pr$ | 20.8 | -1.242 | 0.605 | -0.822 | -10 | 73 | 40 |
| 4 | $R_1$ = n-Bu; $R_2$ = Me | 22.1[c] | -1.360[c] | 0.517[f] | -0.893 | -9.5 | 72 | 40 |
| 5 | $R_1 = PhCH_2$; $R_2$ = Me | 22.0[c] | -1.334[c] | 0.620[f] | -0.835 | -11 | 72.5 | 39 |
| 6 |  | 21.8 | -1.620 | 0.635 | -0.930 | -16 | 66 | 30 |
| 7 |  | 22.2 | -1.553 | 0.455 | -0.980 | -12 | 68 | 35 |
| 8 |  [a] | 22.2 | -1.477 | 0.424 | -0.960 | -10 | 69 | 37.5 |
| 9 |  | 22.5 | -1.382 | 0.605 | -0.831 | -11 | 72 | 39 |
| 10 |  | 21.4 | -1.348[f] | 0.469[f] | -0.839 | -9 | 71.5 | 41 |
| 11 |  | 19.4 | -1.198 | 0.535 | -0.825 | -10 | 72 | 41 |
| 12 |  | 18.2 | -1.166[f] | 0.525[f] | -0.200[i] | -10 | 71 | 54.5 |
| 13 |  | 20.1[d] | -1.208[f] | 0.451[f] | -0.770 | -8 | 73 | 44.5 |

[a] 2,7-Dimethoxy-9-pyrrolidinofluorene. [b] Measured in DMSO against two indicators,[3] unless otherwise indicated. [c] Reference 10. [d] Measured by Dr. T.-Y. Lynch. [e] Reversible redox potentials in DMSO measured by cyclic voltammetry under the reaction conditions described earlier and referenced to the ferrocene–ferrocenium ($Fc/Fc^+$) couple; $E_{1/2}$ reported.[7] The $E_{1/2}$ values reported here are about 25–35 mV more negative than the $E_p$ values, which leads to $BDE_{HA}$ values 0.5–1 kcal/mol lower than previously reported and to p$K_{HA^{+\bullet}}$ values 0.5 p$K_{HA^{+\bullet}}$ units more negative.[3] [f] This work. [g] Irreversible oxidation potentials referenced to the $Fc/Fc^+$ couple; $E_p$ reported. [h] Reversible redox potentials measured by cyclic voltammetry in DMSO under the conditions described earlier and referenced to the $Fc/Fc^+$ couple; $E_{1/2}$ reported unless otherwise indicated. [i] Irreversible oxidation potential and $E_p$ reported. [j] Calculated by using eq 3. [k] Calculated by using eq 2 with $C = 73.3$.[7] [l] Calculated by using eq 1.

The oxidation potentials of the anions derived from 9-$NH_2$-, 9-NHMe-, and 9-NHBu-fluorenes are more negative than that of 9-azetidinylfluorenide ion, and the radical stabilization energies are estimated to be equally large.[10] But the oxidation potentials are irreversible, indicating that the radicals formed are unstable under the reaction conditions. The radicals formed differ from the 9-(dialkylamino)fluorenyl radicals in that they can undergo a hydrogen atom disproportionation, i.e., $2RNHFl^\bullet \rightarrow RN{=}Fl + RNHFlH$. This instability, of course, precludes measurement of $E_{ox}(A^\bullet)$ and estimation of $BDE_{HA^{+\bullet}}$ for the corresponding radical cations, $RNHFlH^{+\bullet}$. It is possible that these CVs could be made reversible by using fast scan techniques, but this has not been attempted as yet.

The $BDE_{HA^{+\bullet}}$ values in Table I vary over a range of about 30 to 55 kcal. One would expect the values to change depending on the stability of the radical cation (4), for which the $E_{ox}(HA)$ values provide a reasonable measure, and the stability of the product cation (5) formed by loss of a hydrogen atom from the radical cation 4, for which $E_{ox}(A^\bullet)$ provides a reasonable measure. In other words, more negative $E_{ox}(A^\bullet)$ values are associated with more stable $A^+$ product cations and lower $BDE_{HA^{+\bullet}}$ values, whereas more negative $E_{ox}(HA)$ values are associated with more stable initial-state radical cations and higher $BDE_{HA^{+\bullet}}$ values. Both the initial-state radical cation 4 and the product cation 5 are subject to steric strains caused by spacial repulsions between the C-1 and C-8 hydrogen atoms on the fluorene ring and the R groups attached to nitrogen, but the strains are greater in 5 because of the shorter C=N than C—N bond length and the rigid structure of the double bond with the consequent much shorter distance between the C-1 and C-8 hydrogen atoms and the R groups in 5.



4 5

The most negative $E_{ox}(A^\bullet)$ values in Table I are those for the radical cations derived from the 9-(dialkylamino)fluorenes bearing the least sterically demanding 9-substituents (nos. 1, 2, 6, 7, and 8). For these, the stability of the product cation (5) appears to be of greater importance than the stability of the initial-state radical cation (4) and the $BDE_{HA^{+\bullet}}$ values are the lowest in the table. The $E_{ox}(A^\bullet)$ values are less negative for radical cations derived from fluorenes with greater steric demands (nos. 3, 4, 5, 9–13). The $BDE_{HA^{+\bullet}}$ values tend to be higher, therefore, and this tendency is not influenced appreciably by the $E_{ox}(HA)$ values, which are usually in the same range as those for fluorenes containing the less sterically demanding substituents. (This is not surprising because the

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(10) Bordwell, F. G.; Lynch, T.-Y. *J. Am. Chem. Soc.* **1989**, *111*, 7558–7562.

**Table II. Acidities and Homolytic Bond Dissociation Energies of 2 and 3 and of the Corresponding Radical Cations**

| compound | $\mathrm{p}K_{\mathrm{HA}}{}^{b}$ | $E_{\mathrm{ox}}(\mathrm{A}^{-})^{c}$ | $E_{\mathrm{ox}}(\mathrm{HA})^{d}$ | $E_{\mathrm{ox}}(\mathrm{A}^{\bullet})^{c}$ | $\mathrm{p}K_{\mathrm{HA}^{+\bullet}}{}^{e}$ | $\mathrm{BDE}_{\mathrm{HA}}{}^{f}$ | $\mathrm{BDE}_{\mathrm{HA}^{+\bullet}}{}^{g}$ |
|---|---|---|---|---|---|---|---|
| **2** (R = Me)$^{a}$ | $27.9^{a}$ | −1.678 | 0.748 | −1.451 | −13 | 73 | 22 |
| **2** (R = Et)$^{a}$ | $27.0^{a}$ | −1.675 | 0.596 | −1.490 | −11 | 72 | 23 |
| **3** (X = $CH_2$) | 25.6 | −1.506 | 0.573 | −1.203 | −9.4 | 74 | 33 |
| **3** (X = O) | 24.4 | −1.360 | 0.747 | −1.080 | −11 | 75 | 33 |

[a] Reference 9. [b] Measured in DMSO against two indicators. [c] Reversible redox potentials were measured by cyclic voltammetry in DMSO under the reaction conditions described earlier and referenced to the ferrocene–ferrocenium couple;[7] $E_{1/2}$ reported. [d] Irreversible oxidation potentials; $E_p$ reported. [e] Calculated by using eq 3. [f] Calculated by using eq 2 with $C = 73.3$.[7] [g] Calculated by using eq 1.

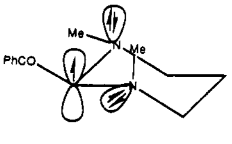
**Table III. $\mathrm{BDE}_{\mathrm{HA}^{+\bullet}}$ Values for Aryl Hydrocarbons and Arylacetonitriles**

| no. | compound | $\mathrm{p}K_{\mathrm{HA}}{}^{a}$ | $E_{\mathrm{ox}}(\mathrm{A}^{-})^{c}$ | $E_{\mathrm{ox}}(\mathrm{HA})^{c}$ | $E_{\mathrm{ox}}(\mathrm{A}^{\bullet})^{c}$ | $\mathrm{p}K_{\mathrm{HA}^{+\bullet}}{}^{p}$ | $\mathrm{BDE}_{\mathrm{HA}}{}^{q}$ | $\mathrm{BDE}_{\mathrm{HA}^{+\bullet}}{}^{r}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | triphenylmethane | 30.6 | −1.486 | 1.415 | $-0.133^{j}$ | −18 | 81 | 45 |
| 2 | *p*-$PhCOC_6H_4CHPh_2$ | 22.4 | $-1.103^{d}$ | 2.005 | $-0.181^{i}$ | −30 | 78.5 | 28 |
| 3 | *p*-$NO_2C_6H_4CHPh_2$ | 16.8 | $-0.791^{d}$ | 2.135 | $-0.063^{d}$ | −32 | 78 | 27 |
| 4 | diphenylmethane | 32.2 | −1.540 | 1.845 | $-0.160^{k}$ | −25 | 82 | 36 |
| 5 | *p*-$NCC_6H_4CH_2Ph$ | 25.3 | −1.138 | 2.035 | $0.210^{l}$ | −28 | 82 | 39.5 |
| 6 | 9,10-dihydroanthracene | 30.1 | −1.575 | 1.618 | $-0.410^{m}$ | −24 | 78 | 31 |
| 7 | xanthene | 30.0 | −1.685 | 1.135 | $-0.347^{j}$ | −18 | 75 | 41 |
| 8 | 9-cyanoxanthene | 13.6 | −0.993 | 1.405 | $0.120^{n}$ | −27 | 69 | 39 |
| 9 | 9-phenylxanthene | 27.9 | −1.531 | 1.215 | $-0.352^{j}$ | −18 | 76 | 40 |
| 10 | 9-(*p*-MeOPh)xanthene | 28.4 | −1.573 | 1.175 | $-0.410^{n}$ | −18 | 76 | 39 |
| 11 | toluene | $\sim 43^{b}$ | $-1.935^{e}$ | $1.955^{i}$ | $0.220^{k}$ | −23 | 88 | $48^{s}$ |
| 12 | fluorene | 22.6 | $-1.069^{f}$ | $1.275^{f}$ | $0.250^{k}$ | −17 | 79.5 | 56 |
| 13 | 9-phenylfluorene | 17.9 | $-1.028^{f}$ | $1.335^{f}$ | $0.110^{n}$ | −22 | 74 | 46 |
| 14 | 9-(*o*-MePh)fluorene | 18.8 | $-0.977^{f}$ | $1.390^{i}$ | $0.180^{n}$ | −21 | 76 | 48 |
| 15 | 9-mesitylfluorene | 18.6 | $-0.997^{d,f}$ | $1.335^{f}$ | $0.217^{i}$ | −21 | 76 | 50 |
| 16 | $PhCH_2CN$ | 21.9 | $-0.923^{g}$ | $2.275^{g}$ | $0.785^{o}$ | −32 | 82 | 47.5 |
| 17 | *p*-$MeOC_6H_4CH_2CN$ | 23.8 | $-1.092^{g}$ | $1.455^{g}$ | $0.195^{o}$ | −19 | 81 | 51.5 |
| 18 | *p*-$NCC_6H_4CH_2CN$ | 16.0 | $-0.538^{g}$ | $2.595^{g}$ | $1.125^{o}$ | −37 | 83 | 49 |

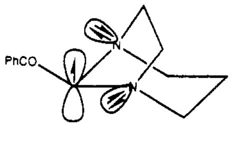
[a] Unless otherwise indicated, these $\mathrm{p}K_{\mathrm{HA}}$ values in DMSO were measured against two indicators and were reported in earlier papers.[12] [b] Estimated.[13] [c] All oxidation potentials of the anions and the corresponding radicals were measured in DMSO, unless otherwise indicated, and were referenced to ferrocene–ferrocenium ($Fc/Fc^+$) couple.[7] [d] This work; reversible oxidation potential; $E_{1/2}$ reported. [e] The $E_{\mathrm{ox}}(\mathrm{A}^-)$ value was measured by using the lithium derivative in THF with HMPA added to dissociate the lithium aggregates.[14] The reduction potential of benzyl radical ($PhCH_2^{\bullet}$) in acetonitrile was measured to be −1.96 V (referenced to $Fc/Fc^+$).[15] [f] Reference 12c. [g] Reference 12d. [h] Irreversible oxidation potentials measured in acetonitrile and referenced to $Fc/Fc^+$ couple.[2b] [i] This work; irreversible oxidation potential; $E_p$ reported. [j] $E_{1/2}$ of the related radicals were measured with SHACV in sulfolane/3-methylsulfolane (5%).[16] [k] Reference 15. [l] Measured in acetonitrile with gold minigrid electrode.[17] [m] measured in acetonitrile.[5] [n] Reference 18. [o] Measured in acetonitrile.[19] [p] Calculated by using eq 3. [q] Calculated by using eq 2 with $C = 73.3$.[7] [r] Calculated by using eq 1. [s] Griller and Wayner[6] et al. estimated the $\mathrm{BDE}_{\mathrm{HA}^{+\bullet}}$ to be 50 kcal/mol.

electron is being removed from a nitrogen atom which evidently can access to the electrode no matter what the size of the group.) The net result is a slight increase in the size of the $\mathrm{BDE}_{\mathrm{HA}^{+\bullet}}$ values.

**Homolytic Bond Dissociation Energies of $HA^{+\bullet}$-Type Radical Cations Derived from 2-Benzoyl-*N*,*N*′-dialkylperhydropyrimidines and α,α-Bis(alkylamino)acetophenones.** Recently we reported that the radical **6$^{\bullet}$** derived from 2-benzoyl-*N*,*N*′-dimethylperhydropyrimidine (**2**, R = Me) is more stable than radical **7$^{\bullet}$** by 16 kcal because **6$^{\bullet}$** is stabilized by one (or two) 3-electron bond(s) formed by lone-pair–odd-electron overlap.[9] In radical **7$^{\bullet}$** formation of a 3-electron bond is precluded by the ethano bridge, which requires the orbitals on the nitrogen atoms holding the lone pairs to be nearly orthogonal to that holding the odd electron. The oxidation potential of the anion derived from **2** is reversible, whereas that from the brided analogue is not.[9] Further oxidation of radical **6$^{\bullet}$** to the corresponding cation has now been found also to be reversible, allowing the $\mathrm{BDE}_{\mathrm{HA}^{+\bullet}}$ values of the C–H bonds in radical cations to be estimated (Table II).

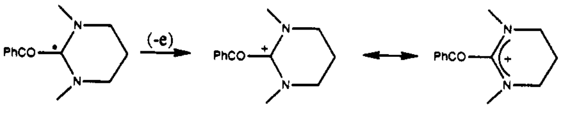


**6$^{\bullet}$**



**7$^{\bullet}$**

Examination of eq 1 shows that the size of the $\mathrm{BDE}_{\mathrm{HA}^{+\bullet}}$ values depends on the size of the $\mathrm{BDE}_{\mathrm{HA}}$, $E_{\mathrm{ox}}(\mathrm{A}^{\bullet})$, and $E_{\mathrm{ox}}(\mathrm{HA})$. Comparison shows that the $\mathrm{BDE}_{\mathrm{HA}}$ and $E_{\mathrm{ox}}(\mathrm{HA})$ values for compounds **1** in Table I and compounds **2** in Table II are for the most part similar in size but that the $E_{\mathrm{ox}}(\mathrm{A}^{\bullet})$ values for the radicals derived from **2** are, on average, about 0.4 V (∼9 kcal) more negative than those for the radicals derived from **1**. This difference accounts for much of the ∼10 kcal lower $\mathrm{BDE}_{\mathrm{HA}^{+\bullet}}$ values for the radical cations derived from **2** than those of the least sterically hindered 9-$R_2NFlH^{+\bullet}$ radical cations in Table I. The assumption that $E_{\mathrm{ox}}(\mathrm{A}^{\bullet})$ values provide a reasonable measure of cation stability leads to the conclusion that the lower $\mathrm{BDE}_{\mathrm{HA}^{+\bullet}}$ values for **2** are due to greater cation stability. This appears reasonable because radical **6$^{\bullet}$**, derived from **2**, gives a cation (**8**) where the positive charge can be delocalized over two nitrogen atoms compared to only one nitrogen atom in the cations derived from 9-$R_2NFl^{\bullet}$ radicals. On the other hand, the presence of a second nitrogen in $(c\text{-}C_5H_{10}N)_2\dot{C}COPh$ does not appear to either stabilize or destabilize the radical (see below).



**6$^{\bullet}$** **8a$^{+}$** **8b$^{+}$**

Compounds **3** in Table II differ from compounds **2** in that the two nitrogen atoms are contained in separate rings. Theoretical calculations for $H\text{–}CH(NH_2)_2$, a model for **3**, predict that the BDE of the H–C bond will be 3.5–4.5 kcal lower than that in $H\text{–}CH_2NH_2$.[11] The BDE for the acidic H–C bond in $(c\text{-}C_5H_{10}N)_2CHCOPh$ is, however, about the same as the BDE for the acidic H–C bond in $c\text{-}C_5H_{10}NCH_2COPh$,[10] i.e., 72 kcal, as estimated by eq 2. This is understandable since an examination of scalar molecular models indicates that only one of the two amino groups can interact with the orbital on carbon bearing the odd electron because of steric constraints. The average $BDE_{HA^{+\bullet}}$ values estimated for the radical cations derived from **3** are about 10 kcal higher than those derived from **2**. Examination of Table II shows that the average $E_{ox}(A^\bullet)$ values for the radicals derived from **3** are less negative by about 7.5 kcal than those for the radicals derived from **2**. Again, the relative stabilities of the cations formed on oxidation of $A^\bullet$ are likely to be the deciding factor. Delocalization of the positive charge between the two nitrogen atoms provides a stabilizing factor in the cations derived from **3**, as well as in those derived from **2**, but delocalization in a single ring is evidently more effective than in separate rings. Still, the $BDE_{HA^{+\bullet}}$ values for the radical cations derived from **3** are among the lowest that we have observed.

**Homolytic Bond Dissociation Energies of $HA^{+\bullet}$-Type Radical Cations Derived from Triphenylmethanes, Other Aryl Hydrocarbons, and Arylacetonitriles.** The oxidation potentials of anions forming radicals wherein the odd electron can be delocalized into three phenyl rings, as in compounds nos. 1–3, 14, and 15 in Table III, are often reversible or partially reversible even under the ordinary conditions (scan rates of 100 mV/s). In this section we have collected data from our laboratory and/or other laboratories in order to estimate $BDE_{HA^{+\bullet}}$ values for the acidic C–H bonds in $HA^{+\bullet}$-type radical cations derived from various such hydrocarbons and related compounds. The $BDE_{HA^{+\bullet}}$ values, together with $pK_{HA}$, $pK_{HA^{+\bullet}}$, and electrochemical data, are summarized in Table III.

In the previous section we have identified two factors that determine the size of $BDE_{HA^{+\bullet}}$ values, as applied to carbon-centered radical cations stabilized by adjacent dialkylamino groups, namely, the size of $E_{ox}(HA)$ and $E_{ox}(A^\bullet)$. We found that the relatively low $BDE_{HA^{+\bullet}}$ values for these radical cations (22–40 kcal) could be correlated primarily with the ability of the adjacent nitrogen atom(s) to stabilize the positive charge in the product cations formed in the reaction $HA^{+\bullet} \rightarrow H^\bullet + A^+$, moderated by the effects on the radical cation stabilities. The principal factor associated with stabilization of the product cations was the highly negative $E_{ox}(A^\bullet)$ values (in the range of −0.8 to −1.5 V referenced to the $Fc/Fc^+$ couple). Examination of Table III shows that the first ten entries have $BDE_{HA^{+\bullet}}$ values that average 36.5 kcal, which is close to the average for the first 10 entries in Table I (37.8 kcal). But the average $E_{ox}(A^\bullet)$ value for the first 10 entries in Table III is −0.17 V compared to −0.88 V for the first 10 entries in Table I. The difference of about 16 kcal shows that the product cations derived from these hydrocarbons are much less stable than those derived from compounds where the positive charge can be delocalized to nitrogen. Further examination shows that the $E_{ox}(HA)$ values for the first 10 hydrocarbons in Table III average 1.6 V compared to 0.56 V for the 9-(dialkylamino)fluorenes. This difference of 24 kcal more than compensates for the less negative $E_{ox}(A^\bullet)$ values. In other words, entries 1–10 in Table III have $BDE_{HA^{+\bullet}}$ values comparable to those of the 9-(dialkylamino)fluorenes because their radical cations are much less stable, leading to facile loss of a hydrogen atom. Introduction of the electron-withdrawing *p*-PhCO or *p*-$NO_2$ groups into triphenylmethane evidently lowers the $BDE_{HA^{+\bullet}}$ values by further destabilizing the radical cations. On the other hand, the *p*-CN group in $p\text{-}CNC_6H_4CH_2Ph$ appears to destabilize the product cation more than it destabilizes the radical cation [the $\Delta E_{ox}(A^\bullet)$ and $\Delta E_{ox}(HA)$ values, relative to those for diphenylmethane, are 0.37 V and 0.19 V, respectively].

The stronger H–A bond strengths for the radical cations derived from entries 11–18 in Table III, compared to nos. 1–10, appear to be a consequence primarily of the relative instability of the cations that would be formed by loss of a hydrogen atom. Note that introduction of mesityl (no. 15) and phenyl (no. 13) groups into the 9-position of fluorene appears to lower the $BDE_{HA^{+\bullet}}$ values of the radical cations by 6 and 10 kcal, respectively, presumably because of their ability to stabilize the corresponding product cations.

Substitution of an α-CN group into toluene weakens the acidic C–H bond in the neutral molecule by 6 kcal because of its ability to stabilize the radical $10^\bullet$. On the other hand, the $BDE_{HA^{+\bullet}}$ for the acidic C–H bond in the phenylacetonitrile radical cation (**11**) is essentially identical with that for the toluene radical cation. Evidently the 7.4 kcal higher $E_{ox}(HA)$ value for $PhCH_2CN$ than $PhCH_3$ is compensated by a comparable destabilizing effect of the cyano group in cation **12**.

$$PhCH_2CN \xrightarrow{(-H^\bullet)} Ph\dot{C}H\text{-}C\equiv N \leftrightarrow PhCH{=}C{=}N^\bullet$$

**9** **10a•** **10b•**

**11** **12a** **12b** **12c**

Introduction of a *p*-MeO group into phenylacetonitrile stabilizes the product cation by about 0.59 V (~13.5 kcal) but stabilizes the radical cation by an even larger amount (0.82 V or ~19 kcal). As a consequence, the $BDE_{HA^{+\bullet}}$ value increases slightly (by ~4 kcal). Introduction of a *p*-CN group into phenylacetonitrile destabilizes the radical cation slightly (by 0.32 V or 7.4 kcal) and destabilizes the product cation by 0.34 V or ~7.8 kcal. The net result is a small increase of 1.5 kcal $BDE_{HA^{+\bullet}}$ (accentuated by the slightly higher $BDE_{HA}$ for $p\text{-}CNC_6H_4CH_2CN$).

**Radical Cation Acidities.** The estimates of radical cation acidities by eq 3 indicate that all are strongly acidic. Structural changes that stabilize the radical cation are expected to weaken the acidity by shifting the equation $HA^{+\bullet} \rightleftarrows H^+ + A^\bullet$ to the left, whereas those that stabilze the product $A^\bullet$ radical should shift the equilibrium to the right. For compounds in Tables I and II the radical cations are formed by loss of an electron from a nitrogen lone pair and the positive charge in the radical cation resides on nitrogen. These radical cations are all more stable than those in Table III where loss of an electron usually occurs from an aromatic π bond and the positive charge resides on carbon. (Note the higher $E_{ox}(HA)$ values in Table III.) The $pK_{HA^{+\bullet}}$ values usually fall in the range of −10 to −12 for the radical cations in Tables I and II compared to a range of −18 to −32 for the radical cations derived from the hydrocarbons in Table III.

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[11] (a) Leroy, G.; Peeters, D.; Sana, M.; Wilante, C. In *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janousek, Z., Merenyl, R., Eds.; D. Reidel Publishing Co.: Boston, 1986; pp 1–48. (b) Leroy, G.; Sana, M.; Wilante, C. *J. Mol. Struct.* (*Theochem*) 1991, *24*, 303–328. The "extra" stabilization of −2.42 for $(NH_2)_2CH^\bullet$ given in Table 4, p 308, should read +2.42.

## Experimental Section

**General.** NMR spectra were recorded on a Varian EM-390 spectrometer (90 MHz) or a Varian XLA-400 MHz spectrometer. Mass spectra were kindly measured by Dr. H. L. Hung on a HP5985 GC/MS system. Melting points were obtained on a Thomas Hoover capillary melting point apparatus and were not corrected. Elemental analyses were obtained from G.D. Searle, Skokie, IL.

**Materials.** 9-(Dialkylamino)fluorenes, triphenylmethanes, xanthenes, 9-phenylfluorenes, and phenylacetonitriles have been synthesized according to the literature methods and are described in the previous papers.[3,10,12b–d]

9-(Dicyclohexylamino)fluorene was kindly synthesized by Dr. T.-Y. Lynch. 9-Bromofluorene (3.2 g, 0.013 mol) and dicyclohexylamine (6.0 g, 0.033 mol) in 50 mL of acetonitrile were refluxed for 6 days. The solid precipitate was filtered and recrystallized from 95% ethanol to yield 94% product: mp 130.5–131.5 °C. MS: *m/e* 345 ($M^+$, 40), 180 [$(c\text{-}C_6H_{11})_2N^+$, 100]. $^1H$ NMR ($CDCl_3$): $\delta$ 0.8–1.9 (m, 20 H), 4.9 (s, 1 H), 7.2–7.4 (m, 4 H), 7.5–7.8 (m, 4 H).

**2-Benzoyl-*N,N'*-dialkylperhydropyrimidines 2 and *α,α*-Bis(alkylamino)acetophenones 3. General Procedure.** To a degassed solution of phenylglyoxal monohydrate (1.52 g, 0.010 mol) (Aldrich Chemical Co.) in 50 mL of benzene was added 0.010 mol of dialkylamine. The mixture was refluxed and the water was removed by using a Dean–Stark apparatus. After removing the solvent, the residual product, if solid, was recrystallized with 95% ethanol, and, if liquid, was purified by gel column chromatography.

**8-Benzoyl-1,5-diazabicyclo[3.2.1]octane:** mp 148–149 °C. $^1H$ NMR ($CDCl_3$): $\delta$ 0.94–1.45 (m, 1 H), 1.5–2.45 (m, 1 H), 2.8–3.7 (m, 8 H), 5.13 (s, 1 H), 7.2–7.6 (m, 3 H), 7.9–8.3 (m, 2 H). IR: 1680 (s) $cm^{-1}$. Anal. Calcd for $C_{13}H_{16}N_2O$: C, 72.19; H, 7.46; N, 12.95. Found: C, 72.23; H, 7.55; N, 12.71. MS: *m/e* 216 ($M^+$, 100), 111 ($H_2C(CH_2)_2N(CH_2)_2NC^+H$, 30). High resolution MS: calcd for $C_{13}H_{16}N_2O$ 216.1262. Found: 216.1251.

**2-Benzoyl-*N,N'*-dimethylperhydropyrimidine:** mp 60–61 °C (lit.[20] mp 62.5–63.5 °C). $^1H$ NMR ($CDCl_3$): $\delta$ 1.45–2.45 (m, 4 H), 2.13 (s, 6 H), 2.85–3.18 (m, 2 H), 3.19 (s, 1 H), 7.2–7.7 (m, 3 H), 8.4–8.7 (m, 2 H). IR: 1680 (s) $cm^{-1}$. Anal. Calcd for $C_{13}H_{18}N_2O$: C, 71.52; H, 8.31; N, 12.83. Found: C, 71.39; H, 8.41; N, 12.81.

**2-Benzoyl-*N,N'*-diethylperhydropyrimidine:** liquid. $^1H$ NMR ($CDCl_3$): $\delta$ 1.05 (t, 6 H), 1.6–2.0 (m, 2 H), 2.4–2.8 (m, 6 H), 3.1–3.3 (m, 2 H), 4.12 (s, 1 H), 7.4–7.6 (m, 3 H), 8.3–8.5 (m, 2 H). MS: *m/e* 245 [$(M - H^\bullet)^+$, 3.5], 141 $EtN(CH_2)_3N(Et)CH^+$, 100). High resolution MS: calcd for $C_{15}H_{21}N_2O$ [$(M - H^\bullet)^+$] 245.1654. Found: 245.1655.

***α,α*-Dipiperidinoacetophenone:** mp 67–68 °C (lit.[21] mp 62 °C). $^1H$ NMR ($CDCl_3$): $\delta$ 1.3–1.6 (m, 12 H), 2.4–2.6 (m, 8 H), 4.12 (s, 1 H), 7.4–7.6 (m, 3 H), 8.6–8.7 (m, 2 H). MS: *m/e* 285 [$(M - H^\bullet)^+$, 3], 181 [$(c\text{-}C_5H_5N)_2CH^+$, 100]. Anal. Calcd for $C_{18}H_{26}N_2O$: C, 75.48; H, 9.15; N, 9.78. Found: C, 75.25; H, 9.01; N, 9.45.

***α,α*-Dimorpholinoacetophenone:** mp 78–80 °C. $^1H$ NMR ($CDCl_3$): $\delta$ 2.6–2.8 (m, 8 H), 3.4–3.7 (m, 8 H), 4.20 (s, 1 H), 7.3–8.1 (m, 5 H). MS: *m/e* 289 [$(M - H^\bullet)^+$, 10], 185 [$(c\text{-}OC_4H_8N)_2CH^+$, 100]. Anal. Calcd for $C_{16}H_{22}N_2O_3$: C, 66.19; H, 7.64; N, 9.65. Found: C, 65.85; H, 7.65; N, 9.47.

**Equilibrium Acidities.** The equilibrium acidities of 9-(dicyclohexylamino)fluorene, *α,α*-dipiperidinoacetophenones, and *α,α*-dimorpholinoacetophenones in DMSO solution were determined by the overlapping indicator method described previously.[12a]

**Electrochemistry.** The measurements of cyclic voltammograms in DMSO were carried out as previously described.[7]

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**Registry No.** 2 (R = Me), 137233-38-6; $2^{+\bullet}$ (R = Me), 141319-97-3; 2 (R = Et), 137233-39-7; $2^{+\bullet}$ (R = Et), 141319-98-4; 3 (X = $CH_2$), 40991-73-9; $3^{+\bullet}$ (X = $CH_2$), 141319-99-5; 3 (X = O), 6425-12-3; $3^{+\bullet}$ (X = O), 141320-00-5; 9-(dimethylamino)fluorene, 53156-46-0; 9-(dimethylamino)fluorene radical cation, 117065-69-7; 9-(diethylamino)fluorene, 108975-83-3; 9-(diethylamino)fluorene radical cation, 116997-75-2; 9-(diisopropylamino)fluorene, 109495-00-3; 9-(diisopropylamino)fluorene radical cation, 116997-76-3; 9-(butylmethylamino)fluorene, 119454-90-9; 9-(butylmethylamino)fluorene radical cation, 141320-01-6; 9-(benzylmethylamino)fluorene, 102478-64-8; 9-(benzylmethylamino)fluorene radical cation, 141320-02-7; 9-(1-azetidinyl)fluorene, 116997-64-9; 9-(1-azetidinyl)fluorene radical cation, 116997-77-4; 9-pyrrolidinofluorene, 7596-59-0; 9-pyrrolidinofluorene radical cation, 116997-79-6; 2,7-dimethoxy-9-pyrrolidinofluorene, 116997-65-0; 2,7-dimethoxy-9-pyrrolidinofluorene radical cation, 116997-78-5; 9-piperidinofluorene, 3333-06-0; 9-piperidinofluorene radical cation, 116997-80-9; 9-(2-methylpiperidino)fluorene, 116997-85-4; 9-(2-methylpiperidino)fluorene radical cation, 141320-03-8; 9-(2,6-dimethylpiperidino)fluorene, 116997-66-1; 9-(2,6-dimethylpiperidino)fluorene radical cation, 116997-81-0; 9-(2,2,6,6-tetramethylpiperidino)fluorene, 116997-84-3; 9-(2,2,6,6-tetramethylpiperidino)fluorene radical cation, 141320-04-9; 9-(dicyclohexylamino)fluorene, 141320-05-0; 9-(dicyclohexylamino)fluorene radical cation, 141320-06-1; triphenylmethane, 519-73-3; triphenylmethane radical cation, 88424-77-5; 4-(diphenylmethyl)benzophenone, 7375-38-4; 4-(diphenylmethyl)benzophenone radical cation, 141320-07-2; 1-(diphenylmethyl)-4-nitrobenzene, 2945-12-2; 1-(diphenylmethyl)-4-nitrobenzene radical cation, 141320-08-3; diphenylmethane, 101-81-5; diphenylmethane radical cation, 82189-87-5; *p*-benzylbenzonitrile, 23450-31-9; *p*-benzylbenzonitrile radical cation, 141394-67-4; 9,10-dihydroanthracene, 613-31-0; 9,10-dihydroanthracene radical cation, 141394-68-5; xanthene, 92-83-1; xanthene radical cation, 41174-12-3; 9-cyanoxanthene, 85554-24-1; 9-cyanoxanthene radical cation, 130920-17-1; 9-phenylxanthene, 3246-80-8; 9-phenylxanthene radical cation, 141394-69-6; 9-(*p*-methoxyphenyl)xanthene, 19234-05-0; 9-(*p*-methoxyphenyl)xanthene radical cation, 141320-09-4; toluene, 108-88-3; toluene radical cation, 34504-47-7; fluorene, 86-73-7; fluorene radical cation, 34985-70-1; 9-phenylfluorene, 789-24-2; 9-phenylfluorene radical cation, 113566-64-6; 9-(*o*-tolyl)fluorene, 18181-25-4; 9-(*o*-tolyl)fluorene radical cation, 141320-10-7; 9-mesitylfluorene, 18153-40-7; 9-mesitylfluorene radical cation, 113533-48-5; phenylacetonitrile, 140-29-4; phenylacetonitrile radical cation, 94132-26-0; (*p*-methoxyphenyl)acetonitrile, 104-47-2; (*p*-methoxyphenyl)acetonitrile radical cation, 130932-63-7; (*p*-cyanophenyl)acetonitrile, 876-31-3; (*p*-cyanophenyl)acetonitrile radical cation, 130932-70-6; 9-bromofluorene, 1940-57-4; dicyclohexylamine, 101-83-7; phenylglyoxal monohydrate, 1075-06-5.

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