24. We are indebted to Dr. David K. Gosser Jr. for providing us with a version of his *General Program of Simulation.*

Registry No. $Pd^{II}(PPh_3)_2Cl_2$, 13965-03-2; THF, 109-99-9; Bu_4NBF_4, 429-42-5; PPh_3, 603-35-0; Au, 7440-57-5; PhI, 591-50-4; $Pd^{II}(PPh_3)_2Br_2$, 23523-33-3; Bu_4NCl, 1112-67-0; Bu_4NBr, 1643-19-2; $Pd^0(PPh_3)_2$, 31989-57-8; $Pd^0(PPh_3)_4$, 14221-01-3; *p*-I-C_6H_4-NO_2, 636-98-6; *p*-I-C_6H_4-CN, 3058-39-7; *p*-I-CH_4-MeCO, 13329-40-3; *p*-I-C_6H_4-Cl, 637-87-6; *p*-I-C_6H_4-Br, 589-87-7; *p*-I-C_6H_4-Me, 624-31-7; *p*-I-C_6H_4-MeO, 696-62-8; *p*-I-C_6H_4-OH, 54417-81-1; Cl^-, 16887-00-6; Br^-, 24959-67-9; $[Pd^0(PPh_3)_2Cl]_2^{2-}$, 136247-62-6; $[Pd^0(PPh_3)_2Cl]^-$, 136247-63-7; $[Pd^0(PPh_3)_2Cl_2]^{2-}$, 136247-64-8; $LiClO_4$, 7791-03-9.

Observations of Nonadditive Substituent Effects on the Dimethyl Sulfoxide Solution Homolytic Bond Strengths of Anthrylmethyl C–H Bonds

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Abstract: Acid–base and redox data, when incorporated into a thermochemical cycle, enable accurate determination of the effects of substituents on the homolytic strengths of chemical bonds. In this study, the effects of substituents on the dimethyl sulfoxide phase homolytic strengths of labile sp^3 C–H bonds present in 9-methylanthracene, seven variously substituted 9-methylanthracenes, phenylacetonitrile, and α-methoxyphenylacetonitrile are evaluated. The bond-strength data for these species indicate that, when present individually, 10-cyano and α-methoxy substituents weaken the anthrylmethyl C–H bond in 9-methylanthracene (in a homolytic sense) by 1–2 and 4 kcal/mol, respectively. When both 10-cyano and α-methoxy substituents are present in the same molecule, as in 10-cyano-9-(methoxymethyl)anthracene, the anthrylmethyl sp^3 C–H bond is weakened by 8 kcal/mol. Therefore, the bond-weakening effect of a 10-cyano substituent on 9-methylanthracene sp^3 C–H bond strengths is ca. 2 kcal/mol greater when the C–H bond to be cleaved is adjacent to an α-methoxy substituent. A similar and somewhat larger synergism (ca. 4 kcal/mol) is observed when an α-phenoxy substituent is present in place of α-methoxy. In related experiments, an α-cyano substituent is shown to weaken the anthrylmethyl C–H bond in 9-methylanthracene by ca. 3 kcal/mol. These data constitute the first nonkinetic experimental observations of synergistic substituent effects on the homolytic strengths of sp^3 C–H bonds. While not necessarily indicative of a general phenomenon, the observed changes in 9-methylanthracene sp^3 C–H homolytic bond strengths (due to the simultaneous presence of α-methoxy (or α-phenoxy) and 10-cyano substituents) can be rationalized by invoking a solvent-induced stabilization in the incipient anthrylmethyl radicals that results from the presence of both donor and acceptor substituents in conjugation with the unpaired electron.

The fact that Hammett ρ values for plots of pK_a vs Hammett σ for a pair of structurally similar families of acids (e.g., for 4-substituted phenylacetonitriles and 4-substituted phenylmalononitriles dissolved in dimethyl sulfoxide (DMSO) solution) are nonequal (7.0 and 5.5, respectively) requires nonadditive substituent effects on the acid–base equilibria for these species in DMSO solution.[1] Nonadditive substituent effects on the pK_a's for these species are best rationalized by pointing out that the additional α-cyano substituent present in the phenylmalononitrile family acts to reduce the amount of negative charge available for delocalization into the phenyl ring in the conjugate bases derived from the respective phenylmalononitriles relative to the amount of delocalization into the phenyl ring in the conjugate bases derived from the respective phenylacetonitriles. A given electron-accepting substituent, therefore, acidifies phenylmalononitrile to a lesser extent compared to its effect on the acidity of phenylacetonitrile. The pK_a data therefore suggest that interactions between negative charge density and multiple (nonsterically demanding) substituents are not additive and that the nonadditivities affect the stabilization of solution-phase organic anions.

Whereas the effects of multiple substituents on anion stabilities are reasonably well-understood, the effects of multiple substituents on radical stabilities are a source of disagreement and uncertainty. Several investigators have suggested that the simultaneous presence of donor and acceptor groups stabilizes organic radicals greater than would be expected on the basis of the individual contributions of either substituent if present singly.[2-6] The terms "push-pull resonance",[3] "merostabilization",[4] and "captodative"[5] have been used to describe the synergism that results from the presence of both donor and acceptor substituents. Kinetic data have been used to support[7] as well as deny[8] the existence of nonadditive (i.e., synergistic) substituent effects on radical stabilities. More recently, additional theoretical results have been published that cast doubt on the general existence of any dipolar resonance contribution to radical stabilization,[9] in contrast to an earlier report that suggested synergistic substituent effects will be observed only when the appropriately substituted radical is dissolved in a solvent of high polarity.[10] Other investigators, while noting that the absence of saturation effects on homolytic bond dissociation energies (BDEs) indicates that the presence of powerful donor and acceptor groups

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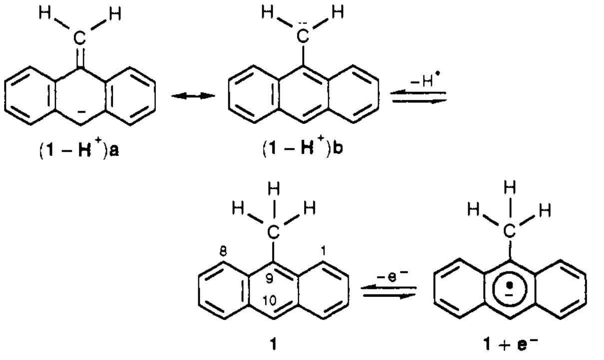
contributes substantially to the stability of radicals, also compare the effects of H_3CO and H_2N substituents on the gas-phase BDEs of X–CH_3 with the effects of H_3CO and H_2N substituents on the DMSO-phase BDEs of X–$CH_2C(O)Ph$ and conclude that there is no captodative effect.[11] In any case, the existence of synergistic stabilization that results from interactions between unpaired electron density and multiple (nonsterically demanding) substituents in solution-phase organic radicals has yet to be clearly demonstrated, since there are no experimental thermodynamic data that definitively indicate the existence of synergistic substituent effects on the homolytic strengths of chemical bonds either in the solution or gas phase.

Reported in this article are results in which the effects of substituents on the homolytic BDEs of variously substituted 9-methylanthracenes are examined. 9-Methylanthracene (**1**) serves as a near-ideal reference compound for several reasons. Most importantly, the two parameters necessary to determine the relative C–H homolytic BDEs for **1** and its derivatives (i.e., the pK_a and the oxidation potential of its conjugate base) are accessible in DMSO. Thus, no comparisons or extrapolations involving gas-phase or other data are necessary in order to evaluate the effect of the substituents, since all of the parameters are collected in DMSO. Secondly, if one intends to examine the effects of substituents on the radicals derived from a given family of molecules, it is advantageous that the radical that serves as the basis for comparison be free of any substituents capable of interacting with the unpaired electron in a way that would mask any of the effects to be examined, since these effects would be present in the reference radical itself. The radical derived from **1** (i.e. the 9-anthrylmethyl radical), composed only of carbon and hydrogen, seems well-suited for this task. Also of importance is the selection of a reference molecule that will be sensitive to substituent effects. The aromatic nature of the anthryl moiety suggests that substituent effects will be relatively large, since the presence of 14 π electrons in anthracene enables facile electron addition to[12,13] (and subtraction from[14]) the anthryl moiety. In addition, analysis of DMSO and gas-phase equilibrium acidity data for variously substituted methanes reveals that 9-methylanthracene (pK_a = 31.1 in DMSO solution[1]) is the most acidic monosubstituted methane (X–CH_3, where X = 9-anthryl), when considering substituents composed of carbon and hydrogen only. Presumably, the inductive effect of the 9-anthryl substituent is small. Therefore, the acidic properties of 9-methylanthracene (**1** in eq 1) and related species are most likely due to the remarkable stability of resonance contributor (**1** – $\mathbf{H^+}$)**a**, a contributor in which substantial negative charge density is present at carbon 10. This supposition is borne out when one considers that a plot of acidities (in DMSO solution) for a selection of 10-substituted varieties of **1** vs Hammett σ yields a ρ of about 10.[1,15] It follows that substantial charge density is also present at carbon 10 in the radical anions derived from **1** (i.e. **1** + e^-), since over a range of 25 kcal/mol a plot of DMSO-phase reduction potentials and pK_a's for 10 variously substituted 9-methylanthracenes is linear with slope 0.75.[16] The acidity and redox data together indicate that substituted 9-methylanthracenes and carbanions derived from substituted 9-methylanthracenes, as well as radical anions derived from substituted 9-methylanthracenes, are well-behaved organic species whose properties are easily understood within the traditional framework of physical organic chemistry. Furthermore, the data suggest that substituents at carbon 10 interact in a similar fashion with carbanions as well as radical anions derived from substituted 9-methylanthracenes.

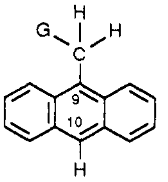


(1)

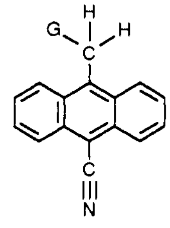
These facts (and the magnitudes of the observed effects) encouraged us to investigate the homolytic strengths of anthrylmethyl sp^3 C–H bonds present in various 10-substituted 9-methylanthracenes in anticipation of similarly large substituent effects on the stabilities of the incipient anthrylmethyl radicals. With the aid of a simple thermochemical cycle, a cycle that incorporates pK_a data for organic acids along with cyclic voltammetric electrochemical data for the conjugate bases derived from these acids,[1,11,17-19] we have now investigated the homolytic strengths of anthrylmethyl sp^3 C–H bonds present in **1** and related species. The homolytic BDE data presented in this article provide the first thermodynamic evidence for the existence of nonadditive effects of donor and acceptor substituents on the strengths of sp^3 C–H bonds when the donor and acceptor substituents are present on species dissolved in DMSO solution.

Results and Discussion

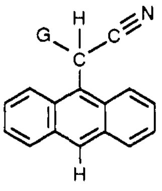
Listed in Table I are six columns of data: (a) equilibrium acidity constants (expressed as pK_a's) for carbon acids **1–10**; (b) cyclic voltammetric (CV) oxidation potentials (E_{ox}) for the conjugate bases derived from carbon acids **1–10**; (c) relative free energies ($\Delta BDE_{(C-H\ het)}$) for sp^3 C–H heterolyses for **2–8** and **10** (relative to **1** and **9**, respectively); (d) relative oxidation potentials ($\Delta E_{ox(C^-)}$) for the carbanions derived from carbon acids **2–8** and **10** (relative to the carbanions derived from **1** and **9**, respectively); and (e) relative free energies ($\Delta BDE_{(C-H\ homo)}$) for sp^3 C–H homolyses for **2–8** and **10** (relative to **1** and **9**, respectively). The entire set of data listed in Table I was collected while utilizing DMSO as the solvent.



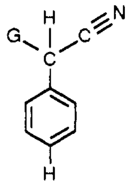
1: G = H
3: G = OCH_3
5: G = OC_6H_5



2: G = H
4: G = OCH_3
6: G = OC_6H_5



7: G = H
8: G = OCH_3



9: G = H
10: G = OCH_3

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Table I. DMSO Solution (25 °C, K^+ Counterion) Equilibrium Acidity Constants for α- and 10-Substituted 9-Methylanthracenes (**1–8**) and α-Substituted Toluenes (**9** and **10**), Cyclic Voltammetric Oxidation Potentials for Carbanions Derived from **1–10**, $\Delta BDE_{(C-H\ het)}$ Values for **1–10**, ΔE_{ox} Values for the Carbanions Derived from **1–10**, and $\Delta BDE_{(C-H\ homo)}$ Values for **1–10**

substrate	$pK_a{}^a$	$E_{ox}{}^b$ (V)	$\Delta BDE_{(C-H\ het)}{}^c$ (kcal/mol)	$\Delta E_{ox(C^-)}{}^d$ (kcal/mol)	$\Delta BDE_{(C-H\ homo)}{}^e$ (kcal/mol)
9-methylanthracene (**1**)	31.1^1	−0.62	(0.0)	(0.0)	(0.0)
10-cyano-9-methylanthracene (**2**)	20.0^1	−0.02	−15.2	13.8	−1.4
9-(methoxymethyl)anthracene (**3**)	$30.6^{15,31}$	−0.76	−0.9	−3.2	−4.1
10-cyano-9-(methoxymethyl)anthracene (**4**)	$17.3_5{}^{31}$	−0.13	−19.1	11.3	−7.8
9-(phenoxymethyl)anthracene (**5**)	$30.2^{15,31}$	−0.68	−1.5	−1.4	−2.9
10-cyano-9-(phenoxymethyl)anthracene (**6**)	14.9^{21}	−0.02	−22.4	13.8	−8.6
9-(cyanomethyl)anthracene (**7**)	$19.7^{15,31}$	−0.05	−15.9	13.1	−2.8
9-(cyanomethoxymethyl)anthracene (**8**)	20.4^{31}	−0.11	−15.3	11.8	−3.5
phenylacetonitrile (**9**)	21.9^1	−0.06	(0.0)	(0.0)	(0.0)
α-methoxyphenylacetonitrile (**10**)	23.0^{31}	−0.31	1.3	−6.6	−5.3

[a] References for pK_a values where appropriate. [b] E_{ox} data are for the cyclic voltammetric oxidations of the carbanions derived from **1–10**. Data collected as described in the Experimental Section. [c] For n = **1–8**: $\Delta BDE_{(C-H\ het)} = 1.37[pK_a(n) - 31.1]$, where 31.1 is the pK_a of 9-methylanthracene (**1**). For **9** and **10**: $\Delta BDE_{(C-H\ het)} = 1.37[pK_a(n) - 21.9]$, where 21.9 is the pK_a of phenylacetonitrile (**9**). At 25 °C, 1 pK_a unit = 1.37 kcal/mol. $\Delta BDE_{(C-H\ het)}$ values are statistically corrected for the number of acidic protons present in **1–10**. [d] For n = **1–8**: $\Delta E_{ox(C^-)} = 23.06[E_{ox}(n - H^+) - {}^-0.62$ where $^-0.62$ is the E_{ox} value (in volts) for the anion derived from 9-methylanthracene ($\mathbf{1} - H^+$). For **9** and **10**: $\Delta E_{ox(C^-)} = 23.06[E_{ox}(\mathbf{n} - H^+) - {}^-0.06]$, where $^-0.06$ is the E_{ox} value (in volts) for the anion derived from phenylacetonitrile ($\mathbf{9} - H^+$). CV E_{ox} values for **1–10** are utilized for these data. At 25 °C, 1 V = 23.06 kcal/mol. [e] $\Delta BDE_{(C-H\ homo)}$ values determined via eq 2. Reproducibilities in $\Delta BDE_{(C-H\ homo)}$ values are ca. 1 kcal/mol.

The $\Delta BDE_{(C-H\ homo)}$ values are determined via eq 2. Equation 2 represents a thermochemical cycle that includes relative acidity data for organic acids ($\Delta BDE_{(C-H\ het)}$ values) and relative oxidation potentials for the conjugate bases derived from each acid [$\Delta E_{ox(C^-)}$ values].[20] At 25 °C, the established reproducibilities in the pK_a

$$\Delta BDE_{(C-H\ homo)} = \Delta BDE_{(C-H\ het)} + \Delta E_{ox(C^-)} \qquad (2)$$

(±0.1 pK unit = ±0.14 kcal/mol) and cyclic voltammetric E_{ox} (±10 mV = ±0.23 kcal/mol)[21] data in Table I therefore suggest reproducibilities of 0.3,[22] 0.5, and ca. 1 kcal/mol in the listed $\Delta BDE_{(C-H\ het)}$, $\Delta E_{ox(C^-)}$, and $\Delta BDE_{(C-H\ homo)}$ values.[1,23] Equation 2 and similar thermochemical cycles have yielded valuable facts regarding the homolytic strengths of C–H, N–H, S–H, and O–H bonds in DMSO and aqueous solution.[24] Several articles have summarized results in which solution-phase relative free energies of homolysis as determined via eq 2 have been converted into solution-phase absolute enthalpies of homolysis.[24,25] Although usually yielding "absolute" solution-phase homolytic enthalpic BDEs that agree nicely (to within ±3 kcal/mol) with gas-phase values for similar processes, the weaknesses and limitations of the assumptions inherent in conversions of these sorts have been explicitly stated.[23,26,27] It is not a goal of this article to directly compare our homolysis data with gas-phase enthalpic results.[28] Rather, it is our aim to analyze solution-phase C–H homolyses in the same way that solution-phase C–H heterolyses are analyzed. Since solution-phase pK_a's yield free energies of proton transfer, the relative free energies of hydrogen-atom transfer (i.e., $\Delta BDE_{(C-H\ homo)}$ values) that result from eq 2 are well-suited for these analyses.[21,23,29]

Synergism in $\Delta BDE_{(C-H\ het)}$ (i.e., ΔpK_a) Data. Analysis of pK_a and $\Delta BDE_{(C-H\ het)}$ (i.e., ΔpK_a) data in Table I reveals that, individually, 10-cyano, α-cyano, α-methoxy, and α-phenoxy substituents acidify the unsubstituted 9-methylanthracene moiety by 15.2, 15.9, 0.9, and 1.5 kcal/mol, respectively. That both 10-cyano and α-cyano substituents acidify 9-methylanthracene to nearly the same extent points to the importance of resonance contributor ($\mathbf{1} - H^+$)**a**.[15] The rather small effects due to α-methoxy and α-phenoxy substituents are similar to the acidifying effects observed when 9-methoxy and 9-phenoxy substituents are present in the fluorenyl moiety (ΔpK_a = 1.1 and 4.0 kcal/mol, respectively).[30] Of particular interest are the synergisms observed when both 10-cyano and α-methoxy (or 10-cyano and α-phenoxy) substituents are present, as in 10-cyano-9-(methoxymethyl)anthracene (**4**) and 10-cyano-9-(phenoxymethyl)anthracene (**6**), since **4** and **6** are 3 and 6 kcal/mol more acidic than expected if it is assumed that the effects of the 10- and α-substituents are additive.[31] In fact, there is no a priori reason to expect that these effects should be additive; such an assumption requires that the sensitivities to changes in pK_a's for families of 10-substituted 9-methylanthracenes and 10-substituted α-methoxy- (or α-phenoxy-) anthracenes (i.e., the Hammett ρ) be equal.

Synergism in $\Delta BDE_{(C-H\ homo)}$ Data. Analysis of the $\Delta BDE_{(C-H\ homo)}$ data in Table I reveals that 10-cyano, α-cyano, α-methoxy, and α-phenoxy substituents weaken the sp^3 C–H bond in 9-methylanthracene by 1.4, 2.8, 4.1, and 2.9 kcal/mol, respectively. That 10-cyano weakens the anthrylmethyl C–H bond to any degree is somewhat surprising, since $\Delta BDE_{(C-H\ homo)}$ data for phenylacetonitrile,[32] benzyl phenyl sulfone,[33] phenylmalononitrile,[34] and their 4-cyano-substituted analogues indicate that the cyano substituent strengthens the benzylic C–H bonds present in these species by 1–2 kcal/mol. The $\Delta BDE_{(C-H\ homo)}$ values for α-cyano, α-methoxy, and α-phenoxy are not unexpected in view of the −6, −7, and −5.5 $\Delta BDE_{(C-H\ homo)}$ values for these "α-substituents" when present in the 9-position of fluorene in DMSO solution.[21] More importantly, the synergism that was observed for the $\Delta BDE_{(C-H\ het)}$ values for 10-cyano-9-(methoxymethyl)anthracene (**4**) and 10-cyano-9-(phenoxymethyl)anthracene (**6**) is also observed for the $\Delta BDE_{(C-H\ homo)}$ values for the same species. Specifically, the $\Delta BDE_{(C-H\ homo)}$ values for 10-cyano-9-(methoxymethyl)anthracene (**4**) and 10-cyano-9-(phenoxymethyl)anthracene (**6**) (−7.8 and −8.6 kcal/mol, respectively) are ca. 2 and 4 kcal/mol more negative than expected, assuming additivities for the individual $\Delta BDE_{(C-H\ homo)}$ values for 10-cyano and α-

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(22) The experimental uncertainties in the pK_a's of 9-(methoxymethyl)anthracene (**3**) and 9-(phenoxymethyl)anthracene (**5**) have been determined to be ±0.2 pK unit (±0.3 kcal/mol).[15] Therefore, the uncertainties in the $\Delta BDE_{(C-H\ het)}$ values for **3** and **5** are ±0.5 kcal/mol.

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methoxy (or α-phenoxy) substituents.

It is a concern that the $\Delta\text{BDE}_{(\text{C-H homo})}$ values for **1–10** depend in part on irreversible cyclic voltammetric (CV) oxidation potentials for the carbanions derived from **1–10**, since comparisons of irreversible electrochemical oxidations are most appropriate if the degrees of irreversibility for the species under comparison are similar.[35] An increase in the lifetime of a given 9-anthrylmethyl radical (in other words, a reduction in its rate of decomposition) is likely to result in an anodic shift in the measured (irreversible) E_{ox} value for the oxidation of its corresponding 9-methylanthracene carbanion compared to the measured E_{ox} value for the oxidation of a 9-methylanthracene carbanion that yields a less persistent 9-anthrylmethyl radical.[36] The magnitudes of the nonadditivites of the $\Delta\text{BDE}_{(\text{C-H homo})}$ data in Table I (2 and 4 kcal/mol) are sufficiently small to demand critical evaluation of the uncertainties in the data due to the incorporation of irreversible redox potentials into eq 2.

The uncertainty introduced by the use of irreversible electrode potentials depends upon the mechanism of further reactions of the radicals formed upon oxidation of the anions. The reaction products for the anodic oxidations listed in Table I have not been determined. Two possible reaction pathways for the various anodically generated anthrylmethyl radicals include (a) hydrogen-atom abstraction from solvent or electrolyte and (b) dimerization. It is reasonable to assume that the relative rate constants for the reactions of the anthrylmethyl radicals in either pathway do not vary by more than a factor of 10^4. The presence of 10-cyano and α–alkoxy substituents on the 9-methylanthracene framework is likely to result in a decrease in the rates of disappearance of the anodically generated anthrylmethyl radicals. A 10-fold decrease in the rate of decomposition of a given anthrylmethyl radical results in anodic shifts of 29.6 mV (mechanism a) or 19.7 mV (mechanism b) in its respective peak potential.[37] Thus, the peak potentials corresponding to the anodic oxidations that result in the least reactive anthrylmethyl radicals (i.e., those derived from 10-cyano-9-(methoxymethyl)anthracene (**4**) and 10-cyano-9-(phenoxymethyl)anthracene (**6**)) are likely to be shifted (*anodically*) by either ca. 118 mV (mechanism a) or 79 mV (mechanism b), assuming that the rates of disappearance of the radicals derived from **4** and **6** are retarded by 10^4 relative to the (less substituted) anthrylmethyl radicals derived from **1–3** and **5**. These shifts correspond to 3.1 (mechanism a) and 2.2 (mechanism b) kcal/mol uncertainties in the derived $\Delta\text{BDE}_{(\text{C-H homo})}$ values for **1–10** when the reproducibilities of the $\Delta\text{BDE}_{(\text{C-H het})}$ and $\Delta E_{\text{ox}(\text{C}^-)}$ data are taken into account.

Careful analysis of eq 2 reveals that an anodic shift for a given carbanion oxidation results in a dimunition (in a negative sense) of the $\Delta\text{BDE}_{(\text{C-H homo})}$ values for any species thus afflicted. Therefore, decreases in the rate of decomposition of the electrochemically generated radicals derived from the disubstituted species 10-cyano-9-(methoxymethyl)anthracene (**4**) and 10-cyano-9-(phenoxymethyl)anthracene (**6**) will result in (a) less negative $\Delta\text{BDE}_{(\text{C-H homo})}$ values for **4** and **6** and (b) a dimunition in the observed synergistic substituent effects in these species. In other words, the uncertainties in the $\Delta\text{BDE}_{(\text{C-H homo})}$ values in Table I that result from the irreversible carbanion oxidations are likely to result in an underestimation of the nonadditivities in the $\Delta\text{BDE}_{(\text{C-H homo})}$ data compared to those that would result if "true" reversible $E_{1/2}$ values were available for the oxidations of **1–10**. We therefore believe that the aforementioned uncertainties in the data listed in Table I do not detract from the meaningfulness of the $\Delta\text{BDE}_{(\text{C-H homo})}$ values.

The anomalous $\Delta\text{BDE}_{(\text{C-H homo})}$ values for **4** and **6** therefore demand elucidation in light of the present interest in the effects of substituents and, in particular, pairs of substituents on the relative thermodynamic stabilities of carbon-centered radicals.[5–11,28] The observed synergism in the $\Delta\text{BDE}_{(\text{C-H homo})}$ values for **4** and **6** must be derived from one or both of the following: (a) a synergistic ground-state destabilization of **4** (and **6**) that results from the simultaneous presence of 10-cyano and α-methoxy (or α-phenoxy) substituents and/or (b) a synergistic stabilization of **4 – H•** (and **6 – H•**) that results from the simultaneous presence of 10-cyano and α-methoxy (or α-phenoxy) substituents. In essence, the presence of both 10- and α-substituents requires a synergistic interaction (either through space, through bonds, and/or with the aid of DMSO solvent molecules) that destabilizes the neutral closed-shell species **4** and **6** and/or stabilizes the open-shell radicals **4 – H•** and **6 – H•**.

Synergistic Destabilization of 4 and 6. Steric interactions in **4** and **6** that result from the simultaneous presence of 10-cyano and α-methoxy (or α-phenoxy) substituents seem implausible due to the small size of the 10-cyano substituent. It is also important to recognize that the α-methoxy and α-phenoxy substituents present in **4** and **6** are also present in **3** and **5**, the species to which their $\Delta\text{BDE}_{(\text{C-H homo})}$ values are compared. Similarly, electronic interactions between the 10- and α-positions in **4** and **6** are largely precluded by the presence of the tetrahedral anthrylmethyl carbon. There is therefore a lack of compelling evidence to suggest that the anomalies observed in the $\Delta\text{BDE}_{(\text{C-H homo})}$ values for **4** and **6** are due to a synergistic ground-state destabilization of these species.

Synergistic Stabilization of 4 – H• and 6 – H•. We are left to consider synergistic stabilization of **4 – H•** and **6 – H•** as likely reasons for the anomalous $\Delta\text{BDE}_{(\text{C-H homo})}$ values for 10-cyano-9-(methoxymethyl)anthracene (**4**) and 10-cyano-9-(phenoxymethyl)anthracene (**6**). Reasoning similar to that outlined previously for **4** and **6** is also appropriate in describing the nature of any steric interactions between the 10-cyano and α-methoxy (or α-phenoxy) substituents present in **4 – H•** (and **6 – H•**). Furthermore, any steric effects that result in a loss of coplanarity between the various substituents would likely result in the thermodynamic destabilization of the radicals rather than the stabilization required by the data. A loss of coplanarity that results from steric interactions is probably operative in **8 – H•**, the radical derived from 9-(cyanomethoxymethyl)anthracene (**8**) (i.e., 9-(α-cyano-α-methoxymethyl)anthracene), since the $\Delta\text{BDE}_{(\text{C-H homo})}$ values for 9-(cyanomethyl)anthracene (**7**) and **8** are −2.8 and −3.5 kcal/mol, respectively. It seems likely that steric interactions between the 1- and 8-hydrogen atoms in the anthryl ring preclude maximum overlap of all three radical-stabilizing substituents (i.e., the anthryl, cyano, and methoxy moieties) bound to the trigonal anthrylmethyl carbon in **8 – H•**. These data indicate that the presence of an adjacent methoxy group has little effect on the strength of the α-cyanoanthrylmethyl C–H bond. On the other hand, the $\Delta\text{BDE}_{(\text{C-H homo})}$ value for α-methoxyphenylacetonitrile (relative to phenylacetonitrile) is −5.3 kcal/mol, a value more in line with published α-methoxy $\Delta\text{BDE}_{(\text{C-H homo})}$ values.[21,30,38]

However, unlike **4** (and **6**), electronic interactions between the 10- and α-positions in **4 – H•** (and **6 – H•**) are *not* precluded, since the anthrylmethyl carbon in both radicals is trivalent. It is therefore proper to consider the viability of a DMSO-induced synergistic stabilization of donor–acceptor-substituted radicals **4 – H•**). It is our supposition that the combination of (a) the unique ability of the 9-anthrylmethyl moiety to delocalize negative charge to the 10-carbon atom and substituents bonded to it and (b) the interaction of dipolar DMSO solvent molecules with donor–acceptor-substituted radicals **4 – H•** and **6 – H•** results in an enhancement of the thermodynamic stability of both **4 – H•** and **6 – H•**. The exact nature of the stabilization is related to the ability of DMSO to solvate the donor–acceptor-substituted radical. With the aid of the DMSO solvent, powerful electron-donating and electron-accepting substituents in conjugation with the unpaired electron act to delocalize the unpaired electron density to a degree greater than the sum of the delocalization offered by either

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electron-donating or electron-accepting substituents when present alone.

Summary

Data presented in this paper constitute the first nonkinetic experimental observations of nonadditive and synergistic substituent effects on the homolytic strengths of labile sp^3 C–H bonds and provide evidence for the significance of solvent-induced stabilization of appropriately substituted carbon-centered radicals. The nonadditivities present in the sp^3 C–H bond strengths for donor–acceptor-substituted species **4** and **6** (2 and 4 kcal/mol, respectively), although small in magnitude, are best explained by postulating that DMSO interacts with the donor–acceptor-substituted radicals **4 – H**$^•$ and **6 – H**$^•$ in a fashion that results in an enhanced stabilization for these species.

Experimental Section

The syntheses of **2–8** and **10** were carried out in our laboratories and have been described previously.[15,16,31] 9-Methylanthracene (**1**, crystallized from EtOH) and phenylacetonitrile (**9**, distilled) were purchased from Aldrich.

All of the pK_a values in Table I have been published previously; appropriate references for these values are listed in Table I.

Dimethyl sulfoxide was purified and potassium dimsylate was synthesized exactly as described by Matthews and Bordwell.[39] $Et_4N^+BF_4^-$ was recrystallized from acetone and was allowed to dry at 110 °C under vacuum prior to dissolution in DMSO. $Et_4N^+ClO_4^-$ was recrystallized from ethanol/water and dried under vacuum overnight prior to dissolution in DMSO.

Electrochemistry conditions: all experiments were carried out in DMSO solution under an argon atmosphere as described previously.[16,17] 0.1 M $Et_4N^+BF_4^-$ and 0.1 M $Et_4N^+ClO_4^-$ were employed as electrolytes. The strongly basic anions derived from 9-methylanthracene, 9-(methoxymethyl)anthracene, and 9-(phenoxymethyl)anthracene were less stable in the presence of $Et_4N^+BF_4^-$, necessitating usage of the perchlorate salt as electrolyte for the anodic oxidations of these species. A standard three-electrode cell consisting of platinum working and auxiliary electrodes and a Ag/AgI reference electrode was used in the cyclic voltammetry (CV) oxidations. The ferrocene/ferrocenium redox couple at +0.875 V provided an internal standard of comparison for the E_{ox} values in Table I. In the electrochemical cell, the carbanions were generated by addition of a stock solution of potassium dimsylate solution (ca. 0.15 M in DMSO) to a 7–8 mL solution of the acid to be deprotonated. The anions were present in 1–2 mM concentrations. The E_{ox} values are the anodic peak potentials (CV sweep rate = 0.1 V/s) as reported by a BAS 100A electrochemical analyzer. The CV anodic peak potentials used in the calculations of the $\Delta E_{ox(C^-)}$ and $\Delta BDE_{(C-H\ homo)}$ values for **1–10** were reproducible to within 10 mV.

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Registry No. 1, 779-02-2; **1** (carbanion), 122128-04-5; **2**, 1467-01-2; **2** (carbanion), 135598-24-2; **3**, 2584-79-4; **3** (carbanion), 135598-25-3; **4**, 133322-46-0; **4** (carbanion), 135598-26-4; **5**, 16430-34-5; **5** (carbanion), 135598-27-5; **6**, 135598-22-0; **6** (carbanion), 135598-28-6; **7**, 2961-76-4; **7** (carbanion), 135598-29-7; **8**, 135598-23-1; **8** (carbanion), 135598-30-0; **9**, 140-29-4; **9** (carbanion), 18802-89-6; **10**, 13031-13-5; **10** (carbanion), 95339-45-0; **4-H**$^•$, 135619-07-7; **6-H**$^•$, 135598-31-1.

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Low-Temperature X-ray and Neutron Diffraction Studies on 18-Crown-6·2Cyanamide Including Electron Density Determination†

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Abstract: Low-temperature (100 K) X-ray and neutron diffraction data have been combined to obtain accurate molecular dimensions and to study the charge density distribution in the neutral complex of 18-crown-6 and cyanamide. Conformational changes in the polyether ring as well as in the cyanamide molecule, due to complex formation, have been analyzed. The leading forces of complexation were found to be cooperative hydrogen bonds of different types and dipole–dipole interactions. Atomic valence deformations, due to chemical bonds and intermolecular interactions, were analyzed in terms of static and dynamic difference densities calculated by the fitted multipole model and X–X Fourier synthesis. In the deformation charge density maps well-defined bond peaks can be observed. Excess density in the regions associated with lone-pair electrons is found for the ether oxygen atoms. For those which participate in hydrogen bonding the maximum charge buildup is located in the direction of the proton. No further density accumulation is observed between the donor and the acceptor which supports the assumption about the electrostatic nature of the hydrogen bond. For the cyanamide molecule the experiment and the theory are in good agreement.

Introduction

Macrocyclic polyethers like 18-crown-6 are known to complex not only cations but also neutral, polarized compounds. Several complexes of this kind with 1:2 stoichiometric ratio of host and guest have been prepared recently. The guest partners usually have high dipole moments and are coordinated above and below the crown in such a way that the dipoles are compensated. To describe this formation, a system of cooperative intermolecular contacts, as dipole–dipole interactions and hydrogen bonds, was postulated.[1]

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† Dedicated to Professor Dr. Erwin Weiß on the occassion of his 65th birthday.

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