kept <20%. After photolysis, the sample was extracted several times with CH_2Cl_2 and conversions analyzed by GC. Excellent material balances were observed, as determined by xanthene external standard. GC responses were essentially identical for all of 1, 6–8.

Fluorescence Measurements. Fluorescence emission spectra (uncorrected) were taken in 3.0-mL quartz cuvettes at $\approx 10^{-4}$ M using a Perkin-Elmer MPF 66 spectrophotometer at ambient temperature (λ_{ex} = 265 nm). Standardized HCl or H_2SO_4 solutions were used for acid quenching experiments. The fluorescence quantum yield of 1 in neutral 1:1 H_2O–CH_3CN was measured relative to diphenyl ether (Φ_f = 0.03 in cyclohexane)[16] as secondary fluorescence standard. Optical densities at λ_{ex} = 260 nm were matched prior to measurement.

Triplet Sensitization. In a typical experiment, a solution of 2 mg of 1 in 150 mL of 1:1 acetone–H_2O was irradiated at 300 nm (Rayonet RPR-100 300-nm lamps) for 2 h, where the sensitizer absorbed >95% of the exciting light. After photolysis, the solution was condensed, saturated with NaCl, and then extracted with 3 × 100 mL of CH_2Cl_2. In all runs, no photoproducts were detected and the starting material was recovered unchanged.

Acknowledgment. This research was supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada. Additional support was provided by the University of Victoria in form of a graduate fellowship (to C.-G.H.).

Thermodynamic Properties of Carbocations and Carbanions. Solvation Effects from an Electrochemical and Theoretical (AM1) Study of Some Substituted Benzyl Radicals[1]

D. D. M. Wayner* and B. A. Sim

Steacie Institute for Molecular Sciences, National Research Council of Canada,
Ottawa, Ontario, Canada K1A 0R6

J. J. Dannenberg

Department of Chemistry, City University of New York-Hunter College and the Graduate School,
695 Park Avenue, New York, New York 10021

Received February 21, 1991

Gas phase ionization potentials (IP) and electron affinities (EA) for a number substituted benzyl radicals have been calculated using the AM1 method. There is a remarkably good correlation between the electrochemical oxidation potentials in acetonitrile and the calculated IP's (slope = 1.03, r = 0.995) and between the reduction potentials in acetonitrile and the calculated EA's (slope = 1.04, r = 0.996). These correlations, which include both monosubstituted radicals and α,para-disubstituted radicals, cover a potential range of ca. 2 eV for both the oxidations and reductions. The relationship between size and solvation energy of a carbocation in acetonitrile is demonstrated. Thus, the solvation free energy of the benzyl cation is ca. −40 kcal mol^{-1} while that for the methoxymethyl cation is −56 kcal mol^{-1}. The data suggest that charge distribution, and not only size, is responsible for the observed differential solvation effects of the benzylic ions. It is concluded that the α-methoxybenzyl cations have solvation free energies that are at least 8 kcal mol^{-1} more exoergonic than either the benzyl or α-cyanobenzyl cations. This solvation effect is the result of a higher localized charge density on the benzylic group in the α-methoxy derivatives. Substituent–substituent interactions in the disubstituted ions are evaluated by using the electrochemical potentials to calculate the free energy change for isodesmic electron transfer reactions. Saturation effects are observed in the interaction of two stabilizing substituents (i.e. two methoxy groups on a cation, two cyano groups on a carbanion). Other substituent–substituent effects appear to be essentially additive.

Introduction

Recently, we reported the half-wave potentials ($E_{1/2}$) for the electrochemical oxidation and reduction of a number of meta- and para-substituted benzyl radicals in acetonitrile.[2] It was found that the oxidation and reduction potentials give linear correlations with σ^+ and σ^-, respectively, implying that the potentials are determined, predominantly, by the substituent effects on the product ions. Comparison of these data with gas-phase ionization potentials (IP) led to a simple relationship between the solvation energy of the ions and the IP of the radical (eqs 1 and 2).

$$\Delta\Delta G^\circ_{\mathrm{sol}}(\mathrm{R}^+) \approx (1 - m)\Delta\mathrm{IP} \tag{1}$$

$$\mathrm{F}\Delta E_{1/2}{}^{\mathrm{ox}} = m\Delta\mathrm{IP} \tag{2}$$

Unfortunately, the number of IP's for radicals that have been reported is limited so it is difficult to test the utility of eq 1. Lossing measured the IP's of a number of substituted benzyl radicals;[3] however, the reliability of these data has been questioned.[4] It was suggested that the substituent effect on the stabilization energy of benzyl carbocations should not be greater than the effect on substituted benzenium ions (ρ^+ = −13).[4a] Using this upper limit for ρ^+, we were able to determine a only lower limit for the value of the slope of eq 2 (m > 0.7).[2]

In view of the dearth of gas-phase data for benzylic radicals we have, initially, attempted to understand these solvation effects by calculating the IP's and electron affinities (EA) using the AM1 molecular orbital method.[5] The electrochemical data have been extended to include a number of α,para-disubstituted benzyl radicals and now

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0022-3263/91/1956-4853$02.50/0 Published 1991 by the American Chemical Society

Table I. Oxidation and Reduction Potentials of Some Substituted Benzyl Radicals in Acetonitrile (0.1 M TBAP)[a]

substituent		V vs SCE		
Y	X	$E_{1/2}^{ox}$	$E_{1/2}^{red}$	ref
CN	*p*-CN	1.63	−0.16	this work
	H	1.29	−0.54	this work
	p-OMe	0.70	−0.73	this work
H	*p*-CN	1.08	−0.77	2
	m-CN	1.11	−1.11	2
	p-COMe	0.90	−0.71	2
	p-Cl	0.80	−1.40	2
	H	0.73	−1.50	2
	m-Me	0.70	−1.50	2
	p-Me	0.51	−1.62	2
	p-OMe	0.26	−1.82	2
OMe	*p*-CN	0.10[b]	−1.13	this work
	H	−0.33	−1.79	this work
	p-OMe	−0.51	<−2.0	this work

[a] Measured by photomodulation voltammetry; ±50 mV. [b] This is the position of the anodic wave on the initial scan using a fresh electrode. On subsequent scans using the same electrode, the wave shifts anodically (to 0.45 V) and broadens (see text).

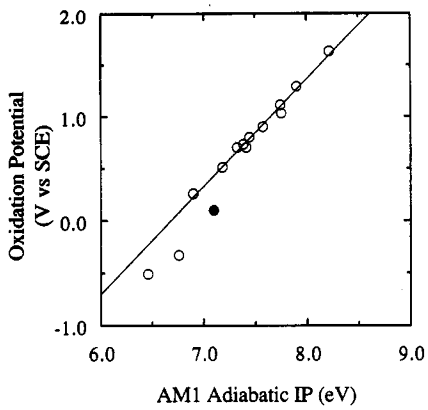
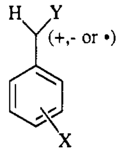


Figure 1. Experimental oxidation potentials ($E_{1/2}$) of some substituted benzyl radicals in acetonitrile (0.1 M TBAP) versus the calculated adiabatic ionization potential, IP_a. The closed circle is the oxidation potential of the *p*-cyano-α-methoxybenzyl radical obtained from the initial scan on a fresh electrode (see text).

cover a range of ca. 2 eV for both the oxidations and reductions. These data will give some insight into the effect of charge delocalization and distribution on the solvation energies of the ions as well as an assessment of the energetics of the substituent–substituent interactions in the disubstituted ions.



Y = H, CN, OMe

Results

The oxidation and reduction potentials of the substituted benzyl radicals (Table I) were measured using the photomodulation voltammetry technique.[6] Radicals were generated by photolysis of di-*tert*-butyl peroxide followed by hydrogen atom abstraction from the substituted toluene (eqs 3 and 4).

$$t\text{-BuOOBu-}t \rightarrow 2t\text{-BuO}^{\bullet} \tag{3}$$

$$t\text{-BuO}^{\bullet} + \text{RH} \rightarrow t\text{-BuOH} + \text{R}^{\bullet} \tag{4}$$

The gas-phase enthalpies of formation of the substituted toluenes and the benzyl radicals, carbocations, and carbanions have been calculated using the AM1 method (Table II). In general, there was reasonable correspondence between the calculated values and experimentally determined values from the literature.[7] These data were used to determine the IP's and EA's of the radicals (both adiabatic and vertical) as well as the bond dissociation enthalpies of the toluenes, BDE(RH), the hydride affinities of the carbocations, $HA(R^+)$, and the proton affinities of the carbanions, $PA(R^-)$ (Table III).

Discussion

Bond Dissociation Enthalpies by AM1. The AM1 method gives a C–H bond dissociation enthalpy (BDE) for toluene that is within 1 kcal mol^{-1} of the most reliable experimental determination.[8] Other semiempirical (MINDO/3 and MNDO) and ab initio (4-31G and 6-31G) methods[9] underestimate the BDE(RH) value for toluene by 6–16 kcal mol^{-1}. The effect of ring substitution on the BDE(RH) values has been addressed by Zavitsas[10] and Pryor.[11] It has been suggested that the C–H bond enthalpies for the substituted toluenes should correlate with the Hammett σ constants (electron-donating substituents making the bond weaker). However, a range of only 2–3 kcal mol^{-1} for the entire series of monosubstituted toluenes is expected. Gilliom[9] found, however, that the correlations of the theoretical data with σ^+ or $\sigma^{\bullet}$ [12] was poor.

Although we see a trend in the AM1 BDE(RH) values in the direction predicted by Pryor (Table III),[11] the range (only 1 kcal mol^{-1}) is too small to be meaningful. For the purposes of this work, these values are considered to be constant.[13] On the other hand, the effect of α-substitution appears to be more significant. Both α-methoxy and α-cyano decrease the BDE(RH) by ca. 5 kcal mol^{-1}.

Proton Affinities. The carbon acidities of 10 of the substituted toluenes (or proton affinities of the carbanions) have been measured experimentally.[7] There is an excellent correlation (r = 0.999) between the calculated and experimental data (eq 5). However, it is clear from these data (slope = 0.84) and from Table II that the AM1 method tends to underestimate the substituent effect on the carbanion.

$$PA(R^-)_{AM1} = (52.8 \pm 0.6) + (0.84 \pm 0.01)PA(R^-)_{expt} \tag{5}$$

Solvation of the Carbocations. The AM1 IP's for the ring-substituted benzyl radicals correlate with the values reported by Lossing and his co-workers,[3] giving a slope of 0.5 (AM1 versus experimental). Although this tends to support the suggestion that the experimental values overestimate the substituent effect,[4] the possibility that the

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(13) There is actually a reasonable correlation of the AM1 BDE's with σ^+ ($\rho^+ = 0.49 \pm 0.07$, $r = 0.934$). This correlation improves significantly when a two parameter plot using σ^+ and $\sigma^{\bullet}$ is used instead ($\rho^+ = 0.49 \pm 0.04$, $\rho^{\bullet} = 3.8 \pm 0.8$, $r = 0.984$; note that the two parameter correlation actually improves the uncertainty in ρ^+). By contrast, it has been reported that the substituent effect on the BDE(OH) of substituted phenols (measured by photoacoustic calorimetry) is large. In this case, the correlation with σ^+ has a ρ^+ value of 7.3. Mulder, P.; Saastad, O. W.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 4090.

Table II. AM1 Heats of Formation (kcal mol^{-1}) of Some Substituted Toluenes and Benzyl Radicals, Carbocations, and Carbanions

substituent		ΔH°_f(RH)		ΔH°_f($R^\bullet$)		ΔH°_f(R^+)		ΔH°_f(R^-)	
Y	X	AM1	lit.[a]	AM1	lit.[a]	AM1	lit.[a]	AM1	lit.[a]
CN	*p*-CN	78.8		111.2		300.7		45.3	45.9
	p-COMe	10.9		43.2		228.9		-21.7	
	p-Cl	39.8	37.0	71.8		254.5		14.0	16.7
	H	46.7	44.5	78.3		260.4		26.9	29.4
	p-OH	2.4		33.8		207.8		-17.2	
	p-OMe	8.8		40.1		210.9		-10.5	-6.9
H	*p*-CN	45.6	44.0	83.7		262.3		33.8	38.7
	m-CN	45.8	44.0	83.6		262.0		41.2	47.3
	p-COMe	-22.0		16.1		190.6		-33.6	-32.5
	p-Cl	7.1	4.0	44.8		216.3		5.6	12.7
	H	14.4	12.0	52.0	49.0	222.1	215.0	20.8	27.0
	m-Me	6.9	4.1	44.6	40.0	213.4	204.0	13.5	
	p-Me	6.9	4.3	44.4	40.0	209.9	200.0	12.2	
	p-OH	-29.7		7.5		169.9	175.0	-25.3	
	p-OMe	-23.4	-24.0	14.0		173.2		-17.0	
OMe	*p*-CN	5.7		37.2		200.9		-9.5	
	p-COMe	-61.1		-30.1		130.1		-76.5	
	p-Cl	-31.8		-1.2		156.9		-38.8	
	H	-25.5	-18.0	6.0		161.9		-24.2	
	p-OH	-68.7		-38.8		113.1		-70.0	
	p-OMe	-63.5		-31.4		117.5		-64.3	

[a] Reference 7.

Table III. Calculated (AM1) Thermodynamic Properties for Some Substituted Toluenes and Benzylic Systems[a]

substituent								
α	ring	$IP_a(R^\bullet)$, eV	$IP_v(R^\bullet)$, eV	$EA_a(R^\bullet)$, eV	$EA_v(R^\bullet)$, eV	BDE(RH), kcal mol^{-1}	HA(R^+), kcal mol^{-1}	PA(R^-), kcal mol^{-1}
CN	*p*-CN	8.22	8.28	2.86	2.81	84.50	255.20	333.60
	p-COMe	8.05	8.14	2.82	2.60	84.42	251.28	334.49
	p-Cl	7.92	8.01	2.51	2.47	84.05	247.96	341.27
	H	7.90	7.97	2.23	2.20	83.70	247.00	347.30
	p-OH	7.55	7.68	2.21	2.18	83.50	238.70	347.50
	p-OMe	7.41	7.58	2.19	2.15	83.40	235.43	347.83
H	*p*-CN	7.75	7.77	2.16	2.08	90.20	250.00	355.30
	m-CN	7.74	7.78	1.84	1.77	89.90	249.50	362.53
	p-COMe	7.57	7.62	2.16	1.89	90.20	245.90	355.50
	p-Cl	7.44	7.49	1.70	1.65	89.76	242.46	365.56
	H	7.38	7.43	1.35	1.29	89.70	241.00	373.50
	m-Me	7.32	7.37	1.35	1.29	89.80	239.80	373.70
	p-Me	7.18	7.23	1.40	1.35	89.67	236.37	372.47
	p-OH	7.04	7.15	1.42	1.30	89.30	232.90	371.50
	p-OMe	6.90	7.03	1.34	1.29	89.43	229.85	373.46
OMe	*p*-CN	7.10	7.19	2.03	1.68	83.60	228.48	351.85
	p-COMe	6.95	7.05	2.01	1.47	83.10	224.54	351.75
	p-Cl	6.86	6.96	1.63	1.26	82.62	221.95	360.10
	H	6.76	6.86	1.31	0.92	83.56	220.73	368.39
	p-OH	6.55	6.69	1.39	0.96	82.85	215.16	365.82
	p-OMe	6.46	6.60	1.42	0.95	84.13	214.22	366.31

[a] Vertical potentials (IP_v and EA_v) are based on the energy of the ion in the optimized geometry of the radical.

AM1 method underestimates the effect (as it does for the proton affinities, vide supra) cannot be ruled out. It is likely, in fact, that both effects contribute to the small slope.

A plot of the electrochemical oxidation potentials for a number of ring substituted and α,para-disubstituted benzyl radicals in acetonitrile versus the calculated adiabatic IP's is a straight line with a slope of 1.03 and correlation coefficient of 0.995 (Figure 1). The data cover a potential range of ca. 2.1 eV. The relaxation energies for the ionizations are small,[14] so the correlation with the vertical IP's is similar, giving a slope of 1.07 and a correlation coefficient of 0.987.

The correlation is remarkable considering the calculations refer to an isolated molecule in the gas phase. However, since we know that the AM1 method overestimates the substituents effect on the carbanions, the quantitative interpretation of the slope for the carbocations is not justified. Nevertheless, the trend is clear and we suggest that the slope of this line is a reasonable upper limit.

The three points that fall off the line in Figure 1 correspond to the three α-methoxybenzyl radicals. These points were not included in the correlation analysis described above. For the oxidation of the *p*-cyano-α-methoxybenzyl radical, the initial scan revealed an anodic wave at 0.10 V (the closed circle in Figure 1). On subsequent scans this wave slowly shifted cathodically and broadened significantly. It appears that in this case some modification of the electrode surface (by the radical, ion or a small amount of impurity in the toluene precursor) is responsible for the cathodic shift and, therefore, the potential obtained from the initial scan was used.

There are three likely explanations for the deviation of these points. The first is that there may be a systematic error in the AM1 calculation for these α-substituted species. The second is that the electrochemical mea-

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Table IV. Solvation Free Energies of Carbocations[a,b]

R^+	$\Delta G°_{sol}(R^+)$, kcal mol^{-1}	R^+	$\Delta G°_{sol}(R^+)$, kcal mol^{-1}
9-fluorenyl	−36.2	Me_2NCH_2	−45.9
$PhCH_2$	−39.3	Me_3C	−47.7
$PhCH_2$	−39.8	$MeOCH_2$	−56.3
PhCHMe	−40.8		

[a] $\Delta G°_{sol} = 23.06(E_{1/2}^{ox} - IP + 4.74)$; refs 2 and 6. [b] Data from refs 6 and 7.

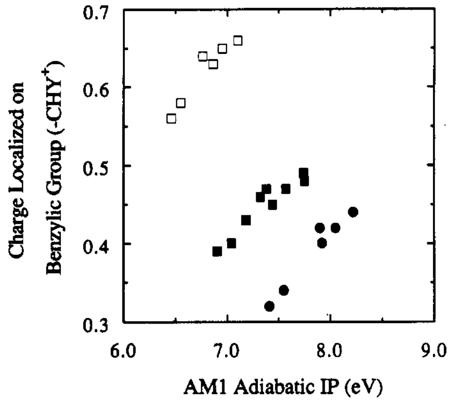

Figure 2. Relationship between charge localization on the benzylic group and the calculated IP_a for some substituted α-methoxybenzyl cations, □; benzyl cations, ■; and, α-cyanobenzyl cations, ●.

surements may be corrupted by a kinetic effect that is not present in any of the other data. Finally, it is possible that these ions may, in fact, have a different (i.e. greater) solvation energy.

It is difficult to test the first two possibilities. However, some observations of the structural effects on the solvation energies of carbocations has led us to a better understanding of those factors that are important. We reported that the benzyl, diphenylmethyl, and 9-fluorenyl carbocations all had approximately the same solvation energy.[6] These values were determined from a comparison of the gas-phase and solution IP's. Using this approach it is possible to estimate the solvation energies of a number of other carbocations in acetonitrle (Table IV). Although a number of assumptions have been made to determine an absolute solvation energy, the relative values are more precise (±2 kcal mol^{-1}).[6] There is a clear relationship between the size of the ion and its solvation energy (Table IV). All of the benzylic ions have about the same solvation energy (−40 kcal mol^{-1}). As the size of the ions decreases, the solvation energy increases, presumably because the stabilization of the charge by interaction with the solvent (as opposed to delocalization) becomes more important as the ion becomes more localized.

This correlation with size can be misleading. Although the substituted benzylic ions in this study are all approximately the same size, the substituents have a significant influence on the charge distribution. While there is a correlation between the charge localized on the benzylic group in the carbocation and the ionization potential of the benzyl radical (Figure 2), each set of α-substituted carbocations forms a different line. Charge localization on the benzylic group is far greater in the case of the α-methoxybenzyl carbocations (ca. 60% of the charge localized outside of the aryl ring system) than it is for either of the other two sets of data (ca. 45% of the charge localized).

This analysis of charge distribution suggests a possible explanation of the systematic deviation of the α-methoxybenzylic systems from the line in Figure 1. The oxidation potentials of the three α-methoxybenzyl radicals lie significantly below, but approximately parallel to, the best-fit line for the rest of the data. The separation between these lines represents a solvation energy difference of ca. 8 kcal mol^{-1}. This difference is not unreasonable as it represents about half of the difference between the solvation of the benzyl and methoxy methyl cations (Table IV).

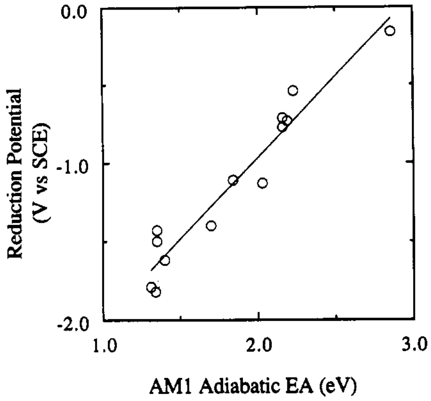

Figure 3. Experimental reduction potentials ($E_{1/2}$) of some substituted benzyl radicals in acetonitrile (0.1 M TBAP) versus the calculated adiabatic electron affinity, EA_a.

Solvation of Carbanions. Plots of the electrochemical reduction potentials versus the AM1 EA's of the radicals are somewhat more scattered than those for the oxidation process. Slopes of 1.04 (r = 0.966, Figure 3) and 0.98 (r = 0.960) are obtained for the adiabatic and vertical EA's, respectively (vertical EA refers to the EA of the carbanion in the geometry of the radical). In this case it is possible to scale the AM1 data using eq 5 (provided the solvation energies of the radical and the toluene derivative are the same). The corrected slopes for the two lines in Figure 3 are 0.87 and 0.82, respectively. This slope indicates that there is a moderate effect of substitution on the solvation energy of the carbanion (eq 1); the more delocalized carbanions have a less exoergonic solvation energy.

It is interesting to point out that while the difference between the adiabatic and vertical EA's are generally small (<0.1 eV), those values for the α-methoxy-substituted radicals are quite large (>0.4 eV). For the α-methoxy-substituted radicals and carbocations, there is a net bonding interaction between the 2p-type lone pair on oxygen and the 2p orbital on C_α; a two-electron bond in the carbocation and a three-electron bond in the radical. A dihedral angle between the O–Me bond and the plane of the aryl ring of 0° is maintained to maximize the orbital overlap in both of these species. However, in the carbanion this geometry leads to a repulsive interaction and consequently, the dihedral angle increases to 86° in order to minimize the overlap. The rotational barrier appears to be as much as 7–10 kcal mol^{-1}.

There also is a correlation between the charge localized on the benzylic group in the carbanion and the EA of the radical (Figure 4). For the carbanions, the charge localized on the α-CN-substituted carbanions is much greater than that for the other two sets. Unfortunately, in this case the scatter in the points precludes the analysis of systematic deviations of these points from the regression line. Furthermore, the differences are expected to be less since acetonitrile solvates carbocations to a greater extent than carbanions.[15]

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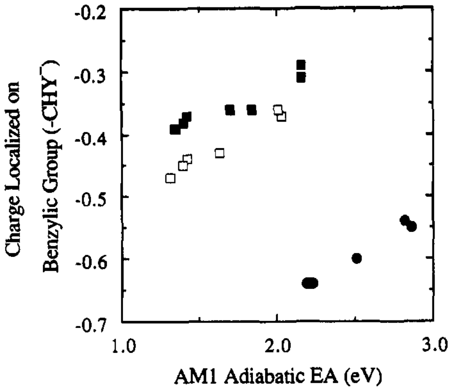

Figure 4. Relationship between charge localization on the benzylic group and the calculated EA_a for some substituted α-methoxybenzyl anions, □; benzyl anions, ■; and, α-cyanobenzyl anions, ●.

Substituent–Substituent Interactions from Isodesmic Electron Transfer Reactions. It is well established that substituent effects are not additive.[16] Recently, Dubois and co-workers[17] have shown that there is a linear correlation between the cross-interaction coefficient (which reflects the sensitivity of Hammett ρ values to substituent effects), and Hammett ρ values. This cross-interaction coefficient is actually a composite parameter that reflects all of the substituent–substituent interactions in a polar species. On the other hand, the magnitude and direction of interactions between specific substituents can be analyzed using isodesmic reactions (eq 6). This approach has been used to determine whether substituent–substituent interactions in free radicals are additive ($\Delta G°_6 = 0$), antagonistic ($\Delta G°_6 < 0$) or synergistic ("captodative"; $\Delta G°_6 > 0$).[18]

$$\mathrm{Ar(X,Y) + Ar(H,H) \rightarrow Ar(X,H) + Ar(H,Y)} \qquad (6)$$

Although the question of the existence and importance of the captodative effect has been a subject of controversy, it is now generally agreed that the energetics of these effects are too small in benzylic systems to measure.[18,19] It should be possible, therefore, to gain some insight into the magnitude and direction of substituent–substituent interactions in the corresponding ions by applying this method of analysis to the redox potentials. Since the redox potentials measure the thermodynamic differences between the ions and the radicals the expected sign of $\Delta G°_6$ will depend not only on the type of interaction (i.e. additive, synergistic or antagonistic), but also on the direction of the electron transfer (oxidation or reduction) and on the whether or not the energetically important species is the oxidized or reduced form (i.e. the ion or the radical).

The sign of $\Delta G°_6$ can easily be summarized if it is assumed that the effects on the ions are energetically more important than those on the radicals. For the oxidation reactions, $\Delta G°_6 < 0$ when the substituent–substituent interactions are antagonistic and $\Delta G°_6 > 0$ when they are synergistic. For the reduction reactions, the opposite is true, i.e. $\Delta G°_6 > 0$ when the interactions are antagonistic and < 0 when they are synergistic. If the effects on the radical are energetically more important then the sign of $\Delta G°_6$ will be opposite to that predicted for the ion. For this reason, the case where $\Delta G°_6 = 0$ may indicate either that the substituent effects are additive or that the effects on the radical and the ions are about the same magnitude (and therefore cancel). Values of $\Delta G°_6$ base on the redox potentials and the AM1 IP's and EA's are given in Table V.

Table V. Isodesmic Reaction Energies (kcal mol^{-1}) for Electron-Transfer Reactions of Some Benzyl Radicals

substituent		$\Delta G°_6$[a]		$\Delta H°_6$[b]	
α	ring	$E_{1/2}^{ox}$	$E_{1/2}^{red}$	IP	EA
CN	*p*-CN	0.0	6.4	1.1	4.2
	p-OMe	2.7	−4.6	0.4	0.6
OMe	*p*-CN	−2.5	0.0	0.8	2.1
	p-OMe	−7.1	−4.1	−3.8	−2.8

[a] Uncertainty ±2 kcal mol^{-1}. [b] Based on AM1 energies.

It is found, as might be expected, that the interaction between two methoxy groups in the carbocation and between two cyano groups in the carbanion is antagonistic, i.e. the second stabilizing substituent is less effective. However, for the first time it is possible to quantify the magnitude of these interactions. For the other three combinations in the carbocations and carbanions the interactions are either moderately synergistic or additive, i.e. saturation effects are not observed.

Conclusions

Ionizaton potentials and electron affinities of α,para-disubstituted benzyl radicals were calculated using the AM1 method. The calculated data give excellent correlations with the corresponding oxidation and reduction potentials measured in acetonitrile.

The solvation energies of the ions depend on the size of the ion as well as the extent of localization of the charge density. Thus, the solvation energy of the methoxymethyl cation is more exoergonic than that benzyl cation by approximately 16 kcal mol^{-1}. The data suggest that the solvation energies of the α-methoxybenzyl-substituted cations are more exoergonic than the α-cyano and unsubstituted ions by 8 kcal mol^{-1} even though all of these ions are approximately the same size. These differences are rationalized in terms of the substituent effects on charge localization. For the α-methoxybenzyl carbocations, the higher localized charge density on the benzylic group is responsible for the higher solvation energy.

The magnitude of the substituent–substituent interactions through the benzylic ring was estimated by using the electrochemical data to calculate the free energy change for a hypothetical isodesmic electron transfer reaction. It was found that these effects were additive or slightly synergistic. Only in those cases where two stabilizing substituents interact were large antagonistic (saturation) effects observed.

Experimental Section

Acetonitrile (HPLC grade) was refluxed for 18 h in an argon atmosphere over calcium hydride (2 g/L) and fractionally distilled prior to use. Tetrabutylammonium perchlorate (Eastman) was recrystallized twice from ethyl acetate/hexane (9:1 v/v) and dried at 40 °C in a vacuum oven for 12 h. All of the substituted toluenes were commercially available and purified by distillation or recrystallization before use with the exceptions listed below.

4-Cyanobenzyl methyl ether and 4-methoxybenzyl methyl ether were prepared by solvolysis of the benzyl bromides (Aldrich) in methanol containing 1 equiv of sodium methoxide. The reactions were followed by capillary gas chromatography and the products characterized by gas chromatography–mass spectrometry. The

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products were isolated by addition of an equivalent volume of water to the reaction mixture followed by extraction into hexane. After drying over magnesium sulfate and removal of the hexane under reduced pressure, the product was purified by vacuum distillation. All of the toluenes were >99% pure by GC analysis.

The redox potentials were measured using the photomodulation voltammetry technique that has been described elsewhere.[6] All measurements were made at a gold minigrid working electrode in acetonitrile containing di-*tert*-butyl peroxide (0.5 M), the substituted toluene (0.3–0.5 M), and tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte. Potentials are reported with respect to the saturated calomel electrode (SCE) as the reference.

Calculational Methods. The various radicals were calculated using the AM1 molecular orbital method and the half electron approximation. This procedure generally gives better energetic results than the alternative UHF procedure for radicals.[20,21] The geometries of the radicals were completely optimized in all internal coordinates. The radicals were first optimized using the MMX molecular mechanics method as incorporated into the PCMODEL program.[22] This geometry was then used as the starting point for the AM1 calculations. Vertical potentials are based on single-point calculations of the ions in the optimized geometry of the radical. All calculations were performed on a Ulysses Systems workstation or an Ogivar Technologies System 386/33 microcomputer.

Acknowledgment. We gratefully acknowledge Dr. D. Griller (NRCC) for helpful discussions.

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Synthesis and Correlation of Electronic Structures and NMR Properties of 10c-Azoniafluoranthene and 12d-Azoniaperylene

Marc Fourmigué,*[,1a] Hanne Eggert,[1b] and Klaus Bechgaard*[,1b]

Laboratoire de Physique des Solides associé au CNRS, Université Paris-Sud, Batiment 510, 91405 Orsay, France, and Kemisk Laboratorium II, H.C.Ørsted Institutet, Universitetsparken 5, 2100 København, Denmark

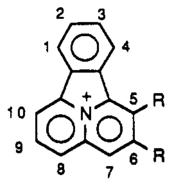
Received February 20, 1990 (Revised Manuscript Received April 9, 1991)

The synthesis of 10b-azoniafluoranthene (**1a**) and 12d-azoniaperylene (**2**) is described. MNDO calculations and ^{1}H, ^{13}C, and ^{15}N NMR data demonstrate that the positive charge in the two cations is delocalized off the nitrogen on the peripheral framework. Also, the fluoranthene derivative **1a** supports an additional ring current not observed in **2**. The two cations are reversibly reduced to the neutral radicals, whose EPR spectra in solution are reported and analyzed.

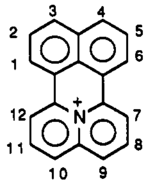
Introduction

Cation radical salts of aromatic hydrocarbons (naphthalene, fluoranthene, etc.) crystallize upon electrochemical oxidation in simple salts like (fluoranthene)$_2$PF$_6$.[2] In these conducting solids, motional narrowing combined with one-dimensional effects results in the observation of extremely narrow solid-state EPR signals.[3] The salts are, however, rather unstable,[4] a feature that prevents several applications of these materials.[5]

We decided to investigate isoelectronic azonia cations of fluoranthene and perylene and targeted 10c-azoniafluoranthene (**1a**)[6] and 12d-azoniaperylene (**2**). In these cations the nitrogen atom is substituted into positions where a minimal effect on the electronic properties of the corresponding radicaloid species is expected (vide infra). Also, light atom substitution was chosen to minimize spin-orbit coupling effects.



R = H **1a**
R = Me **1b**



2

By preserving the geometry of the parent arenes, it was expected that conducting solids exhibiting similar properties could be derived from **1a** and **2**. In addition, it was anticipated that the overall chemical stability might also be enhanced, since the salts would now be obtained by reduction rather than by oxidation.

The cations **1a** and **2** are reminiscent of the well-known cyclazine compounds that have been the object of considerable interest in the past 30 years.[7] The first cyclic π-electron system bridged by a central nitrogen atom, cycl[2.2.3]azine (**3**), was reported by Boekelheide et al.[8] Further compounds in this series became available by the work of Leaver et al.,[7] who reported the highly symmetric cycl[3.3.3]azine (**4**) and several fused derivatives. These compounds, as well as, more recently, several aza derivatives,[8b] were thoroughly studied by means of theoretical calculations and spectroscopic methods (UV–vis, XPS,

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