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Relationships between Carbocation Stabilities and Electrophilic Reactivity Parameters, *E*: Quantum Mechanical Studies of Benzhydryl Cation Structures and Stabilities

Claus Schindele,† K. N. Houk,*,‡ and Herbert Mayr*,†

Contribution from the Department Chemie der Ludwig-Maximilians-Universität München, Butenandtstrasse 5-13 (Haus F), D-81377 München, Germany, and Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569

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Abstract: Quantum chemical calculations of the affinities of benzhydryl cations $(XC_6H_4)_2CH^+$ for the methyl anion, hydroxide, and hydride anion have been performed up to the B3LYP/6-311++G(3df,2pd)//B3LYP/6-31G(d,p) level and compared with rate and equilibrium constants in solution. An excellent linear correlation between the empirical electrophilicity parameter E (by $\log k = s(N + E)$; Mayr, H.; Bug, T.; Gotta, M. F.; Hering, N.; Irrgang, B.; Janker, B.; Kempf, B.; Loos, R.; Ofial, A. R.; Remennikov, R.; Schimmel, H. *J. Am. Chem. Soc.* **2001**, *123*, 9500−9512) and the calculated methyl anion affinities ranging over 46.5 kcal mol^{-1} is found that reproduces the electrophilicity parameters E which range from −10 to +6 with a standard deviation of ±0.26 (11 points). The calculated OH^- and H^- affinities correlate with the calculated CH_3^- affinities with a slope of 1.00, indicating that the relative anion affinities of benzhydrylium ions are independent of the nature of the reference base. Linear correlations of the experimental pK_{R^+} values and chloride ion affinities in solution with the calculated anion affinities in the gas phase indicate that solvation attenuates the differences of carbocation stabilization in the gas phase but does not affect the relative differences. Application of Marcus theory shows that only reaction series with $\alpha = \partial\Delta G^{\ddagger}/\partial\Delta_r G^\circ = 0.5$ corresponding to a slope parameter of $s = 0.67$ can have constant intrinsic barriers. The slope parameters s found for π-nucleophiles and C−H hydride donors ($s \approx 1$) are interpreted by a decrease of the intrinsic barriers with increasing electrophilicities of the carbocations. On the other hand, a value of $s \leq 0.67$ as found for many n-nucleophiles as well as for Si−H, Ge−H, or Sn−H hydride donors is indicative of intrinsic barriers which are constant or slightly increase with increasing electrophilicity of the carbocation.

Introduction

In series of reports published in the past decade, we have established that numerous carbocations and related electrophiles may be characterized by an electrophilic reactivity parameter, E, that is useful for predicting rates of reactions with nucleophiles.[1−3] Similarly, a set of nucleophilic reactivity parameters, N, has been developed and used for quantitative predictions of reactivity of several hundred nucleophiles.[1,2,4]

$$\log k\ (20\ ^\circ\mathrm{C}) = s(N + E) \tag{1}$$

where s is the nucleophile-specific slope parameter, N is the nucleophilicity parameter, and E is the electrophilicity parameter.

Correlation 1, which presently covers a reactivity range of more than 30 orders of magnitude for electrophiles and almost 30 orders of magnitude for nucleophiles, has been reported to reproduce and predict rate constants for electrophile nucleophile combinations from known values of E, N, and s with remarkable precision[5] and has been used for a rational design of organic transformations[6] and of carbocationic polymerizations.[7] When

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* To whom correspondence should be addressed. H.M.: Telefax, (internat.) +49(0)89/2180-7719; E-mail, Herbert.Mayr@cup.uni-muenchen.de. K.N.H.: Telefax, (internat.) +1-310/206-1843; E-mail, houk@chem.ucla.edu.

† Department Chemie der Ludwig-Maximilians-Universität München.

‡ University of California, Los Angeles.

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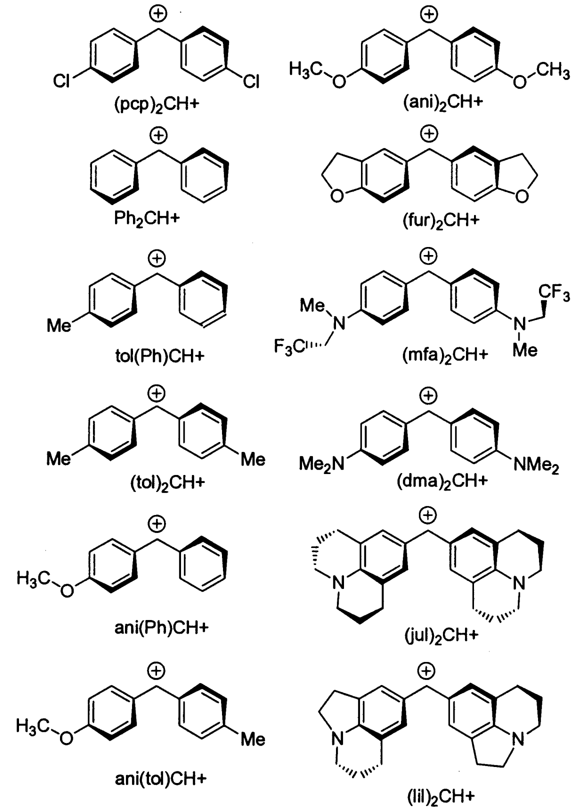
very bulky reagents (e.g., tritylium ions) are excluded, the rate constants calculated by eq 1 were found to reproduce experimental rate constants usually with a deviation of less than a factor of 10−100. This includes the small solvent effects in reactions of carbocations with noncharged π- and σ-nucleophiles,[1,8] but the nucleophilicity parameters for alcohols, amines, and related species have to be defined with respect to specific solvents.[9]

The origins of the linearity of these very general free energy relationships are not known with certainty. Electrophilic reactivity is often considered to be related to the LUMO energy of the electrophile or to the charge density at the reactive center.[10] Such theoretical indices are related to both thermodynamic stabilities and intrinsic electrophilicities of the cations. A complete understanding of these effects will involve computation of transition structures for many examples, including solvation energetics that are quite significant for both ionic and polar species.

Recently, we demonstrated that a straightforward access to *E*-, *N*-, and *s*-parameters is possible when benzhydrylium cations (diarylcarbenium ions) are used as reference electrophiles.[2] We have now undertaken a theoretical investigation of the structures and stabilities of those benzhydryl cations, which have served as the prototypes for the development of these parameters (Scheme 1). We explore the stabilities of cations relative to both the covalent precursors and the products of reaction and investigate the relationships between computed gas-phase stabilities and the solution-phase stabilities from pK_{R^+} values. The results produce significant new insights into the origins of these linear free-energy relationships and to quantitative predictions of *E* values.[11]

Scheme 1. Abbreviations and Calculated Conformations of Benzhydrylium Ions



In a series of related reactions, one generally finds more exothermic reactions to take place faster than less exothermic ones (Bell−Evans−Polanyi principle).[10d] The Brønsted correlation[12] (eq 2) provides a link between structural effects on rates and equilibria of chemical reactions.

$$\delta\Delta G^{\ddagger} = \alpha\delta\Delta G^{\circ} \qquad (2)$$

where $\delta\Delta G^{\ddagger}$ is the change of the activation free enthalpy by structural variation, $\delta\Delta G^{\circ}$ is the change of the reaction free enthalpy by structural variation, and α is the proportionality constant.

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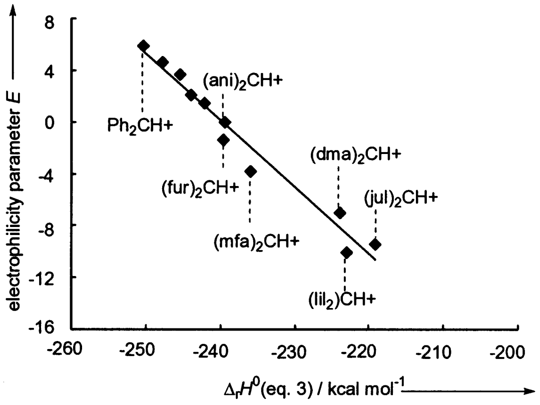

Figure 1. Correlation between the electrophilicity parameter E of various benzhydryl cations and the methyl anion affinities calculated at the AM1 level. $E = -0.51571\ \Delta_rH°(\text{eq } 3) - 123.65$.

Table 1. Calculated Heats of Formation (kcal mol^{-1}/AM1)^{a,b} of Benzhydryl Cations (Ar_2CH^+) and Diarylethanes (Ar_2CHCH_3), and the Corresponding Electrophilicity Parameters E

Ar_2CH^+	$\Delta H_f°$ (Ar_2CH^+)	$\Delta H_f°$ (Ar_2CHCH_3)	E_{exp}	E_{calc} ^{c}	ΔE^d
Ph_2CH^+	232.08	39.433	5.90	5.46	−0.44
tol(Ph)CH^+	221.83	31.782	4.59	4.12	−0.47
$(tol)_2CH^+$	211.86	24.129	3.63	2.92	−0.71
ani(Ph)CH^+	187.83	1.5569	2.11	2.17	0.06
ani(tol)CH^+	178.27	−6.0998	1.48	1.19	−0.29
$(ani)_2CH^+$	145.35	−36.312	0.00	−0.21	−0.21
$(fur)_2CH^+$	153.65	−28.158	−1.36	−0.14	1.22
$(mfa)_2CH^+$	−85.814	−264.00	−3.85	−2.00	1.85
$(dma)_2CH^+$	223.56	57.426	−7.02	−8.22	−1.20
$(jul)_2CH^+$	182.26	20.797	−9.45	−10.62	−1.17
$(lil)_2CH^+$	217.60	52.353	−10.04	−8.68	1.36

[a] 1 au = 627.51 kcal/mol. [b] $\Delta H_f°$ (CH_3^-) = 57.7055 kcal/mol. [c] From correlation in Figure 1. The values of E_{calc} were actually calculated with more decimals of $\Delta H_f°$ than indicated in the table. The use of the $\Delta H_f°$ values given in this table leads to slightly deviating results. [d] $\Delta E = (E_{calc} - E_{exp})$.

In line with this relationship, the electrophilicity parameters E of numerous carbocations have previously been found to correlate moderately with the methyl anion affinities (eq 3) calculated by AM1.[1b] Analogous correlations between experimental rate constants and calculated thermodynamic quantities have been reported.[13]

$$Ar_2CH^+ + CH_3^- \rightarrow Ar_2CH{-}CH_3 \qquad (3)$$

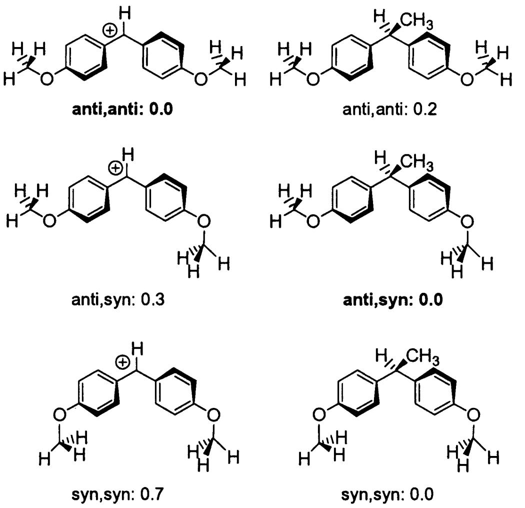

Figure 2. Relative energies (E_0/kcal mol^{-1}) of the various conformers of the bis(4-methoxyphenyl)substituted carbenium ion and 1,1-bis(4-methoxyphenyl)ethane.

Methyl anion affinities calculated by AM1 turned out to be unsuitable, however, for a fine-tuning of reactivity. For example, we were misled when using AM1 data for designing reference benzhydryl cations with distinct electrophilic reactivities. Thus, the methyl anion affinities calculated by AM1 predicted the bis(lilolidin-8-yl)methylium ion $(lil)_2CH^+$ (Figure 1 and Table 1) to be considerably more electrophilic (2 logarithmic units!) than its higher homologue $(jul)_2CH^+$ in contrast to the experimental findings, which revealed $(lil)_2CH^+$ to be less electrophilic than $(jul)_2CH^+$. Analogously, the order of electrophilicities for $(ani)_2CH^+$ and $(fur)_2CH^+$ was incorrectly predicted by the AM1 methyl anion affinities. The AM1 method thus is unable to provide precise estimates of electrophilic reactivities. One goal of this work was to investigate whether DFT methods can better be employed for this purpose.

Computational Methods

All calculations were performed with Gaussian 98.[14] Structures were optimized at the B3LYP level[15] using the 6-31G(d,p) basis set.[16] The B3LYP frequencies (unscaled) were used to calculate the zero-point corrections (ZPE). All energies reported at the B3LYP/6-311++G(3df,2pd) level include ZPE calculated at the B3LYP/6-31G(d,p) level unless otherwise noted.

Conformational Analysis

Various conformers were calculated for the bis(p-methoxyphenyl)methylium ion ($(ani)_2CH^+$, Figure 2) and the bis(2,3-dihydrobenzofuran-5-yl)methylium ion ($(fur)_2CH^+$, Figure 3). The methyl groups were always staggered. As shown in Figures 2 and 3, energy differences among different conformers were generally insignificant, and, for the further analysis, the structures with lowest energies (E_0 marked bold) were used. For the other compounds, only the conformers shown in Scheme 1 have been investigated. For detailed information, see the Supporting Information.

The influence of the basis set on the methyl anion affinities (ΔE_{tot}, eq 3) was examined for five benzhydrylium ions with the B3LYP functional, and 6-31(d,p), 6-311++G(d,p), and 6-311++(3df,2pd) basis sets. While replacement of 6-31(d,p) by 6-311++G(d,p) resulted in a significant change of ΔE_{tot} for

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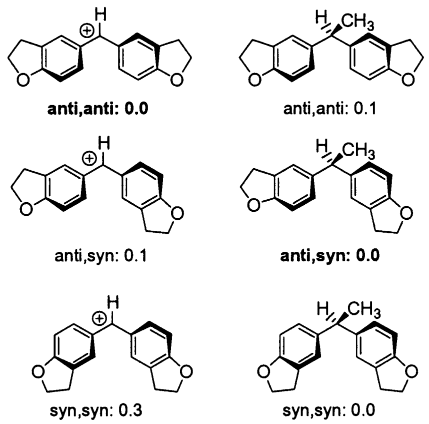


Figure 3. Relative energies (E_0/kcal mol^{-1}) of the various conformers of bis(2,3-dihydrobenzofuran-5-yl) substituted carbenium ions and the corresponding ethanes.

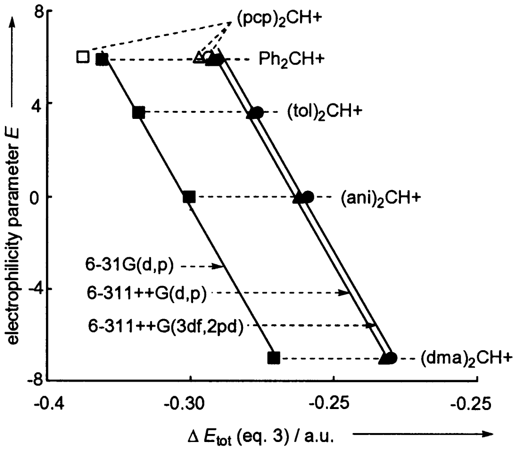
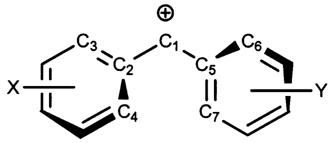


Figure 4. Correlation between the E-parameter and the calculated methyl anion affinities [ΔE_{tot}(eq 3) = $E_{tot}(Ar_2CH{-}CH_3) - E_{tot}(Ar_2CH^+) - E_{tot}(CH_3^-)$] for five benzhydrylium ions at B3LYP/6-311++G(3df,2pd)//B3LYP/6-31G(d,p) [$E = 215.4\Delta E_{tot}(\text{eq }3) - 67.01$, $r^2 = 0.994$], B3LYP/6-311++G(d,p)//B3LYP/6-31G(d,p) [$E = 216.6\Delta E_{tot}(\text{eq }3) - 67.92$, $r^2 = 0.996$], and B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p) [$E = 216.9\Delta E_{tot}(\text{eq }3) - 76.45$, $r^2 = 0.996$] levels. The p-chlorophenyl substituted system $(pcp)_2CH^+$ is not used for the construction of the correlation lines.

Table 2. Calculated Bond Lengths (Å) and Dihedral Angles (deg) of Benzhydrylium Ions (B3LYP/6-31(d,p))



Ar_2CH^+	C_1C_2	C_1C_5	$(C_1C_2 + C_1C_5)/2$	$C_5C_1C_2C_4$	$C_2C_1C_5C_7$	E_{exp}[a]
$(pcp)_2CH^+$	1.4155	1.4155	1.4155	16.9	17.0	6.02
Ph_2CH^+	1.4168	1.4168	1.4168	17.5	17.5	5.90
$tol(Ph)CH^+$ [b]	1.4108	1.4210	1.4159	15.6	18.4	4.59
$(tol)_2CH^+$	1.4150	1.4150	1.4150	16.5	16.3	3.63
$ani(Ph)CH^+$ [b]	1.4019	1.4277	1.4148	13.1	20.2	2.11
$ani(tol)CH^+$ [b]	1.4059	1.4218	1.4138	13.7	18.1	1.48
$(ani)_2CH^+$	1.4126	1.4126	1.4126	15.1	15.1	0.00
$(fur)_2CH^+$	1.4129	1.4129	1.4129	17.1	17.1	−1.36
$(mfa)_2CH^+$	1.4108	1.4109	1.4109	14.3	14.3	−3.85
$(dma)_2CH^+$	1.4106	1.4106	1.4106	14.7	14.7	−7.02
$(jul)_2CH^+$	1.4108	1.4108	1.4108	14.2	14.2	−9.45
$(lil)_2CH^+$	1.4117	1.4115	1.4116	15.7	14.8	−10.04

[a] Electrophilicity parameter according to eq 1; from ref 2. [b] In the case of unsymmetrical benzhydrylium ions, the X-substituted ring refers to the first and the Y-substituted ring refers to the second ring in the formula of the first column of Table 2.

all systems, 6-311++G(3df,2pd) gave nearly the same results as 6-311++G(d,p) for the phenyl-, tolyl-, anisyl-, and dimethylaminophenyl-substituted compounds.

The deviation of the bis(p-chlorophenyl)carbenium ion (pcp)-CH^+ from the correlation line in Figure 4 decreases as the basis set is increased. However, even with the 6-311++G(3df,2pd) basis, the bis(p-chlorophenyl)carbenium ion deviates considerably. The correlation based on methyl anion affinities suggests a higher electrophilicity of the chlorinated compound ($E_{calc} = 7.01$) than that actually observed ($E_{obs} = 6.02$). This deviation is possibly due to an inaccuracy in the experimental E value of this carbocation, which is predominantly derived from fast reactions with rate constants $10^7 < k < 10^8$ L mol^{-1} s^{-1}, a range where the correlations start deviating from the linear relationship described by eq 1.[3c] This interpretation is supported by the fact that ethanolysis rate constants[17a] as well as pK_{R^+} values[18a] suggest a lower stabilization of the bis(p-chlorophenyl)carbenium ion as compared to the nonsubstituted benzhydrylium cation, which should result in a higher electrophilicity of the chlorosubstituted carbocation.

Structure and Reactivity

The structures of the parent benzhydryl cation and the 11 substituted derivatives in Scheme 1 were optimized at the B3LYP/6-31(d,p) level. Some geometric parameters, bonds, and dihedral angles involving the cation center are shown in Table 2, along with the experimental electrophilicity parameters. Accordingly, a slight, but steady, decrease of the bond lengths between the aryl rings and the carbenium center is observed, as the electrophilicity is reduced from $E = 6.02$ (1.416 Å) to $E = -3.85$ (1.411 Å). Further reduction of the electrophilicity by introducing even stronger electron donors did not cause a further shortening of this distance, and the corresponding bond in the bis(lilolidyl)carbenium ion $(lil)_2CH^+$ is even slightly longer than that in the bis(dimethylamino)-substituted analogue $(dma)_2CH^+$ (Figure 5).

As expected, in the unsymmetrical benzhydrylium ions tol-(Ph)CH^+, ani(Ph)CH^+, and ani(tol)CH^+, the aryl rings that are substituted by the better donor contribute more to delocalization of the positive charge as indicated by the shorter distance C_1C_2 as compared to C_1C_5 (Table 2).

There is no significant correlation between electrophilicity and dihedral angles. As shown in Table 2, the benzhydryl cations prefer the propeller-type arrangement, and the deviation of the aryl rings from planarity ranges from 13 to 20°. In the unsymmetrical benzhydrylium ions tol(Ph)CH^+, ani(Ph)CH^+, and ani(tol)CH^+, the ring carrying the weaker donor is twisted more out of the plane to tolerate a smaller distortion of the ring with the better electron donor.[17b]

Correlations between *E* Values and Cation Stabilities

Table 3 lists the total energies of the cations and the corresponding methyl anion adducts, along with experimental

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(17) (a) Ethanolysis rates of diarylmethyl chlorides (25 °C) k_{solv} (Ph_2CHCl) = 5.36×10^{-5} s^{-1}; k_{solv} ($p\text{-}ClC_6H_4)_2CHCl$ = 8.07×10^{-6} s^{-1}: Schade, C.; Mayr, H. *Tetrahedron* **1988**, *44*, 5761−5769. (b) Tsuno, Y.; Fujio, M. *Adv. Phys. Org. Chem.* **1999**, *32*, 267−385.

(18) (a) pK_{R^+} (Ph_2CH^+) = −13.3; pK_{R^+} ($(pcp)_2CH^+$) = −13.96: Deno, N. C.; Schriesheim, A. *J. Am. Chem. Soc.* **1955**, *77*, 3051−3054. (b) Mindl, J.; Vecera, M. *Collect. Czech. Chem. Commun.* **1971**, *36*, 3621−3632. (c) Mindl, J. *Collect. Czech. Chem. Commun.* **1972**, *37*, 585−591.

Table 3. Total Energies and Zero-Point Energies of Diarylcarbenium Ions and the Corresponding 1,1-Diarylethanes; ΔE_0(Eq 3) (kcal mol^{-1}) (B3LYP/6-31G(d,p))

Ar_2CH^+	E_{tot} (Ar_2CH^+)/au	ZPE^a (Ar_2CH^+)/kcal mol^{-1}	E_{tot} (Ar_2CHCH_3)/au	ZPE^a (Ar_2CHCH_3)/kcal mol^{-1}	ΔE_0(eq 3)^b/ kcal mol^{-1}	$E_{calc}{}^c$	ΔE^d
$(pcp)_2CH^+$	−1420.954059	113.155	−1461.137604	137.397	−236.4	7.53	1.51
Ph_2CH^+	−501.7711045	125.326	−541.9483128	149.528	−232.5	6.16	0.26
tol(Ph)CH^+	−541.0983788	142.393	−581.2688332	166.652	−228.2	4.65	0.06
tol_2CH^+	−580.4250766	159.544	−620.5893594	183.803	−224.3	3.30	−0.33
ani(Ph)CH^+	−616.3129847	145.923	−656.473035	169.886	−221.9	2.47	0.36
ani(tol)CH^+	−655.6388507	163.043	−695.793403	187.122	−218.5	1.28	−0.20
$(ani)_2CH^+$	−730.8513487	166.513	−770.997937	190.414	−213.5	−0.46	−0.46
$(fur)_2CH^+$	−807.0798106	175.537	−847.221718	199.508	−210.5	−1.51	−0.15
$(mfa)_2CH^+$	−1443.836269	225.033	−1483.967807	248.419	−204.6	−3.58	0.27
$(dma)_2CH^+$	−769.7762317	217.666	−809.8934242	241.060	−195.6	−6.73	0.29
$(jul)_2CH^+$	−1079.522271	309.906	−1119.625641	332.540	−187.7	−9.49	−0.04
$(lil)_2CH^+$	−1000.876648	272.570	−1040.97813	295.942	−185.9	−10.11	−0.07

[a] 1 au = 627.51 kcal/mol. [b] $E_{tot}(CH_3^-) = -39.796028$ au, $ZPE(CH_3^-) = 17.5$ kcal mol^{-1}. [c] Electrophilicity parameter calculated by eq 4. The values of E_{calc} were actually calculated with more decimals of ΔE_0 than indicated in the table. The use of the ΔE_0 values given in this table leads to slightly deviating results. [d] $\Delta E_{calc} = E_{calc} - E_{exp}$; E_{exp} from Table 2.

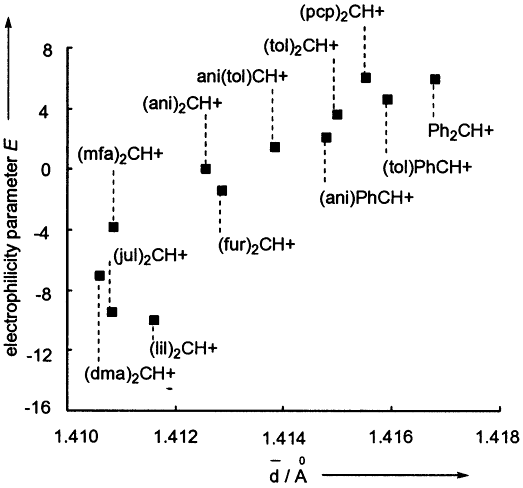

Figure 5. Correlation between the calculated mean distances (($C_1C_2 + C_1C_5$)/2) and the electrophilicity parameters E of the benzhydryl cations.

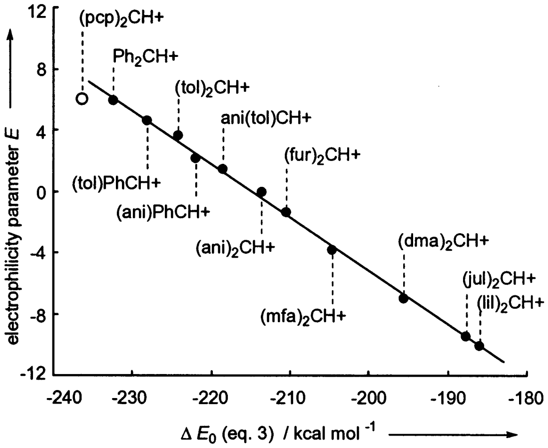

Figure 6. Correlation between the electrophilicity parameters E of various benzhydryl cations with the methyl anion affinities [ΔE_0(eq 3) = $E_0(Ar_2CH{-}CH_3) - E_0(Ar_2CH^+) - E_0(CH_3^-)$] calculated at the B3LYP/6-31G-(d,p) level ($r = 0.9976$), with $(pcp)_2CH^+$ omitted.

E values. Because Figure 4 indicates that the correlation between the electrophilicity parameters E and the methyl anion affinities calculated at the B3LYP/6-31G(d,p) level is of comparable quality to the correlations obtained with larger basis sets, the relatively economical 6-31G(d,p) basis set has been employed for calculations of further benzhydrylium ions.

Figure 6 shows a plot of the E values versus methyl anion affinities (ΔE_0(eq 3)) of 12 benzhydrylium ions covering a range of 16 orders of magnitude in electrophilic reactivity and 46.5 kcal mol^{-1} in gas-phase methyl anion affinities ΔE_0. A least squares line is drawn using 11 benzhydrylium ions (with $(pcp)_2CH^+$ ignored). The linear correlation indicates that differential solvation is negligible. With eq 4 it is now possible to derive electrophilicity parameters E from calculated methyl anion affinities ΔE_0 (in kcal mol^{-1}) with a standard deviation of ±0.26 units in E.

$$E = -0.3496\Delta E_0(\text{eq } 3) - 75.11 \tag{4}$$

where E is the electrophilicity parameter, and ΔE_0(eq 3) is the methyl anion affinity as defined by eq 3.

Only the previously discussed cations $(pcp)_2CH^+$ ($\Delta E = 1.51$) and $(ani)_2CH^+$ ($\Delta E = -0.46$) show deviations larger than 0.4 (last column of Table 4).

Figure 6 correlates kinetic data measured in solution with thermodynamic data calculated for the gas phase. To interpret the slope of this correlation, the effects of solvation must be considered. To explore solvation effects, hydride and hydroxide affinities of some benzhydrylium ions (eqs 5,6) have been computed (Table 4) and compared with equilibrium constants measured in solution.

$$Ar_2CH^+ + H^- \rightarrow Ar_2CH_2 \tag{5}$$

$$Ar_2CH^+ + OH^- \rightarrow Ar_2CH{-}OH \tag{6}$$

Figure 7 is a plot of the hydroxide ion affinities measured in aqueous solution (i.e., pK_{R^+})[18] versus the hydroxide affinities computed for the gas phase. Figure 7 gives a straight line with a slope of 0.72, indicating that solvation attenuates the differences in cation stabilities in water relative to those in the gas phase. That is, the differences in free energies measured in solution are 0.72 of those computed for the gas phase.

Figure 8 shows plots of hydroxide and hydride affinities versus methyl anion affinities discussed earlier. Parallel lines with unit slopes are obtained. This proves that structural variation of the benzhydrylium ions affects their affinities toward H^-, CH_3^-, and OH^- to exactly the same extent. Presumably,

Table 4. Total Energies (au) and Zero-Point Energies (kcal mol^{-1})^a of Diarylmethanes and 1,1-Diarylmethanols; ΔE_0(Eqs 5,6) (kcal mol^{-1}) (B3LYP/6-31G(d,p))

Ar	E_{tot} (Ar_2CH_2)	*ZPE* (Ar_2CH_2)	ΔE_0(eq 5)^b	E_{tot} (Ar_2CHOH)	*ZPE* (Ar_2CHOH)	ΔE_0(eq 6)^c
Ph	−502.634012	131.778	−245.2	−577.8446188	134.607	−214.2
tol	−581.27504	166.001	−237.1	−656.4859277	168.926	−205.6
ani	−731.68358	172.639	−226.3	−806.8950248	175.478	−195.2
mfa	−1444.6534	230.649	−217.4	−1519.864848	233.521	−186.2
dma	−770.57919	223.472	−208.3	−845.7912445	226.204	−177.6

[a] 1 au = 627.51 kcal/mol. [b] E_{tot} (H^-) = −0.4618167 au. [c] E_{tot} (OH^-) = −75.726924 au, *ZPE* (OH^-) = 5.400 kcal mol^{-1}.

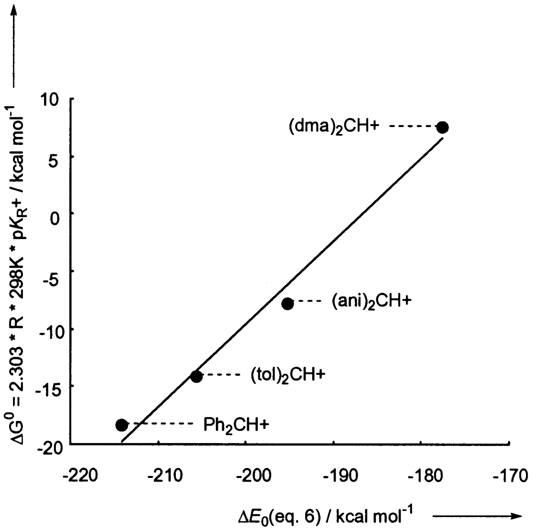

Figure 7. Correlation between $\Delta G°$ (from pK_{R^+}) and calculated hydroxide anion affinities. $\Delta G° = 0.719\Delta E_0$(eq 6) + 134; $pK_{R^+} = 0.527\Delta E_0$(eq 6) + 98.5.

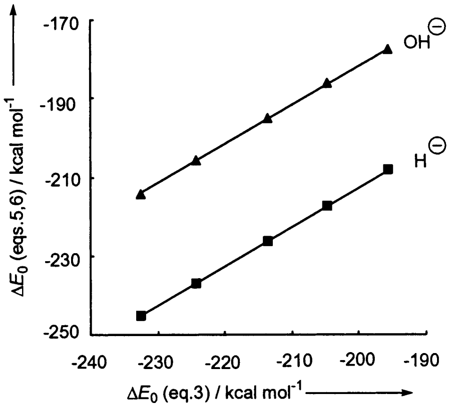

Figure 8. Correlation of calculated hydride (eq 5) and hydroxide ion affinities (eq 6) with calculated methyl anion affinities (eq 3) at B3LYP/6-31G(d,p) level. ΔE_0(eq 5) = $1.00\Delta E_0$(eq 3) − 12.1; ΔE_0(eq 6) = $0.990\Delta E_0$(eq 3) + 16.1.

this will be true for the reactions of the benzhydrylium ions with any other Lewis base (e.g., Cl^-). Figure 9 shows a plot of the relative chloride ion affinities in solution (eq 7)[19] versus the methyl anion affinities in the gas phase (eq 3). Once again, the free-energy change in the solution ionization reaction is less than that for the gas phase, but there is a reasonable linear correlation in agreement with previous reports by Arnett.[20]

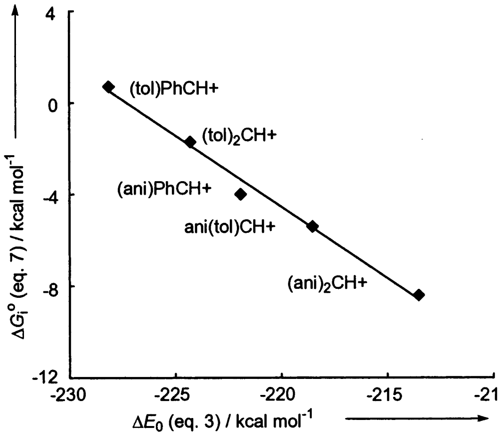

Figure 9. Correlation between ionization free enthalpies of benzhydryl chlorides (CH_2Cl_2, BCl_3, −70 °C) with calculated methyl anion affinities (eq 3). $\Delta G_i° = -0.62\Delta E_0$(eq 3) −141.

Furthermore, the similarity of the slopes in Figures 7 and 9 shows that water and dichloromethane attenuate the differences of carbocation stabilization in the gas phase to similar extents.

$$Ar_2CHCl + BCl_3 \xrightleftharpoons[CH_2Cl_2]{\Delta G_i°} Ar_2CH^+BCl_4^- \tag{7}$$

This series of calculations show the remarkable result that the changes in free energy of ionization of diarylmethanes to cation plus hydride, of diarylmethanols to cation plus hydroxide, and of diarylchloromethanes to cation plus chloride all correlate very well with each other regardless of the series and regardless of whether the reaction is studied in the gas phase or solution. This reflects the fact that most of the energy changes upon substitution occur in the cation and that the neutral reactant changes little. Furthermore, the solvation energy for this series is correlated with the cation stabilities, so solvation reduces differences in anion affinities of the benzhydryl cations, but the carbocations maintain their relative affinities toward Lewis bases.

Rate Equilibrium Relationships

The rate constants (log k) of all reactions of benzhydryl cations with π-nucleophiles, σ-nucleophiles (hydrides), and n-nucleophiles studied so far correlate linearly with the electrophilicity parameters E. Combination of this observation with the linear correlation between the electrophilicity parameter E and the methyl anion affinities ΔE_0 (Figure 6) implies that none of our correlations shows curved rate-equilibrium relationships. The slope (Brønsted coefficient) $\alpha = \partial\Delta G^{\ddagger}/\partial\Delta_r G°$ adopts a characteristic value for each nucleophile.

Substitution of $\partial\Delta G^{\ddagger}$ by $-2.303RT\partial$ log k (Eyring equation) and ∂ log k by $s\partial E$ (eq 1) yields $\partial\Delta G^{\ddagger}$ as a function of the electrophilicity parameter E and the nucleophile-specific slope parameter s (eq 8).

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(19) Schade, C.; Mayr, H.; Arnett, E. M. *J. Am. Chem. Soc.* **1988**, *110*, 567−571.

(20) Arnett, E. M.; Hofelich, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 2889−2895.

$$\partial\Delta G^{\ddagger} = -2.303RTs\partial E(\text{eq }1) \qquad (8)$$

where ∂E is the variation of the electrophilicity parameter defined by eq 1.

The effect of solvation can be derived from the correlation in Figure 9, which is expressed by eq 9.

$$\partial\Delta_r G^{\circ} = 0.62\partial\Delta E_0(\text{eq }3) \qquad (9)$$

where $\partial\Delta_r G^{\circ}$ is the variation of affinities toward Lewis bases in solution, and $\partial\Delta E_0$ is the variation of affinities toward a Lewis base (CH_3^-) in the gas phase.

By the combination of eq 8 with eq 9, we obtain eq 10.

$$\alpha = \frac{\partial\Delta G^{\ddagger}}{\partial\Delta_r G^{\circ}} = \frac{-2.303RTs}{0.62}\cdot\frac{\partial E(\text{eq }1)}{\partial\Delta E_0(\text{eq }3)} \qquad (10)$$

For 293 K and $\partial E(\text{eq }1)/\partial\Delta E_0(\text{eq }3) = -0.3496$ (from eq 4), we arrive at eq 11, which relates Brønsted's α with the nucleophile-specific slope parameter s of eq 1.

$$\alpha = 0.75s \qquad (11)$$

Marcus theory expresses the free-energy barrier of a reaction ($\Delta G^{\ddagger}$) by a combination of thermodynamic ($\Delta_r G^{\circ}$)and intrinsic factors ($\Delta G_0^{\ddagger}$). $\Delta_r G^{\circ}$ is the standard free energy of the reaction in the prevailing medium, and $\Delta G_0^{\ddagger}$ is the intrinsic barrier for the reaction, that is, the barrier for the case where $\Delta_r G^{\circ} = 0$.[21]

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger} + 0.5\Delta_r G^{\circ} + ((\Delta_r G^{\circ})^2/16\Delta G_0^{\ddagger}) \qquad (12)$$

If the intrinsic barrier remains constant within a reaction series, the coefficient α can be derived as shown in eq 13. When the intrinsic barrier $\Delta G_0^{\ddagger}$ is a function of $\Delta_r G^{\circ}$, the more complex eq 14 is obtained.[22]

$$\alpha = \frac{\partial\Delta G^{\ddagger}}{\partial\Delta_r G^{\circ}} = \frac{1}{2} + \frac{\Delta_r G^{\circ}}{8\Delta G_0^{\ddagger}} \qquad (13)$$

$$\alpha = \frac{\partial\Delta G^{\ddagger}}{\partial\Delta_r G^{\circ}} = \frac{1}{2} + \frac{\Delta_r G^{\circ}}{8\Delta G_0^{\ddagger}} + \left[1 - \left(\frac{\Delta_r G^{\circ}}{4\Delta G_0^{\ddagger}}\right)^2\right]\frac{\partial\Delta G_0^{\ddagger}}{\partial\Delta_r G^{\circ}} \qquad (14)$$

In the case of constant intrinsic barriers ($\Delta G_0^{\ddagger}$), that is, when eq 13 holds, plots of $\Delta G^{\ddagger}$ versus $\Delta_r G^{\circ}$ are only linear when $\Delta_r G^{\circ}/8\Delta G_0^{\ddagger} \ll {}^1/_2$. In these cases, $\alpha = 0.5$, corresponding to a value of $s = 0.67$ (from eq 11). As a consequence, only reaction series with $s = 0.67$ (e.g., reactions of a series of benzhydrylium ions with *n*-nucleophiles or Si−H hydride donors) can have constant intrinsic barriers and give rise to linear plots of $\Delta G^{\ddagger}$ versus $\Delta_r G^{\circ}$. When $s \neq 0.67$ (corresponding to $\partial\Delta G_0^{\ddagger}/\partial\Delta_r G^{\circ} \neq 0.5$), as reported in refs 1 and 2, variable intrinsic barriers[23] must occur to compensate for the changes in $\Delta_r G^{\circ}$. This nearly perfect compensation, giving rise to a linear correlation over a phenomenal range of reactivities, suggests that there is a fundamental principle at work here.

As discussed above, in such cases, α is given by eq 14. Most of the reactions of benzhydryl cations, for which we have measured kinetics (i.e., $k = 10^{-4}$ to 10^7 L mol^{-1} s^{-1} or $\Delta G^{\ddagger} =$ 8−22 kcal mol^{-1})$^{1-5}$ are slightly exergonic, which implies that their intrinsic barriers are somewhat larger than 8−22 kcal mol^{-1}. For that reason, we can assume $\Delta_r G^{\circ}/8\Delta G_0^{\ddagger} \ll {}^1/_2$ and $(\Delta_r G^{\circ}/4\Delta G_0^{\ddagger})^2 \ll 1$, which reduces eq 14 to eq 15.

$$\alpha = \frac{\partial\Delta G^{\ddagger}}{\partial\Delta_r G^{\circ}} \approx \frac{1}{2} + \frac{\partial\Delta G_0^{\ddagger}}{\partial\Delta_r G^{\circ}} \qquad (15)$$

As derived from eq 13, one again comes to the conclusion that in the case of a constant intrinsic barrier, α will be 0.5 (i.e., $s = 0.67$) because the last term of eq 15 becomes 0. If $\partial\Delta G_0^{\ddagger}/\partial\Delta_r G^{\circ} < 0$, that is, when the intrinsic barrier increases with increasing exergonicity, it will be recognizable by $\alpha < 0.5$ (eq 15) or $s < 0.67$ (eq 11). On the other hand, if $\partial\Delta G_0^{\ddagger}/\partial\Delta_r G^{\circ} > 0$, that is, when the intrinsic barrier decreases with increasing exergonicity, one will observe a value of $\alpha > 0.5$ (eq 15) or $s > 0.67$ (eq 11).

It is now possible to analyze the slope parameters, s, for different classes of nucleophiles. Slope parameters $s \leq 0.67$ have been found for many *n*-nucleophiles (amines, alkoxides, phosphanes)[9a] and hydride donors (Si−H, Ge−H, Sn−H).[2] In reactions with these heteronucleophiles, the intrinsic barrier increases with increasing exergonicity. Most π-nucleophiles as well as CH-hydride donors, on the other hand, are characterized by slopes around $s = 1$, indicating that the intrinsic barriers decrease as the electrophilicities of the benzhydrylium ions increase. In these reactions, the Hammond effect, which reduces $\partial\Delta G^{\ddagger}/\partial\Delta_r G^{\circ}$ as the transition state is shifted toward reactants in more exergonic reactions, must be overcompensated by a special transition-state stabilizing factor.

It should be noted that the observation of constant intrinsic barriers for reaction series with $s = 0.67$ does not imply constant transition states throughout the reaction series. As explicitly demonstrated for hydride abstractions by experimental[4h] and quantum chemical methods,[24] the position of the transition state may change from early to late within a reaction series as predicted by Hammond's postulate without causing curvature of the $\partial\Delta G^{\ddagger}/\partial\Delta_r G^{\circ}$ correlation. The magnitude of α (or s) thus is totally unrelated to the position of the transition state. Transition-state calculations for reactions of carbocations with different types of nucleophiles (π, σ, n) are now needed to elucidate the information hidden behind the slope parameter s.

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Supporting Information Available: Cartesian coordinates of all reported structures, as well as the total electronic and zero-point vibrational energies (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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