

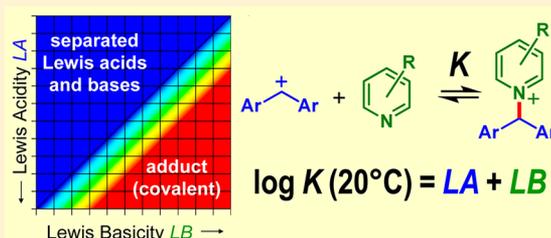
1 Scales of Lewis Basicities toward C-Centered Lewis Acids (Carbocations)

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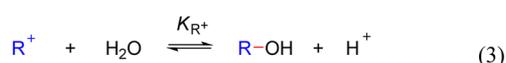
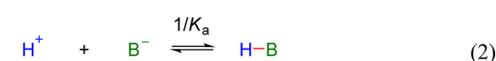
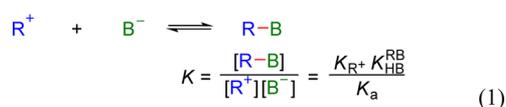
6 **S** Supporting Information

7 **ABSTRACT:** Equilibria for the reactions of benzhydryl cations (Ar_2CH^+)
8 with phosphines, *tert*-amines, pyridines, and related Lewis bases were
9 determined photometrically in CH_2Cl_2 and CH_3CN solution at 20 °C.
10 The measured equilibrium constants can be expressed by the sum of
11 two parameters, defined as the Lewis Acidity (LA) of the benzhydrylium
12 ions and the Lewis basicity (LB) of the phosphines, pyridines, etc. Least-
13 squares minimization of $\log K = \text{LA} + \text{LB}$ with the definition $\text{LA} = 0$ for
14 $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}^+$ gave a Lewis acidity scale for 18 benzhydrylium
15 ions covering 18 orders of magnitude in CH_2Cl_2 as well as Lewis
16 basicities (with respect to C-centered Lewis acids) for 56 bases. The Lewis
17 acidities correlated linearly with the quantum chemically
18 calculated (B3LYP/6-311++G(3df,2pd)//B3LYP/6-31G(d,p) level) methyl
19 anion affinities of the corresponding benzhydrylium
20 ions, which can be used as reference compounds for characterizing a wide
21 variety of Lewis bases. The equilibrium measurements
22 were complemented by isothermal titration calorimetry studies. Rates of $\text{S}_{\text{N}}1$
23 solvolyses of benzhydryl chlorides, bromides, and
24 tosylates derived from $\text{E}(13\text{--}33)^+$, i.e., from highly reactive carbocations,
25 correlate excellently with the corresponding Lewis
acidities and the quantum chemically calculated methyl anion affinities. This correlation does not hold for solvolyses of derivatives of the better stabilized amino-substituted benzhydrylium ions $\text{E}(1\text{--}12)^+$. In contrast, the correlation between electrophilic reactivities and Lewis acidities (or methyl anion affinities) is linear for all donor-substituted benzhydrylium ions $\text{E}(1\text{--}21)^+$, while the acceptor-substituted benzhydrylium ions $\text{E}(26\text{--}33)^+$ react more slowly than expected from their thermodynamic stabilities. The boundaries of linear rate-equilibrium relationships were thus defined.



26 ■ INTRODUCTION

27 Relationships between rate and equilibrium constants are a
28 key, possibly the most important key, for understanding organic
29 reactivity.^{1–5} In this context, Brønsted correlations,^{1,4} i.e.,
30 relationships between rate constants and $\text{p}K_{\text{a}}$ values, play a
31 central role, because $\text{p}K_{\text{a}}$ values are available for most classes
32 of organic compounds.^{6,7} Recently, even a scale of absolute
33 Brønsted acidities has been proposed.⁸ The fundamental
34 problem of these correlations is obvious, however: The $\text{p}K_{\text{a}}$
35 ($-\log K_{\text{a}}$) values of the acids HB express the relative affinities
36 of their conjugate bases (B^-) toward the proton and, therefore,
37 the rates of the reactions of nucleophiles B^- with other classes
38 of electrophiles cannot be expected to be tightly correlated
39 with $\text{p}K_{\text{a}}$.



40 In view of this problem, Parker suggested to compare the
41 nucleophilic reactivities of different bases B^- (i.e., the relative

42 rates of the reactions of a series of B^- with a certain reference
43 electrophile) with the corresponding equilibrium constants and
44 to use the terms hydrogen basicity, carbon basicity, and sulfur
45 basicity for comparing the relative affinities of various bases
46 toward the proton, carbon-centered Lewis acids (e.g.,
47 carbenium ions), or sulfur-centered Lewis acids, respectively.⁹
48 As relative carbon basicities should vary at least somewhat with
49 the nature of the reference carbon acid, for certain purposes a
50 further subdivision into the more specific categories methyl
51 basicity, phenyl basicity, acetyl basicity, etc., may be
52 appropriate.¹⁰ The association constants K for combinations
53 of carbocations R^+ with Lewis bases B^- are given by eq 1.

54 The equilibrium constant K (eq 1) is related to Brønsted
55 basicity $1/K_{\text{a}}$ which describes the affinity of B^- toward the
56 proton (eq 2)^{11,12} and Deno's $\text{p}K_{\text{R}^+}$ values, which describe
57 the equilibrium constants for the reactions of R^+ with water
58 (eq 3).^{13,14}

59 In their seminal 1965 paper, titled “Carbon Basicity”,¹⁵ Hine
60 and Weimar pointed out that the basicities of B^- toward cations
61 R^+ relative to their Brønsted basicities can be expressed by the
62 equilibrium constant $K_{\text{HB}}^{\text{RB}}$ for eq 4,^{12,16} which is accessible from
63 compiled thermodynamic data.

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Table 2. Equilibrium Constants K (M^{-1}) for the Reactions of Benzhydrylium Ions E^+ with Lewis Bases N in CH_2Cl_2 at $20^\circ C$ and Comparison with Equilibrium Constants K_{calc} (M^{-1}) Calculated from Eq 7

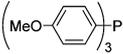
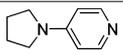
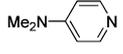
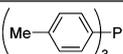
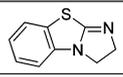
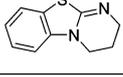
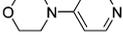
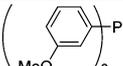
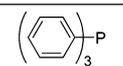
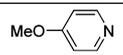
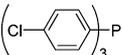
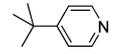
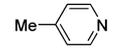
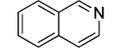
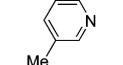
N	Lewis base		E^+	electrophile		experiment		correlation	
	formula	$LB_{CH_2Cl_2}$		abbreviation	$LA_{CH_2Cl_2}$	K^a / M^{-1}	K_{calc}^b / M^{-1}	K_{calc}/K	
N1		17.90	$E1^+$	(lil) $_2CH^+$	-12.76	1.73×10^5 ^c	1.40×10^5	0.81	
			$E2^+$	(jul) $_2CH^+$	-12.62	1.54×10^5 ^c	1.90×10^5	1.23	
N2		17.47	$E1^+$	(lil) $_2CH^+$	-12.76	6.27×10^4 ^d	5.16×10^4	0.82	
			$E2^+$	(jul) $_2CH^+$	-12.62	6.16×10^4 ^d	7.01×10^4	1.14	
			$E3^+$	(ind) $_2CH^+$	-11.16	1.90×10^6 ^d	2.03×10^6	1.07	
N3		17.00	$E1^+$	(lil) $_2CH^+$	-12.76	1.79×10^4 ^e	1.74×10^4	0.97	
			$E2^+$	(jul) $_2CH^+$	-12.62	3.38×10^4 ^e	2.37×10^4	0.70	
			$E3^+$	(ind) $_2CH^+$	-11.16	5.45×10^5 ^e	6.85×10^5	1.26	
			$E4^+$	(thq) $_2CH^+$	-10.92	1.03×10^6 ^e	1.20×10^6	1.17	
N4		16.82	$E1^+$	(lil) $_2CH^+$	-12.76	1.35×10^4	1.15×10^4	0.85	
			$E2^+$	(jul) $_2CH^+$	-12.62	1.33×10^4	1.56×10^4	1.17	
N5		16.42	$E1^+$	(lil) $_2CH^+$	-12.76	5.70×10^3 ^f	4.57×10^3	0.80	
			$E2^+$	(jul) $_2CH^+$	-12.62	5.85×10^3 ^f	6.20×10^3	1.06	
			$E3^+$	(ind) $_2CH^+$	-11.16	1.71×10^5 ^f	1.79×10^5	1.05	
			$E4^+$	(thq) $_2CH^+$	-10.92	2.81×10^5 ^f	3.15×10^5	1.12	
N6		16.02	$E1^+$	(lil) $_2CH^+$	-12.76	1.38×10^3 ^e	1.82×10^3	1.32	
			$E2^+$	(jul) $_2CH^+$	-12.62	2.41×10^3 ^e	2.47×10^3	1.02	
			$E4^+$	(thq) $_2CH^+$	-10.92	1.69×10^5 ^e	1.25×10^5	0.74	
N7		15.40	$E3^+$	(ind) $_2CH^+$	-11.16	2.00×10^4 ^d	1.71×10^4	0.85	
			$E4^+$	(thq) $_2CH^+$	-10.92	2.56×10^4 ^d	3.00×10^4	1.17	
N8		15.39	$E3^+$	(ind) $_2CH^+$	-11.16	2.02×10^4 ^d	1.69×10^4	0.84	
			$E4^+$	(thq) $_2CH^+$	-10.92	2.75×10^4 ^d	2.96×10^4	1.08	
			$E5^+$	(pyr) $_2CH^+$	-10.46	7.73×10^4 ^d	8.58×10^4	1.11	
N9		15.04	$E3^+$	(ind) $_2CH^+$	-11.16	9.96×10^3	7.58×10^3	0.76	
			$E4^+$	(thq) $_2CH^+$	-10.92	1.27×10^4	1.33×10^4	1.05	
			$E5^+$	(pyr) $_2CH^+$	-10.46	3.07×10^4	3.85×10^4	1.25	
N10		14.29	$E3^+$	(ind) $_2CH^+$	-11.16	1.08×10^3	1.33×10^3	1.23	
			$E4^+$	(thq) $_2CH^+$	-10.92	2.60×10^3	2.34×10^3	0.90	
			$E5^+$	(pyr) $_2CH^+$	-10.46	7.03×10^3	6.77×10^3	0.96	
			$E6^+$	(dma) $_2CH^+$	-9.30	1.03×10^5	9.63×10^4	0.94	
N11		14.27	$E1^+$	(lil) $_2CH^+$	-12.76	1.91×10^1 ^e	3.27×10^1	1.71	
			$E2^+$	(jul) $_2CH^+$	-12.62	5.57×10^1 ^e	4.44×10^1	0.80	
			$E3^+$	(ind) $_2CH^+$	-11.16	1.21×10^3	1.28×10^3	1.06	
			$E4^+$	(thq) $_2CH^+$	-10.92	2.27×10^3 ^e	2.26×10^3	0.99	
			$E5^+$	(pyr) $_2CH^+$	-10.46	6.94×10^3	6.53×10^3	0.94	
			$E6^+$	(dma) $_2CH^+$	-9.30	1.26×10^5 ^e	9.29×10^4	0.74	
N12		11.99	$E5^+$	(pyr) $_2CH^+$	-10.46	4.30×10^1	3.41×10^1	0.79	
			$E6^+$	(dma) $_2CH^+$	-9.30	4.06×10^2	4.84×10^2	1.19	
			$E7^+$	(mpa) $_2CH^+$	-7.72	1.81×10^4	1.88×10^4	1.04	
			$E8^+$	(mor) $_2CH^+$	-6.82	1.46×10^5	1.49×10^5	1.02	
N13		11.65	$E4^+$	(thq) $_2CH^+$	-10.92	6.22 ^e	5.42	0.87	
			$E7^+$	(mpa) $_2CH^+$	-7.72	8.52×10^3 ^e	8.65×10^3	1.02	
			$E9^+$	(dpa) $_2CH^+$	-5.72	7.58×10^5 ^e	8.58×10^5	1.13	
N14		11.41	$E6^+$	(dma) $_2CH^+$	-9.30	1.19×10^2	1.27×10^2	1.06	
			$E7^+$	(mpa) $_2CH^+$	-7.72	4.74×10^3	4.91×10^3	1.04	
			$E8^+$	(mor) $_2CH^+$	-6.82	4.29×10^4	3.89×10^4	0.91	
N15		11.31	$E6^+$	(dma) $_2CH^+$	-9.30	8.70×10^1	1.00×10^2	1.15	
			$E7^+$	(mpa) $_2CH^+$	-7.72	3.68×10^3	3.90×10^3	1.06	
			$E8^+$	(mor) $_2CH^+$	-6.82	2.87×10^4	3.08×10^4	1.07	
			$E9^+$	(dpa) $_2CH^+$	-5.72	5.07×10^5 ^f	3.86×10^5	0.76	
N16		10.92	$E6^+$	(dma) $_2CH^+$	-9.30	4.82×10^1	4.14×10^1	0.86	
			$E7^+$	(mpa) $_2CH^+$	-7.72	1.43×10^3	1.61×10^3	1.12	
			$E8^+$	(mor) $_2CH^+$	-6.82	1.23×10^4	1.27×10^4	1.03	
N17		10.76	$E6^+$	(dma) $_2CH^+$	-9.30	2.74×10^1	2.84×10^1	1.04	
			$E7^+$	(mpa) $_2CH^+$	-7.72	1.03×10^3	1.10×10^3	1.07	
			$E8^+$	(mor) $_2CH^+$	-6.82	9.63×10^3	8.71×10^3	0.90	

Table 2. continued

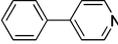
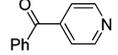
N	Lewis base		electrophile		experiment		correlation	
	formula	$LB_{CH_2Cl_2}$	E^+	abbreviation	$LA_{CH_2Cl_2}$	K^a / M^{-1}	K_{calc}^b / M^{-1}	K_{calc}/K
N18		10.71	$E6^+$	(dma) ₂ CH ⁺	-9.30	2.29×10^1	2.55×10^1	1.11
			$E7^+$	(mpa) ₂ CH ⁺	-7.72	9.77×10^2	9.87×10^2	1.01
			$E8^+$	(mor) ₂ CH ⁺	-6.82	8.78×10^3	7.82×10^3	0.89
N19		10.48	$E7^+$	(mpa) ₂ CH ⁺	-7.72	6.57×10^{2g}	5.81×10^2	0.88
			$E8^+$	(mor) ₂ CH ⁺	-6.82	4.07×10^{3g}	4.60×10^3	1.13
N20		10.17	$E7^+$	(mpa) ₂ CH ⁺	-7.72	2.90×10^2	2.83×10^2	0.97
			$E8^+$	(mor) ₂ CH ⁺	-6.82	1.87×10^3	2.24×10^3	1.20
			$E10^+$	(mfa) ₂ CH ⁺	-5.39	6.94×10^4	5.95×10^4	0.86
N21		10.02	$E7^+$	(mpa) ₂ CH ⁺	-7.72	1.92×10^2	2.03×10^2	1.06
			$E8^+$	(mor) ₂ CH ⁺	-6.82	1.54×10^3	1.61×10^3	1.05
			$E9^+$	(dpa) ₂ CH ⁺	-5.72	2.23×10^{4f}	2.02×10^4	0.90
N22		9.65	$E8^+$	(mor) ₂ CH ⁺	-6.82	6.38×10^{2g}	6.79×10^2	1.06
			$E9^+$	(dpa) ₂ CH ⁺	-5.72	7.20×10^{3g}	8.50×10^3	1.18
			$E10^+$	(mfa) ₂ CH ⁺	-5.39	2.27×10^{4g}	1.81×10^4	0.80
N23		9.16	$E7^+$	(mpa) ₂ CH ⁺	-7.72	3.54×10^1	2.77×10^1	0.78
			$E8^+$	(mor) ₂ CH ⁺	-6.82	1.71×10^2	2.19×10^2	1.28
N24		8.78	$E9^+$	(dpa) ₂ CH ⁺	-5.72	1.33×10^3	1.14×10^3	0.86
			$E10^+$	(mfa) ₂ CH ⁺	-5.39	2.25×10^3	2.42×10^3	1.08
			$E11^+$	(pfa) ₂ CH ⁺	-4.47	1.87×10^4	2.03×10^4	1.08
N25		8.74	$E8^+$	(mor) ₂ CH ⁺	-6.82	1.33×10^2	8.35×10^1	0.63
			$E9^+$	(dpa) ₂ CH ⁺	-5.72	8.47×10^2	1.05×10^3	1.23
			$E10^+$	(mfa) ₂ CH ⁺	-5.39	1.99×10^3	2.22×10^3	1.12
			$E11^+$	(pfa) ₂ CH ⁺	-4.47	1.61×10^4	1.86×10^4	1.16
N26		7.93	$E10^+$	(mfa) ₂ CH ⁺	-5.39	3.11×10^2	3.45×10^2	1.11
			$E11^+$	(pfa) ₂ CH ⁺	-4.47	3.20×10^3	2.89×10^3	0.90
N27		7.92	$E9^+$	(dpa) ₂ CH ⁺	-5.72	1.54×10^2	1.58×10^2	1.03
			$E10^+$	(mfa) ₂ CH ⁺	-5.39	4.04×10^2	3.36×10^2	0.83
			$E11^+$	(pfa) ₂ CH ⁺	-4.47	2.41×10^3	2.82×10^3	1.17
N28		7.44	$E10^+$	(mfa) ₂ CH ⁺	-5.39	1.13×10^2	1.12×10^2	0.99
			$E11^+$	(pfa) ₂ CH ⁺	-4.47	9.37×10^2	9.42×10^3	1.01
N29		6.71	$E10^+$	(mfa) ₂ CH ⁺	-5.39	1.55×10^1	2.06×10^1	1.33
			$E11^+$	(pfa) ₂ CH ⁺	-4.47	1.40×10^2	1.73×10^2	1.23
			$E13^+$	(fur) ₂ CH ⁺	-1.29	4.31×10^5	2.63×10^5	0.61
N30		6.21	$E11^+$	(pfa) ₂ CH ⁺	-4.47	5.56×10^1	5.50×10^1	0.99
			$E13^+$	(fur) ₂ CH ⁺	-1.29	1.03×10^5	8.38×10^4	0.81
			$E15^+$	(ani) ₂ CH ⁺	0.00	1.30×10^6	1.62×10^6	1.24
N31		6.08	$E11^+$	(pfa) ₂ CH ⁺	-4.47	6.59×10^1	4.07×10^1	0.62
			$E13^+$	(fur) ₂ CH ⁺	-1.29	6.19×10^4	6.20×10^4	1.00
			$E15^+$	(ani) ₂ CH ⁺	0.00	7.41×10^5	1.20×10^6	1.62
N32		4.28	$E13^+$	(fur) ₂ CH ⁺	-1.29	8.86×10^2	9.85×10^2	1.11
			$E15^+$	(ani) ₂ CH ⁺	0.00	3.04×10^4	1.90×10^4	0.63
			$E16^+$	ani(pop)CH ⁺	0.90	1.05×10^5	1.51×10^5	1.44
N33		4.06	$E13^+$	(fur) ₂ CH ⁺	-1.29	7.94×10^2	5.95×10^2	0.75
			$E15^+$	(ani) ₂ CH ⁺	0.00	1.22×10^4	1.15×10^4	0.94
			$E16^+$	ani(pop)CH ⁺	0.90	6.43×10^4	9.11×10^4	1.42
N34		3.83	$E13^+$	(fur) ₂ CH ⁺	-1.29	2.16×10^2	3.52×10^2	1.63
			$E15^+$	(ani) ₂ CH ⁺	0.00	8.91×10^3	6.78×10^3	0.76
			$E16^+$	ani(pop)CH ⁺	0.90	6.67×10^4	5.38×10^4	0.81
N35		3.64	$E13^+$	(fur) ₂ CH ⁺	-1.29	1.52×10^2	2.25×10^2	1.48
			$E15^+$	(ani) ₂ CH ⁺	0.00	6.15×10^3	4.35×10^3	0.71
			$E16^+$	ani(pop)CH ⁺	0.90	3.61×10^4	3.45×10^4	0.96
N36		2.98	$E15^+$	(ani) ₂ CH ⁺	0.00	9.50×10^2	9.57×10^2	1.01
			$E16^+$	ani(pop)CH ⁺	0.90	7.65×10^3	7.59×10^3	0.99

Table 2. continued

N	Lewis base		electrophile			experiment	correlation	
	formula	$LB_{CH_2Cl_2}$	E^+	abbreviation	$LA_{CH_2Cl_2}$	K^a / M^{-1}	K_{calc}^b / M^{-1}	K_{calc}/K
N37	BCl_4^-	-4.04	$E15^+$	(ani) ₂ CH ⁺	0.00	$5.82 \times 10^{-5}^h$	9.06×10^{-5}	1.56
			$E16^+$	ani(pop)CH ⁺	0.90	$1.12 \times 10^{-3}^h$	7.19×10^{-4}	0.64
			$E17^+$	ani(tol)CH ⁺	2.00	$9.06 \times 10^{-3}^h$	— ⁱ	— ⁱ
			$E18^+$	ani(Ph)CH ⁺	3.10	$1.15 \times 10^{-1}^h$	— ⁱ	— ⁱ
			$E19^+$	pop(Ph)CH ⁺	4.42	2.41 ^h	— ⁱ	— ⁱ
			$E20^+$	(tol) ₂ CH ⁺	4.82	5.94 ⁱ	— ⁱ	— ⁱ

^aPhotometric determination from this work unless indicated otherwise. ^bCalculated from eq 7 using $LA_{CH_2Cl_2}$ from Table 1 and $LB_{CH_2Cl_2}$ from this table. ^cFrom ref 31. ^dFrom ref 30. ^eFrom ref 28. ^fFrom ref 29. ^gFrom ref 32. ^hThe $\Delta\Delta G_i^0$ ($-70^\circ C$) values and $\Delta\Delta S_i^0 \approx 0$ have been reported for the reverse (ionization) reactions $E(15-20)-Cl + BCl_3 \rightleftharpoons E(15-20)^+ + BCl_4^-$.³⁴ These values were combined with ΔG_i^0 ($-70^\circ C$) and ΔS_i^0 for the ionization of $E20-Cl$ (see footnote *j*) to calculate the ionization equilibrium constants $1/K$ at $20^\circ C$. ⁱOnly one equilibrium constant was used for the determination of $LA_{CH_2Cl_2}$. ^j $1/K$ ($20^\circ C$) was calculated from the thermodynamic parameters of the ionization reaction $E20-Cl + BCl_3 \rightleftharpoons E20^+ + BCl_4^-$: $\Delta H_i^0 = -32.6 \text{ kJ mol}^{-1}$ (ref 34) and ΔG_i^0 ($-70^\circ C$) = -7.0 kJ mol^{-1} (ref 35) (and thus $\Delta S_i^0 = -126 \text{ J K}^{-1} \text{ mol}^{-1}$).

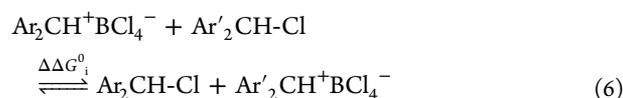
124 less accurate due to the occurrence of slow subsequent
125 reactions, or which were determined indirectly from the ratio
126 of rate constants $k_{forward}/k_{backward}$ (Scheme 1), are not included
127 in Table 2.

128 In order to link the previously reported equilibrium constants
129 with each other, we have now employed the same method to
130 determine further 74 equilibrium constants for the reactions of
131 benzhydrylium ions with pyridines, pyrimidine, quinoline, and
132 isoquinoline, as well as with phosphines, sulfides, and dimethyl
133 selenide in CH_2Cl_2 (Table 2; details in section S8 of the
134 Supporting Information). For these measurements, we likewise
135 applied the strict requirement that the determination of the
136 equilibrium constant should not be disturbed by subsequent
137 reactions. This restriction implies that in CH_2Cl_2 at $20^\circ C$ only
138 equilibrium constants for reactions of the benzhydrylium ions
139 $E(1-16)^+$ were determined, because at room temperature, the
140 more reactive benzhydrylium ions $E(17-33)^+$ react too quickly
141 with traces of impurities which are present in our highly
142 purified CH_2Cl_2 .³³

143 The equilibrium constants K ($20^\circ C$) for the reactions of
144 $E(15-20)^+$ with BCl_4^- in CH_2Cl_2 (N37), which are listed in
145 Table 2, were calculated from the previously reported equilib-
146 rium constants for the ionization reactions (eq 5) at $-70^\circ C$.³⁴



147 For the reaction of $E20-Cl$ with BCl_3 , an ionization free
148 energy of ΔG_i^0 ($-70^\circ C$) = -7.0 kJ mol^{-1} was measured
149 conductometrically in CH_2Cl_2 solution at $-70^\circ C$.³⁵ This value
150 can be combined with the calorimetrically determined heat
151 of ionization of $E20-Cl$ in CH_2Cl_2/BCl_3 at $-70^\circ C$ ($\Delta H_i^0 =$
152 $-32.6 \text{ kJ mol}^{-1}$)³⁴ to calculate the ionization entropy in
153 CH_2Cl_2 as $\Delta S_i^0 = -126 \text{ J K}^{-1} \text{ mol}^{-1}$. As the differences of
154 the entropies for the ionizations of $E(16-18)-Cl$ are small
155 ($\Delta\Delta S_i^0 \approx 0$),³⁴ the value of $\Delta S_i^0 = -126 \text{ J K}^{-1} \text{ mol}^{-1}$ was
156 assumed to hold also for the ionizations of $E(15-19)-Cl$
157 by BCl_3 in CH_2Cl_2 . The differences in free energy $\Delta\Delta G_i^0$
158 ($-70^\circ C$) determined by NMR spectroscopic measurements
159 of ionization equilibria for $E(15-20)-Cl$ (eq 6)³⁴ were then
160 anchored to the directly measured ionization free energy ΔG_i^0
161 ($-70^\circ C$) for $E20-Cl$.³⁵



The ionization entropy of $\Delta S_i^0 = -126 \text{ J K}^{-1} \text{ mol}^{-1}$ was then
used to convert the ΔG_i^0 ($-70^\circ C$) values to $20^\circ C$ and to
calculate the equilibrium constants $1/K$ for the reactions of eq 5
at $20^\circ C$; the inverse values (K) yield the required equilibrium
constants for the combination reactions (Table 2). Due to the
absence of side-reactions at low temperatures ($-70^\circ C$), we
could thus extend the experimental Lewis acidity scale in
 CH_2Cl_2 to benzhydrylium ions as reactive as $E20^+$. The more
electrophilic benzhydrylium ions $E(21-33)^+$ undergo side
reactions so readily (e.g., Friedel-Crafts-type reactions with the
Lewis adducts) that we were not able to find conditions which
allowed us to determine equilibrium constants for the reactions
of these carbocations with Lewis bases.

Correlation Analysis of the Equilibrium Constants in
 CH_2Cl_2 . The equilibrium constants K for the reactions of
benzhydrylium ions with Lewis bases listed in Table 2 can be
described by the two-parameter equation (eq 7), which
characterizes benzhydrylium ions by the parameter LA (Lewis
acidity) and Lewis bases by the parameter LB (Lewis basicity).

$$\log K = LA + LB \quad (7)$$

The LA parameters of $E(1-20)^+$ listed in Table 1 and the LB
parameters of $N(1-37)$ in CH_2Cl_2 listed in Table 2 were
calculated by a least-squares minimization: For that purpose, we
minimized Δ^2 specified by eq 8 using the nonlinear solver
program "What's Best! 7.0" by Lindo Systems Inc.³⁶ In the
following, we will use subscripts to indicate the solvent to
which the LA and LB parameters refer.

$$\begin{aligned} \Delta^2 &= \sum (\log K - \log K_{calc})^2 \\ &= \sum (\log K - (LA + LB))^2 \end{aligned} \quad (8)$$

A total of 115 equilibrium constants for the reactions
of 18 benzhydrylium ions with 37 Lewis bases were em-
ployed for this correlation analysis; the $LA_{CH_2Cl_2}$ parameter of
the dianisylcarbenium ion ($E15^+$) was set to 0.00, as this
carbocation also served as reference point for the correlations
of our kinetic data.²⁰⁻²³ Table 2 provides a comparison of
the calculated equilibrium constants K_{calc} obtained in this
manner with the experimental values of $K(CH_2Cl_2)$. None of
the calculated values deviates from the experimental values
by more than a factor of 1.7, which corroborates the appli-
cability of eq 7.

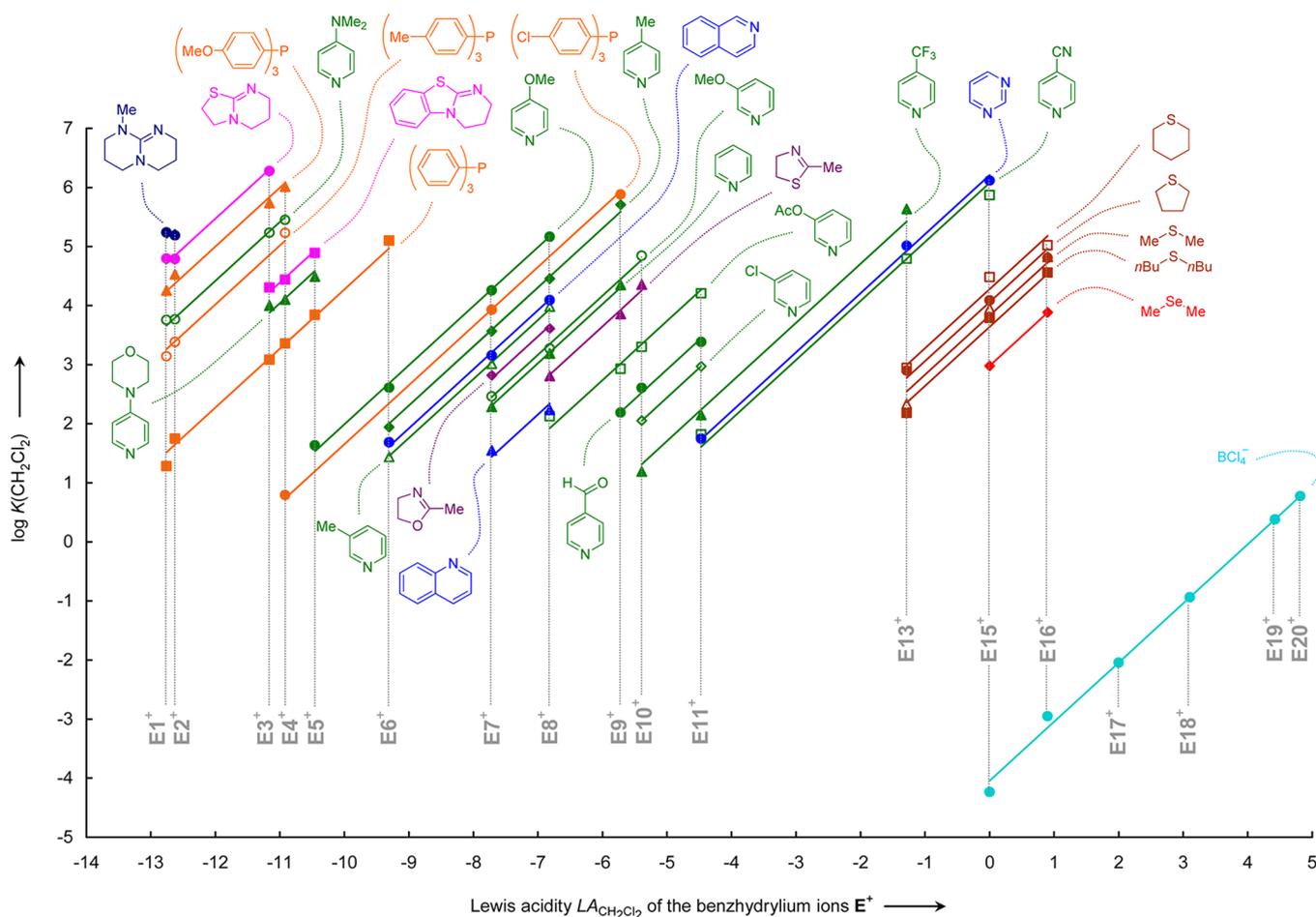


Figure 1. Plot of $\log K$ for reactions of benzhydrylium ions E^+ with Lewis bases in CH_2Cl_2 against the Lewis acidity parameters $LA_{CH_2Cl_2}$ of the benzhydrylium ions. The lines have a slope of unity and were calculated from eq 7. Some correlation lines have been omitted for the sake of clarity (see Figure S1.1 in section S1 of the Supporting Information).

199 The quality of the correlations is illustrated by Figure 1,
 200 which plots $\log K(CH_2Cl_2)$ for the reactions of the
 201 benzhydrylium ions (E^+) with Lewis bases against the $LA_{CH_2Cl_2}$
 202 parameters of the benzhydrylium ions. Equation 7 implies that
 203 the correlation lines for all Lewis bases are parallel to each
 204 other. The good agreement between experimental and cal-
 205 culated values shown in Figure 1 for all investigated classes of
 206 compounds confirms that, unlike in the analogous treatment of
 207 the corresponding rate constants,^{20–23} sensitivity parameters
 208 are not needed. Thus, the parameters $LA_{CH_2Cl_2}$ and $LB_{CH_2Cl_2}$
 209 of the two reaction partners, which adopt the dimension of a reac-
 210 tion free energy when multiplied with $-RT \ln(10)$, combine
 211 additively to describe the Gibbs free energies of the combina-
 212 tion reactions ($-RT \ln K$).

213 The fact that a sensitivity parameter is not required is due
 214 to the fact that the steric surroundings of the reaction centers
 215 of the benzhydrylium ions are kept constant (only *p*- and
 216 *m*-substituents) and furthermore indicates that the electron
 217 densities in the benzhydrylium fragments of the different Lewis
 218 adducts are not significantly altered.

219 **Equilibrium Constants in CH_3CN at 20 °C.** In order to
 220 study the role of the solvent, we have also investigated the
 221 reactions of $E(1–8)^+$ with Lewis bases in CH_3CN solution.
 222 Table 3 lists 96 equilibrium constants, 56 of which have been
 223 determined in this work, while the others have previously been
 224 reported.^{37–40} Again we have employed only the most reliable

225 equilibrium constants for the correlation analysis. Therefore,
 226 equilibrium constants for reactions of benzhydrylium ions
 227 which are more reactive than $E8^+$ are not included in Table 3,
 228 because these benzhydrylium ions were found to undergo slow
 229 reactions with impurities that remain present in highly purified
 230 CH_3CN .

231 A comparison of Tables 2 and 3 shows that the equilibrium
 232 constants K are generally 1.3–9 times (reactions of $E7^+$, 12–38
 233 times) larger in CH_3CN than in CH_2Cl_2 solution, i.e., the
 234 formation of adducts from benzhydrylium ions and neutral
 235 Lewis bases is more favorable in CH_3CN than in CH_2Cl_2 . This
 236 difference indicates that the onium salts generated by the
 237 reaction of the benzhydrylium ions with the neutral Lewis bases
 238 (Scheme 1) are better stabilized by the polar solvent CH_3CN
 239 than the benzhydrylium ions, in which the charge is highly
 240 dispersed. The equilibrium constants for the combinations of
 241 the benzhydrylium ions E^+ with the anions $N(45–47)$ are so
 242 large in CH_2Cl_2 that their magnitude could not be measured by
 243 the photometric method employed in this work.

244 A closer look at the data is provided by Figure 2, which plots
 245 $\log K(CH_3CN)$ for reactions of benzhydrylium ions E^+ with
 246 pyridines and phosphines in CH_3CN (Table 3) against $\log K$
 247 (CH_2Cl_2) for the same reactions in CH_2Cl_2 (Table 2). Two
 248 observations can be made: (a) the equilibrium constants for the
 249 reactions of pyridines (green circles) experience a larger solvent
 250 effect (further remote from the dashed unity line) than those

Table 3. Equilibrium Constants K (M^{-1}) for the Reactions of the Benzhydrylium Ions E^+ with Lewis Bases N in CH_3CN at 20 °C and Comparison with the Equilibrium Constants K_{calc} (M^{-1}) Calculated from Eq 7

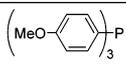
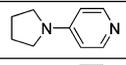
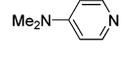
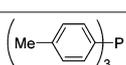
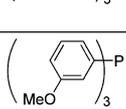
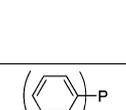
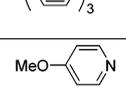
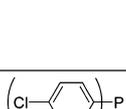
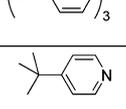
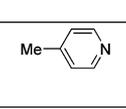
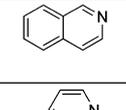
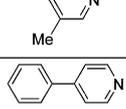
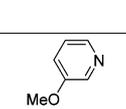
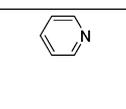
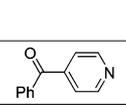
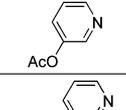
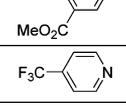
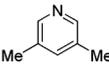
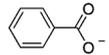
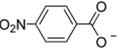
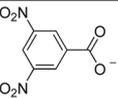
N	Lewis base		electrophile		experiment		correlation	
	formula	LB_{CH_3CN}	E^+	abbreviation	LA_{CH_3CN}	K^a / M^{-1}	K_{calc}^b / M^{-1}	K_{calc}/K
N3		17.26	$E1^+$	(lil) ₂ CH ⁺	-12.76	2.78×10^4	3.15×10^4	1.13
			$E2^+$	(jul) ₂ CH ⁺	-12.61	5.00×10^4	4.42×10^4	0.88
N4		17.39	$E1^+$	(lil) ₂ CH ⁺	-12.76	5.08×10^4	4.27×10^4	0.84
			$E2^+$	(jul) ₂ CH ⁺	-12.61	5.03×10^4	5.99×10^4	1.19
N5		17.13	$E1^+$	(lil) ₂ CH ⁺	-12.76	2.44×10^4 ^{c,d,e}	2.33×10^4	0.96
			$E2^+$	(jul) ₂ CH ⁺	-12.61	2.60×10^4 ^{c,d,f}	3.28×10^4	1.26
			$E3^+$	(ind) ₂ CH ⁺	-11.46	5.60×10^5 ^c	4.65×10^5	0.83
N6		16.13	$E1^+$	(lil) ₂ CH ⁺	-12.76	1.87×10^3	2.33×10^3	1.24
			$E2^+$	(jul) ₂ CH ⁺	-12.61	3.63×10^3	3.27×10^3	0.90
			$E3^+$	(ind) ₂ CH ⁺	-11.46	5.19×10^4	4.63×10^4	0.89
N10		14.85	$E1^+$	(lil) ₂ CH ⁺	-12.76	9.67×10^1	1.24×10^2	1.29
			$E2^+$	(jul) ₂ CH ⁺	-12.61	2.31×10^2	1.75×10^2	0.76
			$E3^+$	(ind) ₂ CH ⁺	-11.46	1.68×10^3	2.48×10^3	1.47
			$E4^+$	(thq) ₂ CH ⁺	-11.27	4.87×10^3	3.88×10^3	0.80
			$E5^+$	(pyr) ₂ CH ⁺	-10.83	1.22×10^4	1.07×10^4	0.88
N11		14.72	$E1^+$	(lil) ₂ CH ⁺	-12.76	7.77×10^1 ^{d,g}	9.04×10^1	1.16
			$E2^+$	(jul) ₂ CH ⁺	-12.61	1.66×10^2	1.27×10^2	0.76
			$E3^+$	(ind) ₂ CH ⁺	-11.46	1.60×10^3	1.80×10^3	1.12
N12		13.41	$E2^+$	(jul) ₂ CH ⁺	-12.61	9.20	6.28	0.68
			$E3^+$	(ind) ₂ CH ⁺	-11.46	7.02×10^1 ^c	8.90×10^1	1.27
			$E4^+$	(thq) ₂ CH ⁺	-11.27	1.31×10^2 ^c	1.39×10^2	1.06
			$E5^+$	(pyr) ₂ CH ⁺	-10.83	3.70×10^2 ^c	3.85×10^2	1.04
			$E6^+$	(dma) ₂ CH ⁺	-9.82	3.75×10^3	3.92×10^3	1.05
N13		12.84	$E6^+$	(dma) ₂ CH ⁺	-9.82	1.00×10^3	1.07×10^3	1.07
			$E7^+$	(mpa) ₂ CH ⁺	-7.87	1.06×10^5	9.46×10^4	0.89
			$E8^+$	(mor) ₂ CH ⁺	-7.52	2.01×10^5	2.11×10^5	1.05
N14		12.71	$E5^+$	(pyr) ₂ CH ⁺	-10.83	6.83×10^1	7.61×10^1	1.11
			$E6^+$	(dma) ₂ CH ⁺	-9.82	7.25×10^2	7.76×10^2	1.07
			$E7^+$	(mpa) ₂ CH ⁺	-7.87	8.23×10^4	6.89×10^4	0.84
N15		12.80	$E5^+$	(pyr) ₂ CH ⁺	-10.83	8.67×10^1	9.36×10^1	1.08
			$E6^+$	(dma) ₂ CH ⁺	-9.82	8.08×10^2	9.54×10^2	1.18
			$E7^+$	(mpa) ₂ CH ⁺	-7.87	1.08×10^5	8.47×10^4	0.78
N16		12.23	$E6^+$	(dma) ₂ CH ⁺	-9.82	2.97×10^2	2.62×10^2	0.88
			$E7^+$	(mpa) ₂ CH ⁺	-7.87	2.07×10^4	2.32×10^4	1.12
			$E8^+$	(mor) ₂ CH ⁺	-7.52	5.14×10^4	5.19×10^4	1.01
N17		12.27	$E6^+$	(dma) ₂ CH ⁺	-9.82	2.52×10^2	2.86×10^2	1.13
			$E7^+$	(mpa) ₂ CH ⁺	-7.87	2.71×10^4	2.54×10^4	0.94
			$E8^+$	(mor) ₂ CH ⁺	-7.52	6.00×10^4	5.66×10^4	0.94
N18		12.12	$E6^+$	(dma) ₂ CH ⁺	-9.82	1.83×10^2	2.00×10^2	1.09
			$E7^+$	(mpa) ₂ CH ⁺	-7.87	1.67×10^4	1.78×10^4	1.06
			$E8^+$	(mor) ₂ CH ⁺	-7.52	4.62×10^4	3.97×10^4	0.86
N20		11.50	$E6^+$	(dma) ₂ CH ⁺	-9.82	7.00×10^1	4.83×10^1	0.69
			$E7^+$	(mpa) ₂ CH ⁺	-7.87	3.45×10^3	4.29×10^3	1.24
			$E8^+$	(mor) ₂ CH ⁺	-7.52	8.23×10^3	9.58×10^3	1.16
N21		11.82	$E3^+$	(ind) ₂ CH ⁺	-11.46	2.78	2.28	0.82
			$E4^+$	(thq) ₂ CH ⁺	-11.27	4.11	3.57	0.87
			$E5^+$	(pyr) ₂ CH ⁺	-10.83	1.02×10^1	9.85	0.97
			$E6^+$	(dma) ₂ CH ⁺	-9.82	8.45×10^1	1.00×10^2	1.19
			$E7^+$	(mpa) ₂ CH ⁺	-7.87	7.29×10^3	8.92×10^2	1.22
N24		10.49	$E7^+$	(mpa) ₂ CH ⁺	-7.87	4.22×10^2	4.22×10^2	1.00
			$E8^+$	(mor) ₂ CH ⁺	-7.52	9.41×10^2	9.42×10^2	1.00
N25		9.85	$E7^+$	(mpa) ₂ CH ⁺	-7.87	9.00×10^1	9.57×10^1	1.06
			$E8^+$	(mor) ₂ CH ⁺	-7.52	2.27×10^2	2.14×10^2	0.94
N26		9.44	$E7^+$	(mpa) ₂ CH ⁺	-7.87	3.59×10^1	3.69×10^1	1.03
			$E8^+$	(mor) ₂ CH ⁺	-7.52	8.46×10^1	8.24×10^1	0.97
N29		9.00	$E7^+$	(mpa) ₂ CH ⁺	-7.87	1.45×10^1	1.34×10^1	0.92
			$E8^+$	(mor) ₂ CH ⁺	-7.52	2.76×10^1	2.99×10^1	1.08

Table 3. continued

N	Lewis base		electrophile			experiment		correlation	
	formula	LB_{CH_3CN}	E^+	abbreviation	LA_{CH_3CN}	K^a / M^{-1}	K_{calc}^b / M^{-1}	K_{calc}/K	
N30		8.59	$E7^+$	(mpa) $_2CH^+$	-7.87	5.68	5.24	0.92	
			$E8^+$	(mor) $_2CH^+$	-7.52	1.08×10^1	1.17×10^1	1.08	
N38		13.20	$E3^+$	(ind) $_2CH^+$	-11.46	4.68×10^{1c}	5.43×10^1	1.16	
			$E4^+$	(thq) $_2CH^+$	-11.27	8.04×10^{1c}	8.51×10^1	1.06	
			$E5^+$	(pyr) $_2CH^+$	-10.83	2.60×10^2	2.35×10^2	0.90	
			$E6^+$	(dma) $_2CH^+$	-9.82	2.66×10^3	2.39×10^3	0.90	
N39		12.76	$E4^+$	(thq) $_2CH^+$	-11.27	3.02×10^{1c}	3.13×10^1	1.04	
			$E5^+$	(pyr) $_2CH^+$	-10.83	9.52×10^{1c}	8.64×10^1	0.91	
			$E6^+$	(dma) $_2CH^+$	-9.82	8.28×10^2	8.81×10^2	1.06	
N40		15.48	$E4^+$	(thq) $_2CH^+$	-11.27	1.68×10^{4c}	1.65×10^4	0.98	
			$E5^+$	(pyr) $_2CH^+$	-10.83	4.49×10^{4c}	4.56×10^4	1.02	
N41		14.49	$E4^+$	(thq) $_2CH^+$	-11.27	1.56×10^{3c}	1.66×10^3	1.07	
			$E5^+$	(pyr) $_2CH^+$	-10.83	4.89×10^{3c}	4.59×10^3	0.94	
N42		15.14	$E1^+$	(lil) $_2CH^+$	-12.76	2.44×10^{2h}	2.39×10^2	0.98	
			$E2^+$	(jul) $_2CH^+$	-12.61	2.42×10^{2h}	3.63×10^2	1.39	
			$E3^+$	(ind) $_2CH^+$	-11.46	5.56×10^{3h}	4.76×10^3	0.86	
			$E4^+$	(thq) $_2CH^+$	-11.27	8.69×10^{3h}	7.46×10^3	0.86	
N43		13.49	$E3^+$	(ind) $_2CH^+$	-11.46	9.08×10^{1h}	1.07×10^2	1.18	
			$E4^+$	(thq) $_2CH^+$	-11.27	1.83×10^{2h}	1.68×10^2	0.92	
			$E5^+$	(pyr) $_2CH^+$	-10.83	4.72×10^{2h}	4.63×10^2	0.98	
			$E6^+$	(dma) $_2CH^+$	-9.82	4.99×10^{3h}	4.72×10^3	0.95	
N44		13.77	$E3^+$	(ind) $_2CH^+$	-11.46	1.86×10^{2h}	2.06×10^2	1.11	
			$E4^+$	(thq) $_2CH^+$	-11.27	2.60×10^{2h}	3.23×10^2	1.24	
			$E5^+$	(pyr) $_2CH^+$	-10.83	9.99×10^{2h}	8.90×10^2	0.89	
			$E6^+$	(dma) $_2CH^+$	-9.82	1.11×10^{4h}	9.07×10^3	0.82	
N45		17.45	$E1^+$	(lil) $_2CH^+$	-12.76	6.20×10^{4i}	4.87×10^4	0.79	
			$E2^+$	(jul) $_2CH^+$	-12.61	5.38×10^{4i}	6.84×10^4	1.27	
N46		15.41	$E1^+$	(lil) $_2CH^+$	-12.76	5.79×10^{2j}	4.44×10^2	0.77	
			$E2^+$	(jul) $_2CH^+$	-12.61	5.18×10^{2j}	6.24×10^2	1.20	
			$E3^+$	(ind) $_2CH^+$	-11.46	1.08×10^{4j}	8.84×10^3	0.82	
			$E4^+$	(thq) $_2CH^+$	-11.27	1.13×10^{4j}	1.39×10^4	1.23	
			$E5^+$	(pyr) $_2CH^+$	-10.83	3.20×10^{4j}	3.82×10^4	1.19	
			$E6^+$	(dma) $_2CH^+$	-9.82	4.32×10^{5j}	3.90×10^5	0.90	
N47		13.63	$E3^+$	(ind) $_2CH^+$	-11.46	1.99×10^{2j}	1.47×10^2	0.74	
			$E4^+$	(thq) $_2CH^+$	-11.27	2.33×10^{2j}	2.30×10^2	0.99	
			$E5^+$	(pyr) $_2CH^+$	-10.83	5.48×10^{2j}	6.35×10^2	1.16	
			$E6^+$	(dma) $_2CH^+$	-9.82	5.46×10^{3j}	6.47×10^3	1.19	
N48 (N)	SCN ⁻ 	11.47	$E7^+$	(mpa) $_2CH^+$	-7.87	3.70×10^{3j}	3.99×10^3	1.08	
			$E8^+$	(mor) $_2CH^+$	-7.52	9.60×10^{3j}	8.91×10^3	0.93	

^aPhotometric determination from this work unless indicated otherwise. ^bCalculated from eq 7. ^cFrom ref 37. ^d ΔH^0 and ΔS^0 were determined from a van't Hoff analysis of the photometrically determined equilibrium constants at different temperatures ranging from -10 to +20 °C, this work; see end of section S8 in the Supporting Information for details. ^e $\Delta H^0 = -53.5 \text{ kJ mol}^{-1}$ and $\Delta S^0 = -99.2 \text{ J K}^{-1} \text{ mol}^{-1}$. ^f $\Delta H^0 = -50.7 \text{ kJ mol}^{-1}$ and $\Delta S^0 = -88.7 \text{ J K}^{-1} \text{ mol}^{-1}$. ^g $\Delta H^0 = -40.5 \text{ kJ mol}^{-1}$ and $\Delta S^0 = -101.4 \text{ J K}^{-1} \text{ mol}^{-1}$. ^hFrom ref 38. ⁱEquilibrium constants at 25 °C, from ref 39. ^jFrom ref 40.

for the reactions of phosphines (orange triangles), and (b) the equilibrium constants for reactions of the phenylamino-substituted benzhydrylium ion $E7^+$ (open symbols) experience an unusually large solvent effect. Possibly, $n-\pi^*$ interactions in the pyridinium fragments account for the fact that Lewis adducts generated from pyridines are better stabilized by acetonitrile than other Lewis adducts.

Correlation Analysis of the Equilibrium Constants in CH_3CN . Although Figure 2 indicates that the equilibrium constants for the reactions in CH_3CN correlate with those for the reactions in CH_2Cl_2 , we did not make any *a priori* assumptions about the effect of the solvent on the Lewis acids and bases. Instead, we subjected the CH_3CN data to an independent correlation analysis, and subsequently compared the results. We thus performed another least-squares optimization according to eq 7 for the equilibrium constants from Table 3

by minimizing Δ^2 as defined in eq 8. As precise equilibrium constants for the reactions of $E15^+$ ($LA_{CH_2Cl_2} = 0$) with Lewis bases could not be determined in CH_3CN (Table 3), we defined $LA_{CH_3CN}(E1^+) = -12.76$ (i.e., the same value as obtained for $E1^+$ in CH_2Cl_2) as the reference point. The good agreement between calculated and experimental equilibrium constants (last column of Table 3) shows that eq 7 also holds in CH_3CN and allows us to derive the LA_{CH_3CN} and LB_{CH_3CN} parameters for CH_3CN solution which are listed in Table 3. A graphical illustration of the correlations is given in Figure 3, which plots $\log K(CH_3CN)$ for the reactions of benzhydrylium ions with Lewis bases in CH_3CN against the LA_{CH_3CN} parameters of the benzhydrylium ions E^+ in CH_3CN .

Remarkably, also the benzoate anions $N(45-47)^{39}$ and thiocyanate anion ($N48$, reaction at N)⁴⁰ follow the same

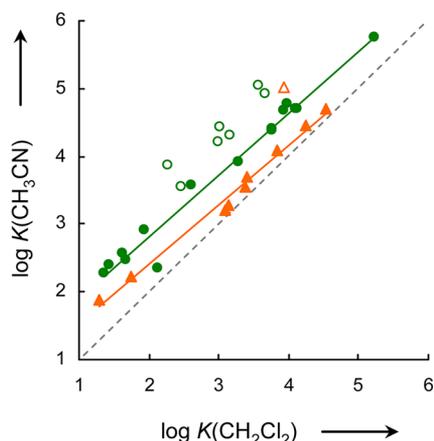


Figure 2. Plot of $\log K(\text{CH}_3\text{CN})$ for reactions of benzhydrylium ions E^+ with pyridines (green circles) and phosphines (orange triangles) in CH_3CN against $\log K(\text{CH}_2\text{Cl}_2)$ for the same reactions in CH_2Cl_2 . Pyridines: $\log K(\text{CH}_3\text{CN}) = 0.913 \log K(\text{CH}_2\text{Cl}_2) + 0.984$, $R^2 = 0.977$. Phosphines: $\log K(\text{CH}_3\text{CN}) = 0.872 \log K(\text{CH}_2\text{Cl}_2) + 0.673$, $R^2 = 0.990$. The data points for $\text{E}7^+$ (empty symbols) were not used for the correlations.

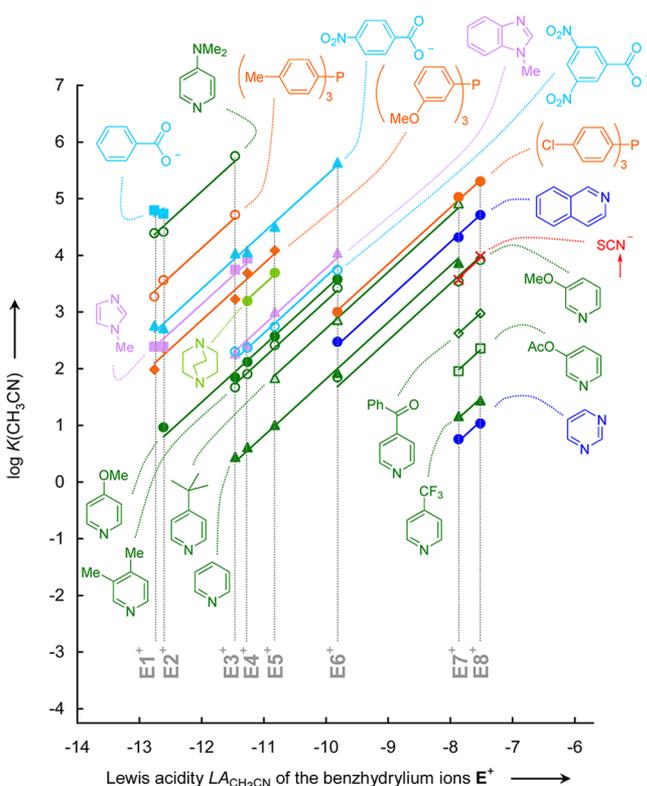


Figure 3. Plot of $\log K(\text{CH}_3\text{CN})$ for reactions of benzhydrylium ions E^+ with Lewis bases in CH_3CN against the Lewis acidity parameters $\text{LA}_{\text{CH}_3\text{CN}}$ of the benzhydrylium ions in CH_3CN calculated from eq 7. Some correlation lines have been omitted for the sake of clarity (see Figure S1.2 in section S1 of the Supporting Information).

282 correlation as the pyridines and phosphines (Table 3 and
283 Figure 3).

284 **Methyl Anion Affinities of the Benzhydrylium Ions in**
285 **the Gas Phase.** In order to investigate the effect of solvation
286 on the relative Lewis acidities of benzhydrylium ions and to
287 extend the Lewis acidity scale, we performed quantum chemical
288 calculations. The methyl anion affinities, defined as the Gibbs

free energies ΔG_{MA} (eq 9) in the gas phase, were calculated for
32 benzhydrylium ions on the B3LYP/6-311++G(3df,2pd)//
B3LYP/6-31G(d,p) level (see sections S9–S11 in the
Supporting Information).⁴¹



Full geometry optimizations and vibrational analyses were
performed at the B3LYP/6-31G(d,p) level of theory. The un-
scaled harmonic vibrational frequencies were used to calculate
the thermal corrections to 298.15 K, which were applied to
single point energies from B3LYP/6-311++G(3df,2pd) level to
give H_{298} and G_{298} . The Boltzmann distribution was used to
calculate the statistical weights of the individual conformers,
and averaged energies were used for the calculations of the
methyl anion affinities ΔG_{MA} , which are listed in Table 1.

Zhu et al. have previously calculated the free energies
 ΔG_{g}^* for hydride transfer from the diarylmethanes E-H to the
benzyl cation in the gas phase (eq 10) on the BLYP/6-311++G
(2df, 2p) level.⁴² The reverse reaction of eq 10 provides the
relative hydride affinities of the benzhydrylium ions E^+ .



Figure 4 shows a linear correlation with unity slope between
the relative hydride anion affinities in the gas phase ($-\Delta G_{\text{g}}^*$)

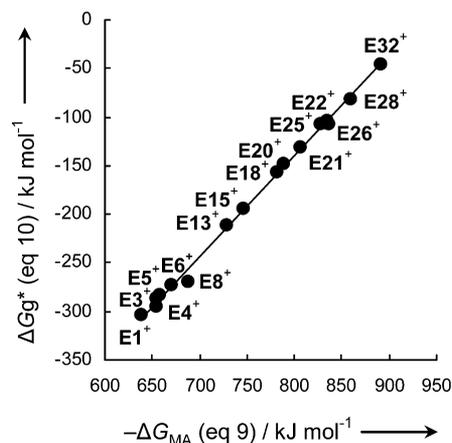


Figure 4. Correlation of the calculated free energies ΔG_{g}^* (kJ mol^{-1}) for hydride transfer from the diarylmethanes Ar_2CH_2 (E-H) to the benzyl cation in the gas phase (eq 10)⁴² with the calculated methyl anion affinities ΔG_{MA} (kJ mol^{-1}) of the benzhydrylium ions E^+ in the gas phase (eq 9) from this work ($\Delta G_{\text{g}}^* = -1.04\Delta G_{\text{MA}} - 971$; $R^2 = 0.998$).

reported by Zhu⁴² and the methyl anion affinities ΔG_{MA} in
the gas phase calculated in this work. This correlation implies
that structural variation of the benzhydrylium ions affects their
affinities toward different anions (CH_3^- or H^-) to equal ex-
tents, in line with previous analyses which also included hydrox-
ide affinities.⁴³ This behavior reflects the fact that variation of
the substituents affects the free energies of the neutral adducts
E- CH_3 and E-H almost equally.

Quantum Chemical Calculations and Solvation Ef-
fects. Figure 5 illustrates that the Lewis acidity parameters
 $\text{LA}_{\text{CH}_2\text{Cl}_2}$ of the benzhydrylium ions $\text{E}(1-20)^+$, which were
derived from equilibrium constants in CH_2Cl_2 , correlate linearly
with the methyl anion affinities ΔG_{MA} of these benzhydrylium

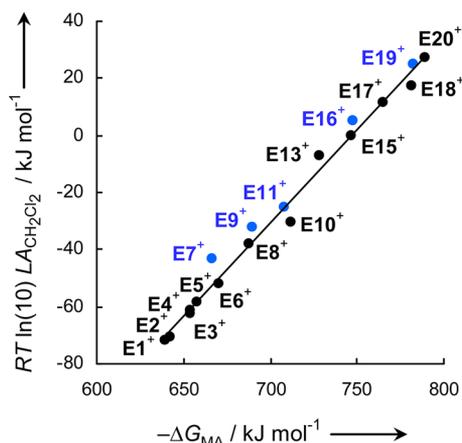


Figure 5. Correlation of the Lewis acidities $LA_{CH_2Cl_2}$ of the benzhydrylium ions E^+ (eq 7) with calculated methyl anion affinities ΔG_{MA} (eq 9) of E^+ ($-RT \ln(10) LA_{CH_2Cl_2} = 0.652 \Delta G_{MA} + 487$; $R^2 = 0.987$). Blue symbols: *p*-phenylamino- and *p*-phenoxy-substituted benzhydrylium ions.

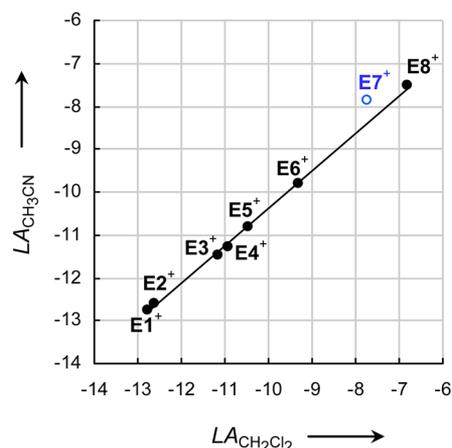


Figure 6. Plot of the LA_{CH_3CN} parameters for benzhydrylium ions in CH_3CN versus their $LA_{CH_2Cl_2}$ parameters in CH_2Cl_2 . The point for $E7^+$ (open blue circle) was not used for the correlation: $LA_{CH_3CN} = 0.878 LA_{CH_2Cl_2} - 1.60$; $R^2 = 0.999$.

ions in the gas phase. This correlation implies that there is generally no differential solvation of the benzhydrylium ions $E(1-20)^+$; i.e., the solvation energies change linearly with the thermodynamic stabilities of the carbocations, in line with previous conclusions.⁴²⁻⁴⁵

The slope of the correlation in Figure 5 (0.65 at 20 °C) shows that substituent variation affects the Lewis acidities of benzhydrylium ions in CH_2Cl_2 by approximately 65% of the anion affinities in the gas phase. This value is in agreement with earlier results for a smaller series of carbenium ions.⁴³

As mentioned above (Figure 2), the equilibrium constants for the reactions of $E7^+$ with pyridines and phosphines show an unusual solvent dependence. The deviating behavior of $E7^+$ is also evident in Figure 5: Although $E6^+$ and $E7^+$ have similar methyl anion affinities ΔG_{MA} , the *p*-N(Me)(Ph)-substituted benzhydrylium ion $E7^+$ has a considerably higher Lewis acidity $LA_{CH_2Cl_2}$ than the *p*-NMe₂-substituted analogue $E6^+$. Similarly, the other *p*-phenylamino- and *p*-phenoxy-substituted benzhydrylium ions (blue symbols in Figure 5) also have $LA_{CH_2Cl_2}$ values which are about one unit larger than those of carbocations with comparable ΔG_{MA} having only *p*-alkylamino or *p*-alkoxy substituents (compare $E9^+/E8^+$, $E11^+/E10^+$, $E16^+/E15^+$, $E19^+/E18^+$).⁴⁶

Figure 6 correlates the LA_{CH_3CN} parameters for $E(1-8)^+$ obtained from the equilibrium constants in CH_3CN (Table 3) with the $LA_{CH_2Cl_2}$ parameters obtained from the equilibrium constants in CH_2Cl_2 (Table 2). Again an excellent linear correlation with a slope of 0.88 is observed, indicating that variation of the substituents affects the Lewis acidities LA of the benzhydrylium ions $E(1-8)^+$ in the better solvating solvent CH_3CN slightly less than in CH_2Cl_2 . Only $E7^+$ shows a noticeable upward deviation in Figure 6, consistent with a less efficient solvation of this benzhydrylium ion in CH_3CN compared to the other benzhydrylium ions (see above). The linear correlations shown in Figures 5 and 6 imply that there is also a linear correlation of the Lewis acidities LA_{CH_3CN} with the methyl anion affinities in the gas phase (Figure S1.3 in section S1 of the Supporting Information), the slope of which shows that solvation by CH_3CN attenuates the substituent effects to 60% of the anion affinities observed in the gas phase.

The LB_{CH_3CN} parameters derived from the equilibrium constants in CH_3CN (Table 3) also correlate linearly with the corresponding $LB_{CH_2Cl_2}$ parameters in CH_2Cl_2 (Table 2). In Figure 7, which spans almost 10 orders of magnitude in

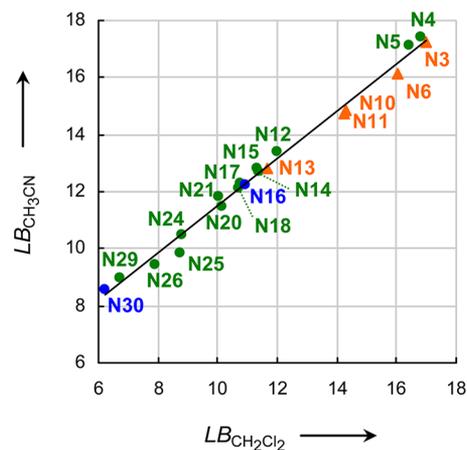


Figure 7. Plot of the LB_{CH_3CN} parameters for pyridines (green circles) and phosphines (orange triangles) in CH_3CN versus their $LB_{CH_2Cl_2}$ parameters in CH_2Cl_2 : $LB_{CH_3CN} = 0.828 LB_{CH_2Cl_2} + 3.22$; $R^2 = 0.991$.

reactivity, the small differences of solvation on the reactions of pyridines and phosphines, which have been displayed in Figure 2, are hardly noticeable. Figure 7 shows that the order of Lewis basicities is more or less the same for neutral Lewis bases in CH_3CN and in CH_2Cl_2 . The observation that, in contrast to the behavior in CH_3CN (Figure 3), all benzhydrylium ions E^+ investigated in this work combine quantitatively with the carboxylate anions N(45-47) in CH_2Cl_2 to give covalent esters⁴⁸ indicates, however, that anionic Lewis bases generally cannot be expected to follow the correlation shown in Figure 7.

The slopes in Figures 6 and 7 are difficult to interpret, as the effects of the solvent on the Lewis acids and Lewis bases cannot be separated unambiguously. However, by setting $LA_{CH_3CN}(E1^+) = LA_{CH_2Cl_2}(E1^+)$, the bulk of the solvent effects is shifted into the LB_{CH_3CN} terms. The larger equilibrium constants observed in

Table 4. Equilibrium Constants K (M^{-1}) for the Reactions of Benzhydrylium Ions E^+ with the Lewis Bases N48 (S-Terminus) and N(49-55) in CH_3CN at 20 °C (Laser Flash Photolysis) and LB_{CH_3CN} Parameters Determined from Eq 7

N	Lewis base		electrophile		experiment	correlation		
	formula	LB_{CH_3CN}	E^+	abbreviation	LA_{CH_3CN}	K^a / M^{-1}	K_{calc}^b / M^{-1}	K_{calc}/K
N48 (S)		10.27	$E8^+$	(mor) $_2CH^+$	-7.52	2.00×10^{2c}	5.63×10^2	2.82
			$E9^+$	(dpa) $_2CH^+$	-6.63 ^d	2.80×10^{4c}	4.37×10^3	0.16
			$E10^+$	(mfa) $_2CH^+$	-6.34 ^d	3.75×10^{3c}	8.53×10^3	2.27
N49		12.92	$E5^+$	(pyr) $_2CH^+$	-10.83	1.3×10^{2e}	1.23×10^2	0.95
N50		12.42	$E6^+$	(dma) $_2CH^+$	-9.82	1.2×10^{3e}	1.26×10^3	1.05
			$E5^+$	(pyr) $_2CH^+$	-10.83	3.3×10^{1e}	3.89×10^1	1.18
N51		4.34	$E13^+$	(fur) $_2CH^+$	-2.73 ^d	1.9×10^{1e}	4.11×10^1	2.16
			$E14^+$	fur(ani) CH^+	f	1.1×10^{2e}	f	f
			$E15^+$	(ani) $_2CH^+$	-1.60 ^d	1.2×10^{3e}	5.55×10^2	0.46
N52		3.92 ^g (in CH_2Cl_2)	$E13^+$	(fur) $_2CH^+$	-1.29 ^g	$3.08 \times 10^{2g,h}$	5.15×10^2	1.67
			$E14^+$	fur(ani) CH^+	f	$1.40 \times 10^{3g,h}$	f	f
			$E15^+$	(ani) $_2CH^+$	0.00 ^g	$1.16 \times 10^{4g,h}$	6.94×10^3	0.60
N53		4.27 ^{g,i} (in CH_2Cl_2)	$E13^+$	(fur) $_2CH^+$	-1.29 ^g	$9.46 \times 10^{2g,h}$	f	f
			$E14^+$	fur(ani) CH^+	f	$7.71 \times 10^{3g,h}$	f	f
N54	Cl^-	(11) ^j	$E9^+$	(dpa) $_2CH^+$	-6.63 ^d	7.5×10^{4k}	2.28×10^4	0.30
			$E10^+$	(mfa) $_2CH^+$	-6.34 ^d	5.9×10^{3k}	4.43×10^4	7.52
			$E11^+$	(pfa) $_2CH^+$	-5.53 ^d	6.5×10^{5k}	2.85×10^5	0.44
N55	Br^-	(8) ^{h,j}	$E11^+$	(pfa) $_2CH^+$	-5.53 ^d	5.5×10^{2l}	f	f

^aPhotometric determination from laser flash photolysis experiments in CH_3CN unless noted otherwise. ^bCalculated from eq 7. ^cFrom ref 40. ^dExtrapolated from $LA_{CH_2Cl_2}$ parameters using the correlation given in Figure 6. ^eFrom ref 49. ^fThe $LA_{CH_2Cl_2}$ parameter of $E14^+$ has not been determined, but the experimentally determined equilibrium constants K (CH_3CN) are given for comparison with the other experimental values. ^gSolvent: CH_2Cl_2 . ^hFrom ref 51. ⁱ $K = K_{calc}$ because the LB_{CH_3CN} parameter was calculated from only one equilibrium constant. ^j LB_{CH_3CN} parameters calculated from the equilibrium constants in this table. For independent examination see below. ^kFrom ref 52, conventional photometric titration. ^lData from ref 52 re-evaluated for this work; see end of section S8 in the Supporting Information.

383 CH_3CN (see Figure 2) are, therefore, predominantly reflected by
384 the higher LB_{CH_3CN} values in CH_3CN .

385 **Further Lewis Basicities in CH_3CN .** As already mentioned,
386 in CH_3CN only equilibrium constants for reactions of $E(1-8)^+$
387 have been measured directly, because the K values for the
388 reactions with these carbenium ions are not affected by
389 uncontrolled side-reactions. Yet, less precise equilibrium
390 constants for reactions of more reactive benzhydrylium ions
391 have been obtained by fast measurement techniques. Thus,
392 benzhydrylium ions have been generated laser-flash-photolyti-
393 cally in the presence of variable concentrations of Lewis bases,
394 and the equilibrium constants K listed in Table 4 have been
395 derived from the absorbances of the carbocations immediately
396 after irradiation with a 7 ns laser pulse and the stationary
397 absorbances which were measured as soon as the equilibrium
398 for the reaction of interest was established.^{40,49-51}

399 Subjecting the equilibrium constants thus obtained to a least-
400 squares optimization according to eq 7 yielded the LB_{CH_3CN} param-
401 eters for the S-terminus of the thiocyanate ion (N48),⁴⁰ for
402 trimethylamine (N49),⁴⁹ the hydrazines N(50,51),⁴⁹ and the
403 hydrazones N(52,53).⁵¹ The equilibrium constants calculated
404 by substituting LA_{CH_3CN} (Table 1) and LB_{CH_3CN} (Table 4) into eq
405 7 show a good agreement with the experimental values (Table 4).
406 Again, the relatively large deviation between experimental and
407 calculated values for the series including the *N*-phenylamino-
408 substituted benzhydrylium ions ($E9^+$, $E11^+$) can be explained by
409 the different solvation of these benzhydrylium ions (see previous
410 section).

411 The direct determination of equilibrium constants for the
412 reactions of chloride (N54) and bromide (N55) ions with
413 benzhydrylium ions (Table 4) was only possible with

$E(9-11)^+$ or $E11^+$, respectively, since benzhydrylium ions of
414 lower Lewis acidity do not show sufficient conversion (adduct
415 formation) whereas the more acidic $E13^+$ reacts almost
416 quantitatively. Since the *N*-phenylamino-substituted benzhy-
417 drylium ions $E9^+$ and $E11^+$ show untypical solvation effects, as
418 described above, the LB_{CH_3CN} values determined in this way are
419 not very reliable. Because of the great importance of the Lewis
420 basicities of halide ions we sought further confirmation of the
421 data for Cl^- and Br^- listed in Table 4 by relating the Lewis
422 basicity of Br^- (N55) to the strengths of neutral Lewis bases.
423

424 For that purpose, we investigated the equilibria for the
425 reactions of benzhydryl halides with Lewis bases in CD_3CN
426 solution (eq 11) by NMR spectroscopy.



428 A major problem of these investigations was the identi-
429 fication of systems which do not show side reactions while
430 having suitable equilibrium constants (see section S5 of the
431 Supporting Information for details). We were able to determine
432 the equilibrium constants K for the reaction of $E17-Br$ with
433 pyrimidine (N30) at different temperatures from -20 °C to
434 +20 °C, from which we obtained the thermodynamic param-
435 eters $\Delta H^0 = -62.7 \text{ kJ mol}^{-1}$ and $\Delta S^0 = -210.2 \text{ J mol}^{-1} \text{ K}^{-1}$
436 (see section S5 of the Supporting Information). The large nega-
437 tive reaction entropy is explained by the increased solvation
438 of the generated ions, which requires strong organization of
439 the solvent. The equilibrium constant $K = 1.6$ shows that the
440 bromide ion (N55) is slightly less Lewis basic than pyrimidine
441 (N30, $LB_{CH_3CN} = 8.59$) in acetonitrile at 20 °C. Further ¹H
442 NMR (CD_3CN) measurements for the reactions of $E17-Br$
443 with the pyridines N26 and N29 at 20 °C (Table 5) confirm

Table 5. Equilibrium Constants K (Dimensionless) for the Reactions of the Benzhydryl Halides E17-Br and E14-Cl with Azines in CD_3CN at 20 °C

benzhydryl halide	Lewis base		equilibrium constant K^b	$\text{LB}_{\text{CH}_3\text{CN}}$ of halide ion ^c
	formula	$\text{LB}_{\text{CH}_3\text{CN}}^a$		
E17-Br	N26	9.44	1.0×10^2	7.4
	N29	9.00	16	7.8
	N30	8.59	1.6^{d1}	8.4
E14-Cl	N21	11.82	1.5×10^3	~9
	N24	10.49	4.8	9.8

^aFrom Table 3. ^bDetermined from ^1H NMR (200 MHz, 23 °C). ^c $\text{LB}_{\text{CH}_3\text{CN}}(\text{halide}) = -\log K + \text{LB}_{\text{CH}_3\text{CN}}(\text{N})$. ^dDetermined from ^1H NMR (400 MHz, 20 °C); a van't Hoff plot shows good linearity and yields the thermodynamic parameters $\Delta H^0 = -62.7 \text{ kJ mol}^{-1}$ and $\Delta S^0 = -210.2 \text{ J mol}^{-1} \text{ K}^{-1}$ (see section S5 of the Supporting Information).

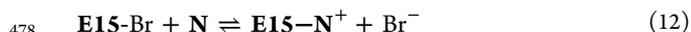
444 the value of $\text{LB}_{\text{CH}_3\text{CN}} \approx 8$ for Br^- (N55) derived from the laser
445 flash photolysis experiment (Table 4).

446 Analogous NMR experiments were performed to study the
447 equilibria of the reactions of E14-Cl with N21 and N24 in
448 CD_3CN at 20 °C (Table 5). From these data, one can derive
449 $\text{LB}_{\text{CH}_3\text{CN}} \approx 9$ for Cl^- (N54), again in fair agreement with the
450 value from the laser flash photolysis experiments (Table 4).
451 Thus, the chloride ion is about 20 times more Lewis basic than
452 the bromide ion in acetonitrile.

453 **Calorimetric Data.** An independent access to relative
454 strengths of Lewis bases is provided by isothermal titration
455 calorimetry (ITC). For that purpose, we investigated the heats
456 of the reactions of the dimethoxybenzhydryl bromide E15-Br
457 with various Lewis bases in CH_3CN (eq 12) by adding small
458 amounts (10 μL of a $2 \times 10^{-3} \text{ M}$ solution) of the Lewis bases N
459 to a large excess (1.4 mL of a $2 \times 10^{-3} \text{ M}$ solution) of E15-Br.
460 The sample cell and a reference cell filled with CH_3CN were
461 both thermostated to 20 °C, and the differences in the heat
462 energies required for maintaining the temperature constant in
463 both cells were recorded in order to determine the reaction
464 enthalpies ΔH^0 , which are listed in Table 6.

465 Since the equilibrium constant for eq 12 does not depend on
466 the substitution pattern of the benzhydryl fragment,⁵³ the value
467 of $K = 1.6$, which was measured for the reaction of E17-Br
468 with pyrimidine N30 (Table 5) should also hold for the
469 reaction of E15-Br with N30. As a consequence, this reaction
470 proceeds almost quantitatively at the concentrations em-
471 ployed in the ITC experiment (>99% for the first addition,
472 >95% for the 10th addition), and the heats measured in the
473 calorimetric experiments with N30 and stronger Lewis bases
474 correspond to the reaction enthalpies ΔH^0 for the reactions
475 with E15-Br.

476 The reaction (eq 12) can be split up into two steps (eqs 12a
477 and 12b), and ΔH^0 (eq 12) can be expressed by eq 12c.



$$481 \quad \Delta H^0(\text{eq 12}) = \Delta H^0(\text{eq 12a}) + \Delta H^0(\text{eq 12b}) \quad (12c)$$

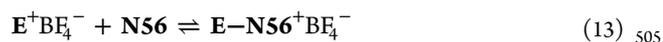
482 As ΔH^0 (eq 12a) is a constant term for all calorimetrically
483 investigated reactions of Table 6, one obtains a linear correla-
484 tion between the enthalpies ΔH^0 for the reactions of E15-Br

with the Lewis bases N in CH_3CN at 20 °C with the cor- 485
responding $\text{LB}_{\text{CH}_3\text{CN}}$ parameters from Table 3 (Figure 8). 486

There is a difference of 10 kJ mol^{-1} , however, between the 487
calorimetrically determined value ($\Delta H^0 = -52.7 \text{ kJ mol}^{-1}$) for 488
the reaction of E15-Br with N30 (Table 6) and the value of 489
 $\Delta H^0 = -62.7 \text{ kJ mol}^{-1}$ obtained from the temperature-dependent 490
NMR measurements of equilibrium constants for the reaction of 491
E17-Br with N30 (see above), showing a discrepancy between the 492
two methods, the origin of which is not yet clear. 493

Equilibrium constants $K(\text{CH}_3\text{CN})$ for the reactions of 494
benzhydrylium ions E^+ with 1,8-diazabicycloundec-7-ene 495
(DBU, N56) could not be determined with the photometric 496
method because even the least reactive benzhydrylium ions E1^+ 497
and E2^+ react quantitatively with DBU (N56).⁵⁴ We can use 498
the correlation given in Figure 8, however, to calculate $\text{LB}_{\text{CH}_3\text{CN}} =$ 499
19.7 for DBU (N56) from the heat of the reaction of DBU with 500
E15-Br in CH_3CN (Table 6). 501

The ITC method was also used to study ΔH^0 for the 502
reactions of N56 with the benzhydrylium tetrafluoroborates 503
 $\text{E(1-8)}^+ \text{BF}_4^-$ in CH_3CN (eq 13), which are listed in Table 7. 504



Subtracting ΔH^0 for the reaction of a covalent benzhydryl 506
bromide with DBU (eq 12, N = N56, last entry of Table 6) 507
from the values for ΔH^0 for the reaction of a benzhydryl cation 508
with DBU (eq 13, Table 7) provides ΔH^0 for the combinations 509
of E(1-8)^+ with Br^- , from which we can also estimate the 510
corresponding reaction entropies, as elaborated in section S7 of 511
the Supporting Information. Figure 9 shows that the $\text{LA}_{\text{CH}_3\text{CN}}$ 512
parameters of E^+ correlate linearly with the enthalpies ΔH^0 for 513
the reactions of E^+ with N56 in CH_3CN at 20 °C which are 514
listed in Table 7. 515

As the terms $-RT \ln(10)\text{LA}$ and $-RT \ln(10)\text{LB}$ correspond 516
to the fractions of ΔG^0 for the Lewis acid–Lewis base co- 517
ordinations which are allotted to the Lewis acid or Lewis base, 518
respectively, the deviations of the slopes of the correlations in 519
Figures 8 and 9 from $-RT \ln(10)$ reveal the contributions of 520
the reaction entropy ΔS^0 to the Lewis acidity and Lewis basicity 521
parameters. 522

Though the slope of the correlation in Figure 9 should be 523
considered with caution because of the moderate quality of 524
this correlation, it is interesting to note that multiplication of 525
 $\text{LA}_{\text{CH}_3\text{CN}}$ with $-RT \ln(10)$ yields a value of 1.18; i.e., the 526
increasing negative value of ΔH^0 with increasing Lewis acidity 527
is enhanced by the entropy term. As the benzhydrylium ions' 528
need for solvation increases when the positive charge of the 529
benzhydrylium ions is less delocalized (e.g., E1^+ is less solvated 530
than E8^+), less ordering of the solvent molecules is given up in 531
the combination of a Lewis base with a better stabilized 532
benzhydrylium ion (e.g., E1^+), and the formation of the Lewis 533
adduct proceeds with a more negative reaction entropy than an 534
analogous reaction with a less stabilized benzhydrylium ion 535
(e.g., E8^+). As a result, substituent variation in Figure 9 affects 536
 ΔG^0 more than ΔH^0 . The same line of arguments was used to 537
rationalize why the equilibrium constants for the reactions of 538
benzhydrylium ions with neutral Lewis bases are larger in the 539
more polar solvent CH_3CN than in CH_2Cl_2 (Figure 2). 540

When $\text{LB}_{\text{CH}_3\text{CN}}$ is expressed in units of kJ mol^{-1} (by 541
multiplication with $-RT \ln(10)$), the slope of the correlation in 542
Figure 8 is 0.83; i.e., the substituent effect on reaction enthalpy 543
 ΔH^0 is attenuated by a compensating entropy effect. More 544
specifically: As the enthalpy term ΔH^0 becomes more negative, 545

Table 6. Reaction Enthalpies ΔH^0 (kJ mol⁻¹) for the Reactions of E15-Br with Different Lewis Bases N (Eq 12) in CH₃CN at 20 °C

N	Lewis base		ΔH^0 ^c / kJ mol ⁻¹
	formula	$LB_{CH_2Cl_2}$ ^a LB_{CH_3CN} ^b	
N1		17.90 - ^d	-131.4 (±2.9)
N2		17.47 - ^d	-113.0 (±0.4)
N4		16.82 17.39	-113.8 (±0.2)
N5		16.42 17.13	-111.3 (±0.3)
N6		16.02 16.13	-103.5 (±1.0)
N8		15.39 - ^d	-113.0 (±0.3)
N9		15.04 - ^d	-105.4 (±0.7)
N11		14.27 14.72	-103.6 (±1.1)
N12		11.99 13.41	-87.8 (±0.2)
N13		11.65 12.84	-86.5 (±0.6)
N14		11.41 12.71	-84.1 (±1.9)
N15		11.31 12.80	-83.6 (±1.6)
N16		10.92 12.23	-80.2 (±0.3)
N17		10.76 12.27	-80.4 (±0.6)
N18		10.71 12.12	-80.7 (±0.1)
N20		10.17 11.50	-74.9 (±1.0)

N	Lewis base		ΔH^0 ^c / kJ mol ⁻¹
	formula	$LB_{CH_2Cl_2}$ ^a LB_{CH_3CN} ^b	
N21		10.02 11.82	-79.8 (±0.3)
N22		9.65 - ^d	-79.4 (±1.4)
N24		8.78 10.49	-70.7 (±0.6)
N25		8.74 9.85	-66.8 (±0.0)
N26		7.93 9.44	-64.9 (±1.3)
N29		6.71 9.00	-55.7 (±0.4)
N30		6.21 8.59	-52.7 (±0.3)
N38		- ^d 13.20	-87.8 (±0.3)
N39		- ^d 12.76	-86.2 (±0.1)
N41		- ^d 14.49	-98.3 (±2.3)
N42		- ^d 15.14	-96.6 (±0.7)
N43		- ^d 13.49	-87.9 (±1.6)
N44		- ^d 13.77	-84.7 (±1.1)
N56		- ^d (19.7) ^e	-130.5 (±1.2)

^aFrom Table 2. ^bFrom Tables 3 and 4. ^cIsothermal titration calorimetry, this work (see section S6 of the Supporting Information). Average values from 3–4 individual runs; values in parentheses are standard deviations. ^dNot available. ^eCalculated from ΔH^0 in this table and the correlation shown in Figure 8.

17% of the decrease of ΔH^0 is compensated by an increase of the $-T\Delta S^0$ term, so that only 83% of the change in ΔH^0 is reflected by changes of ΔG^0 . This means that the formation of Lewis adducts from stronger Lewis bases (more negative ΔH^0) is associated with a more negative value of ΔS^0 , i.e., a larger increase of ordering during the reaction. This implies a weaker solvation of the stronger Lewis bases and/or that stronger Lewis bases form Lewis adducts which have higher need for solvation. Overall, we thus observe a linear correlation between enthalpy and entropy effects (compensation effect⁵⁵) for the combinations of Lewis acids and Lewis bases.

Correlation of LA and ΔG_{MA} with pK_R^+ of the Benzhydrylium Ions. Deno's pK_R^+ values,^{13,14} which reflect the equilibrium constants for the reactions of carbocations with water (eq 3), are a well-known measure for the stabilities of carbocations. Figure S1.4 in section S1 of the Supporting Information plots the available $\log K_R^+$ versus the $LA_{CH_2Cl_2}$ parameters of the benzhydrylium ions, as well as versus their methyl anion affinities ΔG_{MA} in the gas phase.

The interpretation of the slopes of these correlations is not unambiguous due to the fact that the highly negative

pK_R^+ values of the less stabilized carbocations refer to sulfuric acid solutions of variable concentration, i.e., a change of the solvent (from water to concentrated Brønsted acids) is unavoidable when determining pK_R^+ values of carbocations with widely differing reactivities. Because of this ambiguity and the nonavailability of pK_R^+ values for $E(7-14)^+$, we refrain from discussing the correlations of $LA_{CH_2Cl_2}$ (eq 14) and ΔG_{MA} (eq 15) with pK_R^+ ; see Figure S1.4 in section S1 of the Supporting Information.

$$pK_R^+ = -1.15LA_{CH_2Cl_2} - 5.28; \quad R^2 = 0.998 \quad (14)$$

$$pK_R^+ = 0.112\Delta G_{MA} + 79.0; \quad R^2 = 0.968 \quad (15)$$

Correlation of the Lewis Basicities with pK_a Values. Figure 10a illustrates that the LB_{CH_3CN} parameters of the Lewis bases in CH_3CN do not follow a common correlation with their pK_a values in CH_3CN . Instead, we observe separate correlation lines for Lewis bases belonging to different classes of compounds, such as pyridines, tertiary amines, phosphines, or benzoates. From the fact that the slopes of the individual correlations are close to 1.0, one can conclude

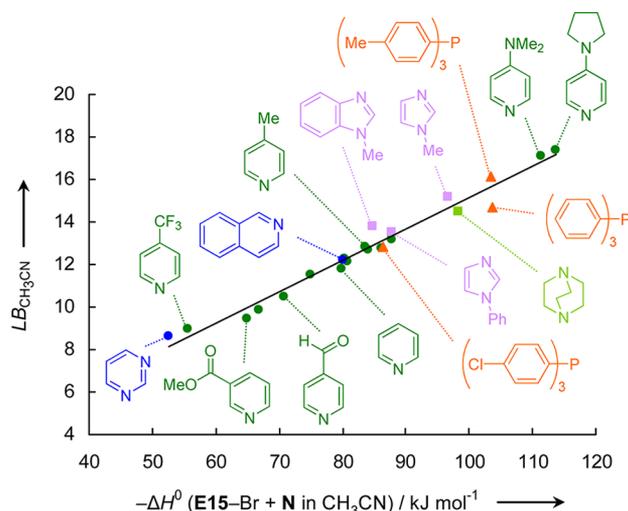


Figure 8. Plot of LB_{CH_3CN} parameters of Lewis bases N versus the enthalpies ΔH^0 for their reactions with E15-Br in CH_3CN at 20 °C ($LB_{CH_3CN} = -0.148\Delta H^0 + 0.317$; $R^2 = 0.970$).

Table 7. Reaction Enthalpies ΔH^0 ($kJ\ mol^{-1}$) for the Reactions of the Benzhydrylium Tetrafluoroborates E(1–8) $^+BF_4^-$ with 1,8-Diazabicycloundec-7-ene (DBU, N56) in CH_3CN at 20 °C

Lewis acid		$\Delta H^{0a}/kJ\ mol^{-1}$
E $^+$	abbreviation	
E1 $^+$	(lil) $_2CH^+$	-73.2 (± 0.6)
E2 $^+$	(jul) $_2CH^+$	-73.3 (± 0.3)
E3 $^+$	(ind) $_2CH^+$	-77.1 (± 0.3)
E4 $^+$	(thq) $_2CH^+$	-81.4 (± 0.5)
E5 $^+$	(pyr) $_2CH^+$	-81.4 (± 0.5)
E6 $^+$	(dma) $_2CH^+$	-89.9 (± 0.3)
E8 $^+$	(mor) $_2CH^+$	-95.3 (± 0.5)

^aIsothermal titration calorimetry, this work (see section S6 of the Supporting Information). Average values from 3–4 individual runs; values in parentheses are standard deviations.

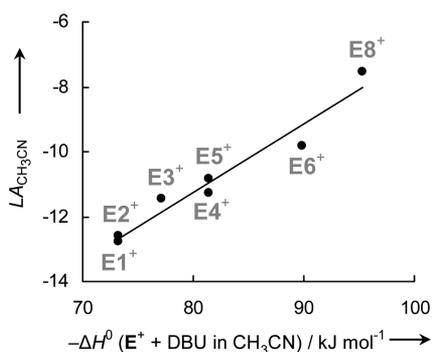


Figure 9. Plot of the LA_{CH_3CN} parameters of the benzhydrylium ions E(1–8) $^+$ versus the enthalpies ΔH^0 for the reactions of E(1–8) $^+BF_4^-$ with 1,8-diazabicycloundec-7-ene (DBU, N56) in CH_3CN at 20 °C ($LA_{CH_3CN} = -0.211\Delta H^0 - 28.1$; $R^2 = 0.951$).

586 that structural variation within one class of compounds has
587 the same effect on Brønsted basicity and on Lewis basicity
588 toward C-centered Lewis acids. Similar plots with near-unity
589 slopes were previously observed between Lewis basicity and
590 Brønsted basicity for different classes of anions in the gas
591 phase.⁴

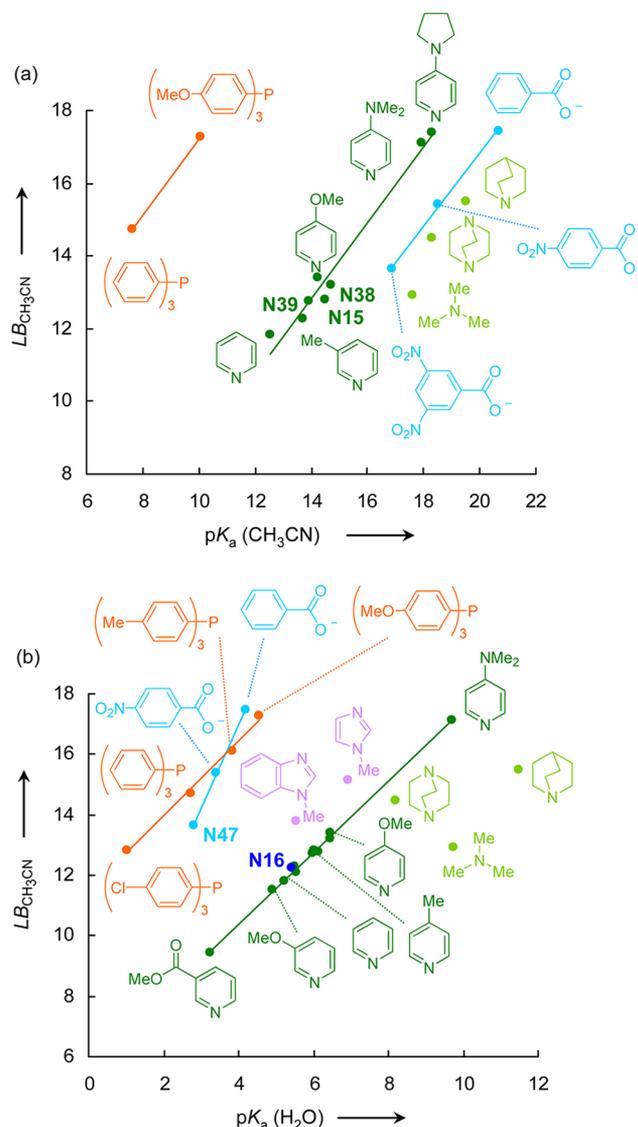


Figure 10. Plot of Lewis basicities LB_{CH_3CN} in CH_3CN versus pK_a values of the Lewis bases in CH_3CN (a) and H_2O (b). The pK_a values were taken from refs 7 and 59.

One factor which accounts for the occurrence of separate
592 correlation lines in Figure 10a is the difference in bond
593 dissociation energies.^{56,57} Since the average N–H vs N–C
594 bond energies differ by $\sim 86\ kJ\ mol^{-1}$ while the P–H and P–C
595 bond energies differ by only $\sim 58\ kJ\ mol^{-1}$,⁵⁸ one can already
596 explain why phosphines are stronger bases toward Ar_2CH^+ than
597 amines of comparable pK_a (the difference of $28\ kJ\ mol^{-1}$
598 corresponds to ca. 5 units of LB_{CH_3CN} in Figure 10a). Similarly,
599 the O–H and O–C bond energies differ by $\sim 104\ kJ\ mol^{-1}$,⁵⁸
600 which is an even larger difference than that between N–H vs
601 N–C bonds. However, bond energies vary widely depending
602 on the exact structure of the compound,^{56,57} and this may
603 contribute to the large gap (several units of LB_{CH_3CN}) between
604 the correlation lines for pyridines and tertiary amines.
605

As pK_a values are strongly solvent-dependent, it is clear that the
606 more readily available pK_a values in water cannot be used for esti-
607 mating Lewis basicities in acetonitrile. Still, we observe correlations of
608 LB_{CH_3CN} with $pK_a(H_2O)$ within some series of related compounds
609 such as pyridines, phosphines, and benzoates (Figure 10b).
610

611 ■ RELATIONSHIPS BETWEEN KINETIC AND
612 THERMODYNAMIC PARAMETERS

613 **Heterolysis Rate Constants (S_N1 Solvolyses).** In
614 previous work, we have compiled rate constants k_s (corre-
615 sponding to k_{backward} in Scheme 1) for solvolysis reactions of
616 benzhydryl derivatives $E(1-33)-X$ ($X = \text{Br}, \text{Cl}, \text{OAc}, \text{OBz}, 3,5$ -
617 dinitrobenzoyl, p -nitrobenzoyl, OCO_2Me , etc.) in hydroxylic
618 solvents.²³ Rate constants k_s for heterolysis reactions of
619 benzhydryl halides in aprotic solvents like CH_2Cl_2 and
620 CH_3CN have subsequently been determined by conductimetry
621 in the presence of amines or triphenylphosphine, which trap the
622 intermediate ion pairs and suppress ion recombination.^{60,61}

623 Figure 11a plots $\log k_s$ for representative examples of
624 solvolysis reactions of $E(13-20)-X$ versus the Lewis acidities
625 $\text{LA}_{\text{CH}_2\text{Cl}_2}$ of E^+ and illustrates excellent linear correlations
626 between kinetic and thermodynamic data for this limited set of
627 systems. Lewis acidities $\text{LA}_{\text{CH}_2\text{Cl}_2}$ of benzhydrylium ions less
628 stabilized than $E20^+$ are not available, but the thermodynamic
629 stabilities of these species can be derived from the calculated
630 methyl anion affinities. Figure 11b shows excellent linear
631 correlations between solvolysis rate constants k_s for the
632 benzhydrylium ions $E(13-33)^+$ and the calculated methyl
633 anion affinities ΔG_{MA} (eq 9) of E^+ ;⁶² data for the p -phenoxy-
634 substituted benzhydrylium ions $E16^+$ and $E19^+$ are not
635 included in Figure 11b, because of the different solvation of
636 these systems (see above).

637 In contrast, the rate constants of solvolyses that proceed via
638 the highly stabilized amino-substituted benzhydrylium ions
639 $E(1-11)^+$ correlate poorly with $\text{LA}_{\text{CH}_2\text{Cl}_2}$ of E^+ (Figure 12),
640 indicating that the rates of these heterolysis reactions are not
641 predominantly controlled by the relative thermodynamic
642 stabilities of the carbocations but are largely affected by the
643 different intrinsic barriers.^{23,39,63}

644 The excellent linear correlations (Figure 11) with slopes
645 close to -1 for leaving groups such as $\text{Cl}^-/\text{CH}_2\text{Cl}_2$ and
646 $\text{Cl}^-/\text{CH}_3\text{CN}$ in Figure 11a are explained by the fact that these
647 heterolyses have small or negligible barriers for the recombina-
648 tion reaction of the carbocation with the leaving group.
649 The slightly smaller slopes for 90A10W and 80AN20W in
650 Figure 11a indicate that the relative Lewis acidities of E^+ are
651 more attenuated in these more polar solvents than in CH_2Cl_2 .
652 (cf. Figure 6). Thus, ΔG^\ddagger corresponds to ΔG^0 for these
653 reactions, as illustrated by the free energy diagram for the
654 solvolysis of $E18\text{-Cl}$ in aqueous acetonitrile (Figure 13a). The
655 reaction of $E18^+$ with Cl^- in this solvent proceeds with a rate
656 constant of $1.02 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$;⁶⁴ i.e., there is only a small free
657 energy barrier for the combination of the ions (Figure 13a,
658 reaction from right to left). The energy barrier ΔG_i^\ddagger for the
659 ionization reaction (Figure 13a, from left to right) thus more or
660 less corresponds to the free ionization energy ΔG_i^0 for the
661 reaction $E18\text{-Cl} \rightleftharpoons E18^+ + \text{Cl}^-$ and for all substrates yielding
662 less stabilized carbenium ions. This conclusion has previously
663 been drawn from Arnett's observation that the differences in
664 activation free enthalpies of ethanolysis reactions of alkyl
665 chlorides reflected 89% of the heats of ionization of the same
666 substrates in superacidic media.⁶⁵

667 Figure 13b, on the other hand, shows the free energy diagram
668 for the solvolysis of $E1\text{-OAc}$ in 80% aqueous acetone. As the
669 combination of E^+ with AcO^- proceeds with a considerable
670 barrier in this solvent (Figure 13b, reaction from right to left),³⁹
671 ΔG_i^\ddagger for the ionization (Figure 13b, from left to right) is much
672 larger than the ionization free energy ΔG_i^0 for the reaction

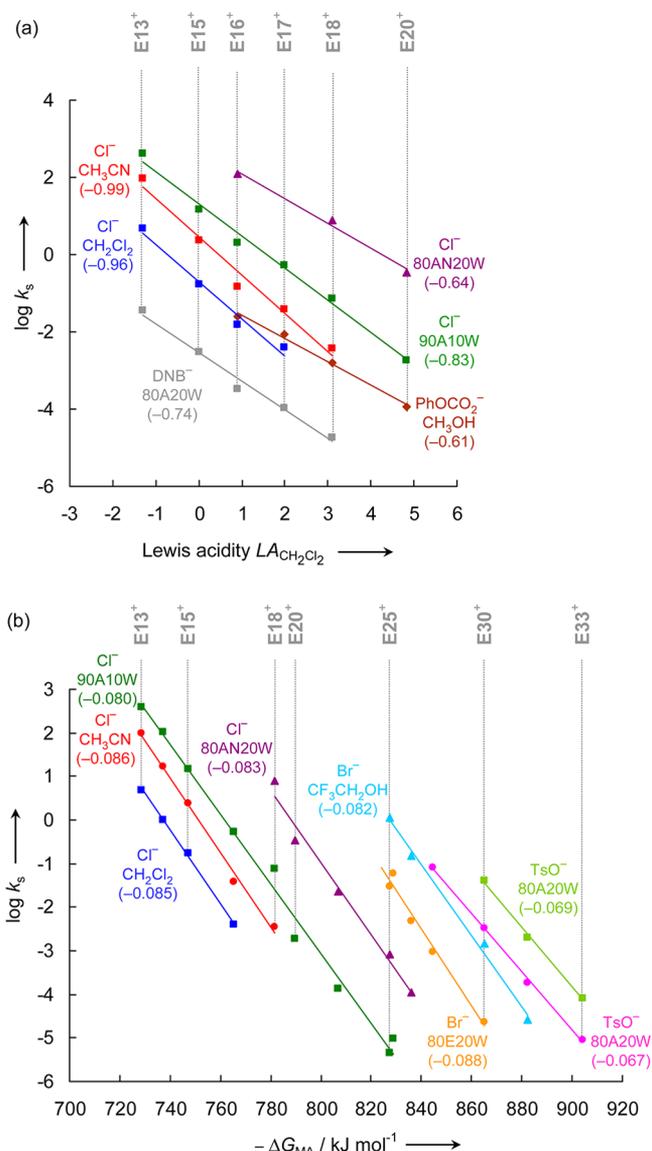


Figure 11. Correlation of $\log k_s$ for solvolysis reactions (25 °C) of $E(13-33)-X$ ^{23,60} versus the Lewis acidities $\text{LA}_{\text{CH}_2\text{Cl}_2}$ (a) and calculated methyl anion affinities ΔG_{MA} (b) of the benzhydrylium ions E^+ . The slopes of the correlation lines are given in parentheses; data for $E16^+$ and $E19^+$ are not shown and were not used for the correlations. Abbreviations: DNB⁻ = 3,5-dinitrobenzoate; mixtures of solvents are given as (v/v), A = acetone, AN = acetonitrile, W = water.

$E1\text{-OAc} \rightleftharpoons E1^+ + \text{AcO}^-$, i.e., there is a significant intrinsic 673
674 barrier, and the solvolysis rates are not predominantly
675 controlled by the relative free energies of the ionization step
($\text{LA}_{\text{CH}_2\text{Cl}_2}$ of E^+ , Figure 12). 676

Solvolysis experiments thus provide information about the 677
678 thermodynamic stabilities of carbocations if the recombination
679 reaction of the carbocation with the leaving group occurs with-
680 out barrier. In our previous work, we have measured diffusion-
681 controlled or almost diffusion-controlled ($>10^8 \text{ M}^{-1} \text{ s}^{-1}$) rate
682 constants for many combination reactions of $E(13-33)^+$ with Cl^-
683 and Br^- in solvolytic media.⁶⁴ In these cases, the Lewis acidities
684 of E^+ can thus be derived indirectly from their solvolysis rate
685 constants k_s . On the other hand, the smaller slopes for $X = \text{OTs}$
686 in Figure 11b might indicate that there is a barrier for the
687 combinations of E^+ with the very weak nucleophile TsO^- so

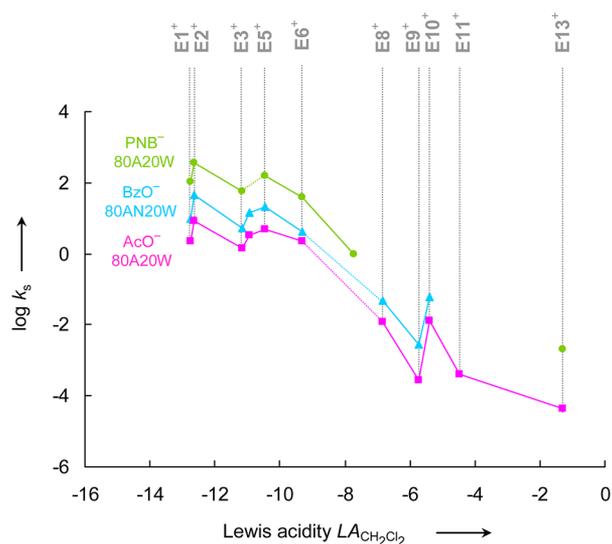


Figure 12. Plot of $\log k_s$ for solvolysis reactions (25 °C) of $E(1-13)-X^{23}$ versus the Lewis acidities $LA_{CH_2Cl_2}$ of the benzhydrylium ions E^+ . Abbreviations: PNB⁻ = *p*-nitrobenzoate; mixtures of solvents are given as (v/v), A = acetone, AN = acetonitrile, W = water.

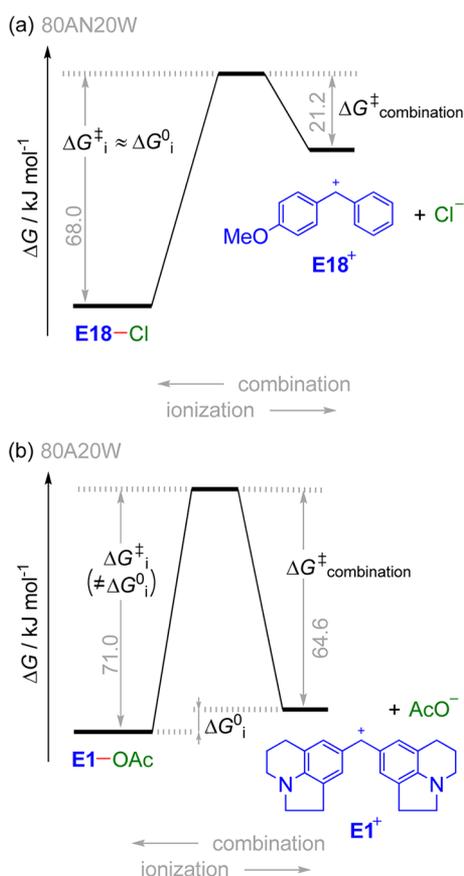


Figure 13. Free energy diagrams for the ionization steps in the solvolyses of $E18-Cl$ in 80% aqueous acetonitrile (80AN20W)⁶⁶ (a) and $E1-OAc$ in 80% aqueous acetone (80A20W)⁶⁷ (b). The subsequent reaction of E^+ with the solvent has been omitted for clarity (this reaction is much faster than the ionization in most S_N1 solvolyses⁶⁸).

688 that the carbocation character is not fully developed in the
689 transition states of the tosylate solvolyses.

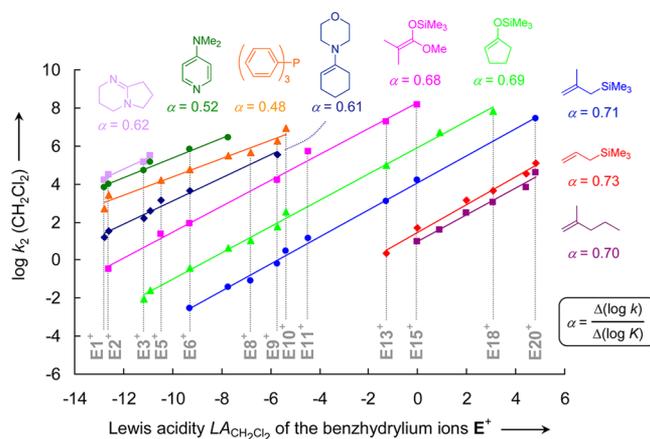


Figure 14. Correlation of $\log k_2$ for the reactions of E^+ with different nucleophiles^{20,22,28,29,31} in CH_2Cl_2 versus the Lewis acidities $LA_{CH_2Cl_2}$ of E^+ (this work).

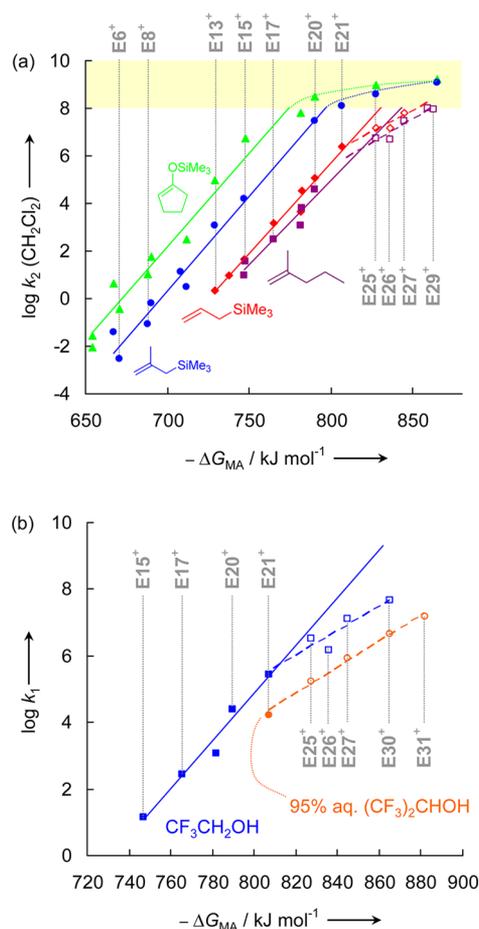


Figure 15. Plots of $\log k_2$ for the reactions of $E(3-30)^+$ with different nucleophiles^{20,22} in CH_2Cl_2 (a) and $\log k_1$ for the reactions of $E(15-31)^+$ with trifluoroethanol^{33,72} and with 95% aqueous hexafluoroisopropanol (w/w)⁷⁴ (b) versus the calculated methyl anion affinities ΔG_{MA} (eq 9) of E^+ . Data for the acceptor-substituted benzhydrylium ions $E(25-29)^+$ (empty symbols) and second-order rate constants $>10^8 M^{-1} s^{-1}$ (shaded area in panel a) were not used for the correlations.⁷⁵

Rate Constants for Combinations of Carbocations with Nucleophiles. Figure 14 illustrates that the rate constants $\log k_2$ for the reactions of E^+ with different nucleophiles

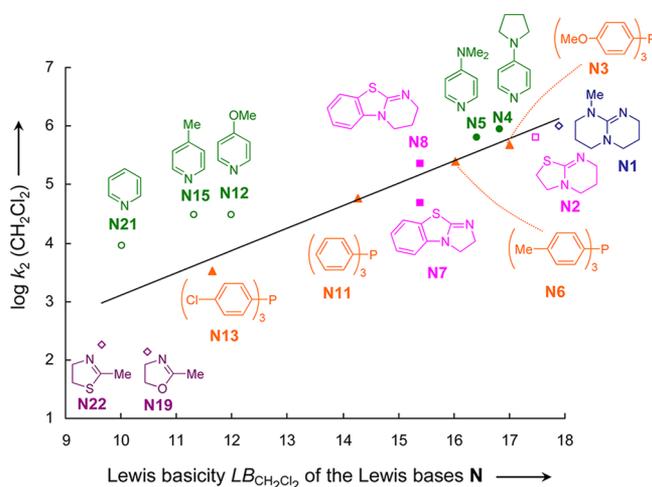


Figure 16. Plot of $\log k_2$ for the reactions of $E6^+$ with different nucleophiles N in CH_3CN ^{28–30} versus the Lewis basicities LB_{CH_3CN} of N (this work). Empty symbols: $\log k_2$ calculated from eq 17 and the reactivity parameters published in refs 29–32. The line shows the correlation for all data points ($\log k_2 = 0.38LB_{CH_2Cl_2} - 0.74$; $R^2 = 0.814$).

693 in CH_2Cl_2 ^{20,22,28,29,31} correlate linearly with the Lewis acidities
694 $LA_{CH_2Cl_2}$ of E^+ from this work.

695 The linearity of these correlations over a wide range—from
696 slow reactions with late transition states at the lower end of the
697 correlation lines to very fast, almost diffusion-controlled
698 reactions with early transition states at the top—again show
699 that the Leffler–Hammond $\alpha = \Delta(\log k)/\Delta(\log K)$ cannot be
700 a measure for the position of the transition state.^{25,69,70}

701 According to Marcus theory (eq 16),^{3,24,25,70,71} rate-
702 equilibrium relationships, i.e., $\log k$ vs $\log K$ correlations
703 ($\Delta\Delta G^\ddagger$ vs ΔG^0 correlations) can only be linear if (a) the
704 intrinsic barrier ΔG_0^\ddagger is very high compared with the reaction
705 free enthalpy $\Delta_r G^0$ or if (b) the intrinsic barriers ΔG_0^\ddagger change
706 proportionally with $\Delta_r G^0$. Our previous conclusion⁴³ that in the
707 reactions of $E(1–20)^+$ with π -nucleophiles the intrinsic barriers

decrease with increasing electrophilicity of the benzhydrylium
708 ions has now obtained a quantitative basis, because Figure 14
709 shows that all π -nucleophiles are characterized by $\alpha > 1/2$. In
710 these series, the Hammond effect, which reduces $\delta\Delta G^\ddagger/\delta\Delta_r G^0$
711 as the transition state is shifted toward reactants in more
712 exergonic reactions, must be compensated by a decrease of the
713 intrinsic barriers with increasing exergonicity.
714

$$\Delta G^\ddagger = \Delta G_0^\ddagger + \frac{1}{2}\Delta G_r^0 + \frac{(\Delta G_r^0)^2}{16\Delta G_0^\ddagger} \quad (16)$$

As $LA_{CH_2Cl_2}$ parameters for the highly reactive benzhydrylium
715 ions $E(21–33)^+$ are not available, we also plotted $\log k_2$ versus
716 the calculated methyl anion affinities ΔG_{MA} (eq 9) of E^+ . While
717 the donor-substituted benzhydrylium ions $E(1–21)^+$ show
718 good linear correlations (Figure 15), a linear extrapolation of
719 this correlation overestimates the rate constants for the acceptor-
720 substituted benzhydrylium ions $E(26–29)^+$ considerably
721 (Figure 15), although several of these rate constants are still
722 below the limit of $10^8 M^{-1} s^{-1}$ where the rate-limiting effect of
723 diffusion begins to play a role (yellow-shaded area in Figure 15).²²
724 Moreover, the same behavior is found for the first-order decay
725 reactions with solvents such as trifluoroethanol (Figure 15b),^{33,72}
726 acetonitrile,^{33,73} or hexafluoroisopropanol–water mixtures,⁷⁴ in
727 which diffusion does not have any limiting effect at all.
728

The deviation of the highly reactive carbocations from the
729 correlation line cannot result from a ground state solvation
730 effect, since the plots of $\log k_s$ for the heterolysis reactions
731 versus the calculated methyl anion affinities ΔG_{MA} of $E(13–33)^+$
732 are perfectly linear (Figure 11b). The bends in Figure 15,
733 panels a and b, thus indicate that the intrinsic barriers of the
734 combination reactions vary in a different way for donor- and
735 acceptor-substituted benzhydrylium ions. A detailed investi-
736 gation of these relationships is in progress.
737

In the discussion so far we have neglected the fact that the
738 quality of the correlations on the left-hand side of Figure 14 is
739 slightly worse than that of those on the right-hand side; the
740

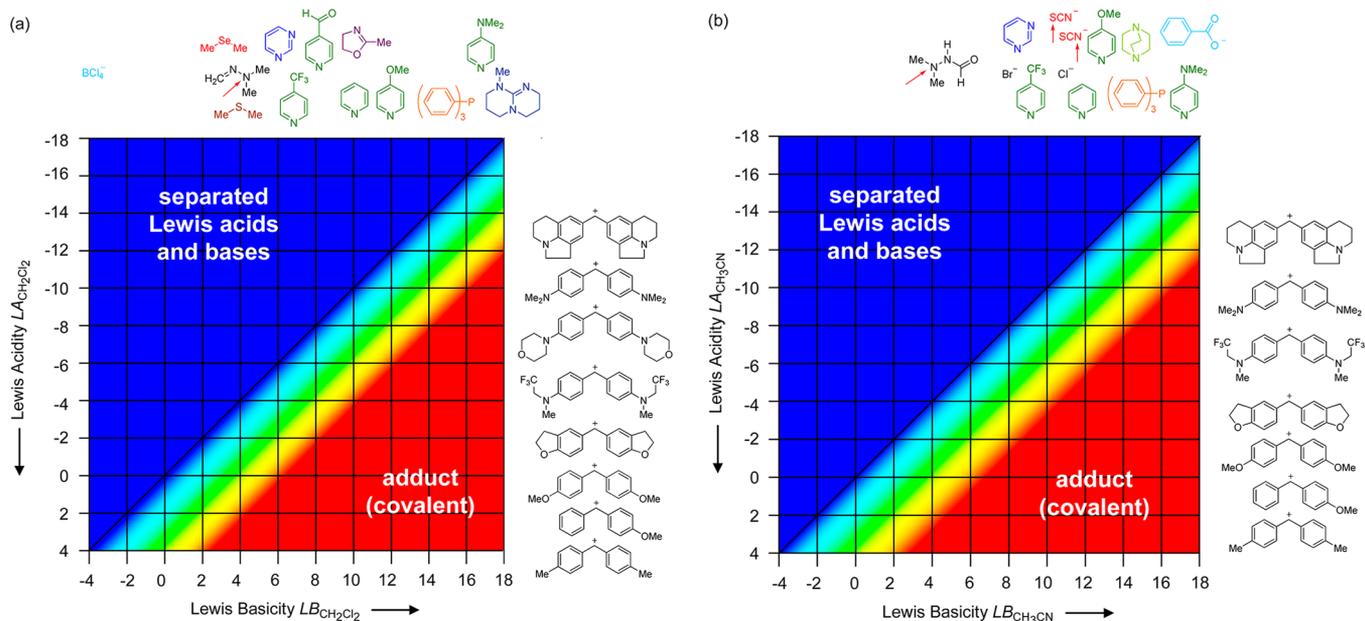


Figure 17. Semiquantitative schemes to estimate equilibria for reactions of Lewis acids (vertical axis) and Lewis bases (horizontal axis) in CH_2Cl_2 (a) and CH_3CN ⁷⁸ (b) at 20 °C. Combinations located in the red area of the figures form Lewis adducts, while combinations located in the blue area do not.

741 deviations show a similar pattern as in Figure 12. For example,
742 while having very similar $LA_{CH_2Cl_2}$ parameters, $E2^+$ is generated
743 faster in S_N1 reactions but also reacts faster in combination
744 reactions than $E1^+$. Similarly, both $E4^+$ and $E5^+$ are generated
745 and consumed faster than $E3^+$, and $E10^+$ is generated and
746 consumed faster than $E9^+$. These discrepancies show that our
747 thermodynamics-coined intuition—the better stabilized a
748 cation, the faster it is formed and the slower it reacts—has to
749 be refined. From the rate-equilibrium relationships in Figures 12
750 and 14, one can clearly see that differences in intrinsic barriers
751 are responsible for the fact that ionization and combination
752 reactions of certain systems deviate from the correlation lines in
753 the same direction.⁷⁶

754 As mentioned in the Introduction, the interpretation of
755 Brønsted correlations—i.e., relationships between nucleophilic
756 reactivities and Brønsted basicities—is hampered by the fact
757 that rate and equilibrium constants refer to interactions with
758 different reaction centers. Using the Lewis basicities derived in
759 this work, one can now correlate nucleophilic reactivities
760 toward C-centered electrophiles with equilibrium constants for
761 reactions with C-centered Lewis acids (benzhydrylium ions).⁷⁷

762 Figure 16 shows that the rate constants for the reactions of
763 various P- and N-centered Lewis bases with $E6^+$ (used as the
764 reference electrophile) correlate only poorly with the
765 corresponding Lewis basicities $LB_{CH_2Cl_2}$. Unlike in Brønsted
766 correlations, where various reasons may account for the scatter,
767 the poor quality of the correlation in Figure 16 must be due to
768 differences in intrinsic barriers because rate ($\log k_2$) and
769 equilibrium constants $\log K = LB_{CH_2Cl_2} + LA_{CH_2Cl_2}(E6^+)$ now
770 correspond to the same reaction. As rate constants for the
771 reactions of nucleophiles with benzhydrylium ions can very
772 reliably be calculated from eq 17,^{20–22} it is now possible to
773 systematically analyze the relationships between structure and
774 intrinsic barriers.

$$\log k_2(20\text{ }^\circ\text{C}) = s_N(N + E) \quad (17)$$

775 ■ CONCLUSION

776 It was demonstrated that the equilibrium constants for the
777 reactions of Lewis acids with Lewis bases in CH_2Cl_2 and
778 CH_3CN can be expressed by $\log K(20\text{ }^\circ\text{C}) = LA + LB$ (eq 7),
779 where LA is a Lewis acidity and LB is a Lewis basicity param-
780 eter. By arranging Lewis bases with increasing LB from left to
781 right and carbocations with increasing Lewis acidity from top to
782 bottom, one arrives at Figure 17, where the diagonals in panels
783 a and b correspond to Lewis adducts which form with $K = 1$.
784 As the equilibrium constants have the dimension liters per
785 mole, $K > 10^2\text{ L mol}^{-1}$ is needed to obtain predominantly
786 covalent adducts in 10^{-2} M solutions, corresponding to the red
787 sectors in panels a and b of Figure 17, while the blue sectors
788 indicate separated Lewis acids and Lewis bases.

789 From the excellent linear correlation of Lewis acidities LA of
790 benzhydrylium ions with calculated methyl anion affinities
791 ΔG_{MA} one can derive that the differences of the Lewis acidities
792 in the gas phase are attenuated to 65% in CH_2Cl_2 solution and
793 to 60% in CH_3CN . The Lewis acidities and Lewis basicities
794 reported in this work can, therefore, be used as a quantitative
795 basis for calibrating semiempirical quantum chemical methods.⁷⁹

796 As expected, the Lewis acidities LA are tightly correlated with
797 pK_R^+ , while the Lewis basicities LB only correlate with the
798 corresponding Brønsted basicities within groups of structurally
799 closely related compounds. A similar situation can be expected

for Lewis acidities, but was not observed in this work as we only
considered benzhydrylium ions, i.e., Lewis acids with similar
structures.

Whereas the electrofugalities of all acceptor-substituted and
weakly donor-substituted benzhydrylium ions $E(13-33)^+$ (S_N1
solvolysis rates) show excellent linear correlations with the
corresponding Lewis acidities (from equilibrium measure-
ments) or methyl anion affinities (from quantum chemical
calculations), these correlations break down for the amino-
substituted benzhydrylium ions $E(1-12)^+$. The rates of
heterolysis of $E(1-12)-O_2CR$ are only weakly correlated
with the corresponding Lewis acidities (i.e., thermodynamic
stabilities) of the resulting benzhydrylium ions, while the
relative magnitudes of the intrinsic barriers play an important
role.^{76,77} As a consequence, it is now clear that rates of solvolyses
of substrates yielding carbocations with $LA_{CH_2Cl_2} \geq -1$ usually
provide direct information about the thermodynamic stabilities
of the resulting carbocations—or vice versa—calculated methyl
anion affinities of carbocations with $\Delta G_{MA} < -720\text{ kJ mol}^{-1}$
provide direct information about the corresponding solvolysis
rates of R-Cl and R-Br, because the ion recombinations of such
systems are diffusion-controlled.

In contrast, the electrophilic reactivities of all donor-
substituted benzhydrylium ions $E(1-20)^+$ correlate excellently
with the corresponding Lewis acidities, while now the highly
acidic, nonstabilized or destabilized benzhydrylium ions
 $E(21-33)^+$ deviate from the linear correlation between rate
and equilibrium constants. These findings explain our previous
observation that only for the narrow group of alkoxy- and alkyl-
substituted benzhydrylium ions $E(13-20)^+$ electrophilicities
(i.e., relative rates of reactions with nucleophiles) are the
inverse of electrofugalities (i.e., relative rates of formation in
 S_N1 reactions).²³

In summary, we have created the thermodynamic counter-
part to our previously published kinetic scales: nucleophilicity
and electrophilicity on one side,^{20–22} and nucleofugality and
electrofugality on the other.²³ By employing the wide-ranging
Lewis acidity scale for benzhydrylium ions reported in this work
it is now possible to determine the Lewis basicity (toward C-
centered acids) for a wide variety of Lewis bases. Combination
of the resulting equilibrium constants with the corresponding
rate constants gives access to a systematic evaluation of intrinsic
barriers—a basis for the understanding of chemical reactivity.

■ ASSOCIATED CONTENT

Supporting Information

Additional tables and figures (section S1) as well as
miscellaneous information mentioned in the text (sections
S2–S4 and S7); experimental details for the NMR equilibrium
measurements (section S5), isothermal titration calorimetry
experiments (section S6), and photometric measurements
(section S8); and details of the quantum chemical calculations
(sections S9 and S10). This material is available free of charge
via the Internet at <http://pubs.acs.org>.

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Notes

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