

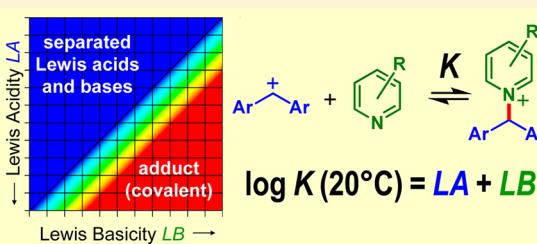
¹ Scales of Lewis Basicities toward C-Centered Lewis Acids (Carbocations)

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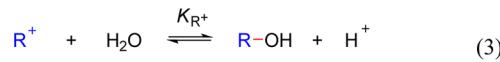
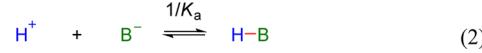
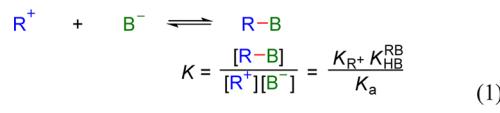
⁶ Supporting Information

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 acidities correlated linearly with the quantum chemically
¹⁷ calculated (B3LYP/6-311++G(3df,2pd)//B3LYP/6-31G(d,p) level) methyl anion affinities of the corresponding benzhydrylium
¹⁸ ions, which can be used as reference compounds for characterizing a wide variety of Lewis bases. The equilibrium measurements
¹⁹ were complemented by isothermal titration calorimetry studies. Rates of $\text{S}_{\text{N}}1$ solvolyses of benzhydryl chlorides, bromides, and
²⁰ tosylates derived from $\text{E}(13-33)^+$, i.e., from highly reactive carbocations, correlate excellently with the corresponding Lewis
²¹ acidities and the quantum chemically calculated methyl anion affinities. This correlation does not hold for solvolyses of derivatives of
²² the better stabilized amino-substituted benzhydrylium ions $\text{E}(1-12)^+$. In contrast, the correlation between electrophilic reactivities
²³ and Lewis acidities (or methyl anion affinities) is linear for all donor-substituted benzhydrylium ions $\text{E}(1-21)^+$, while the acceptor-
²⁴ substituted benzhydrylium ions $\text{E}(26-33)^+$ react more slowly than expected from their thermodynamic stabilities. The boundaries
²⁵ of linear rate-equilibrium relationships were thus defined.



■ INTRODUCTION

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



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

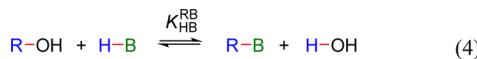
rates of the reactions of a series of B^- with a certain reference electrophile) with the corresponding equilibrium constants and to use the terms hydrogen basicity, carbon basicity, and sulfur basicity for comparing the relative affinities of various bases toward the proton, carbon-centered Lewis acids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

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

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

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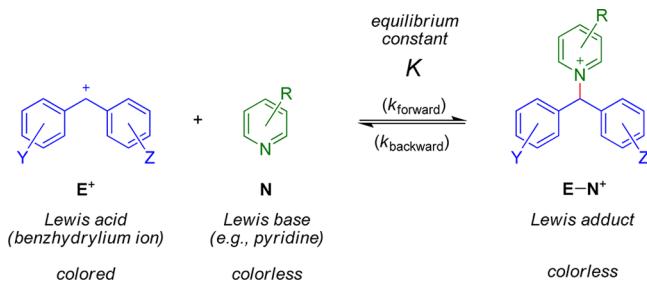


64 Combination of eqs 2–4 gives access to absolute values of
65 Lewis acid/Lewis base association constants (eq 1).^{12,16,17}

66 Kessler and Feigel demonstrated for few systems that
67 equilibrium constants for combinations of carbocations with
68 anions B^- correlate with the pK_{R}^+ values of the carbocations
69 and the pK_a values of the conjugate acids HB .¹⁸ Takeuchi and
70 Kitagawa reported analogous relationships for combinations of
71 carbocations with carbanions.¹⁹

72 However, the calculation of Lewis acid/Lewis base
73 association constants K from eq 1 has not frequently been
74 used in practice, probably because of the lack of a sufficient
75 number of suitable pK_{R}^+ values and the difficulties to properly
76 handle the influence of solvents on these equilibrium constants.
77 We now report on an alternative, easily applicable method for
78 determining Lewis basicities toward C-centered electrophiles
79 which uses benzhydrylium ions as reference Lewis acids
80 (Scheme 1). This method is analogous to that which we have

Scheme 1. Benzhydrylium Ions E^+ as Reference Lewis Acids for the Determination of Lewis Basicities



81 previously used for the construction of comprehensive
82 nucleophilicity^{20–22} and nucleofugality²³ scales where benzhy-
83 drylium ions Ar_2CH^+ (E^+) were employed as reference
84 electrophiles and reference electrofuges, respectively. As the
85 Lewis acidities of Ar_2CH^+ (E^+) can widely be varied by
86 modifying the substituents at the arene rings, strong Lewis
87 bases can be characterized by measuring their coordination
88 equilibria with weakly Lewis-acidic (donor-substituted) benzhy-
89 drylium ions, while weak Lewis bases can be characterized by
90 measuring their coordination equilibria with less stabilized
91 more Lewis-acidic benzhydrylium ions. In order to keep the
92 steric demand of the electrophilic reaction center constant, only
93 *m*- and *p*-substituted benzhydrylium ions have been employed
94 for these equilibrium measurements, as for the previous kinetic
95 investigations (Table 1).^{20–23}

96 By using the method of overlapping correlation lines, we will
97 derive a Lewis acidity scale for benzhydrylium ions in CH_2Cl_2
98 solution, which can be used for the characterization of a large variety
99 of Lewis bases by photometric measurements of equilibrium con-
100 stants. We will then show that the Lewis acidities thus obtained
101 correlate well with quantum chemically calculated methyl anion
102 affinities in the gas phase. Since the term “carbon basicity”, as
103 defined by Parker and Hine,^{9,15} is often misunderstood as
104 “reactivities of carbon bases”, we will avoid this term and instead
105 refer to “Lewis basicity with respect to certain Lewis acids”.

106 Correlating the Lewis acidities and Lewis basicities derived in
107 this work with the corresponding rate constants will provide
108 important insights into the role of intrinsic barriers^{24,25} in polar
109 organic reactivity. We address this aspect only briefly in this

Table 1. Reference Lewis Acids E(1–33)⁺ and Their Lewis Acidities $\text{LA}_{\text{CH}_2\text{Cl}_2}$ and $\text{LA}_{\text{CH}_3\text{CN}}$, Calculated Methyl Anion Affinities ΔG_{MA} , and pK_{R}^+ Values

no. ^a	Y	Z	abbreviation	LA^b CH_2Cl_2	ΔG_{MA}^c CH_3CN	pK_{R}^d
E1 ⁺			(lil) ₂ CH ⁺	-12.76	-12.76	-639.8
E2 ⁺			(jul) ₂ CH ⁺	-12.62	-12.61	-642.2
E3 ⁺			(ind) ₂ CH ⁺	-11.16	-11.46	-654.5
E4 ⁺			(thq) ₂ CH ⁺	-10.92	-11.27	-654.0
E5 ⁺	Y = Z = 4-(<i>N</i> -pyrrolidino)		(pyr) ₂ CH ⁺	-10.46	-10.83	-658.3
E6 ⁺	Y = Z = 4-N(Me) ₂		(dma) ₂ CH ⁺	-9.30	-9.82	-670.7
E7 ⁺	Y = Z = 4-N(Me)(Ph)		(mpa) ₂ CH ⁺	-7.72	-7.87	-667.1
E8 ⁺	Y = Z = 4-(<i>N</i> -morpholino)		(mor) ₂ CH ⁺	-6.82	-7.52	-688.2
E9 ⁺	Y = Z = 4-N(Ph) ₂		(dpa) ₂ CH ⁺	-5.72	^g	-689.9
E10 ⁺	Y = Z = 4-N(Me)(CH ₂ CF ₃)		(mfa) ₂ CH ⁺	-5.39	^g	-711.9
E11 ⁺	Y = Z = 4-N(Ph)(CH ₂ CF ₃)		(pfa) ₂ CH ⁺	-4.47	^g	-708.5
E13 ⁺			(fur) ₂ CH ⁺	-1.29	^g	-728.8
E14 ⁺			fur(ani)CH ⁺	^g	^g	-737.4
E15 ⁺	4-MeO	4-MeO	(ani) ₂ CH ⁺	0.00	^g	-747.2
E16 ⁺	4-MeO	4-PhO	ani(pop) ₂ CH ⁺	0.90	^g	-747.6
E17 ⁺	4-MeO	4-Me	ani(tol) ₂ CH ⁺	2.00	^g	-765.3
E18 ⁺	4-MeO	H	ani(Ph) ₂ CH ⁺	3.10	^g	-781.7
E19 ⁺	4-PhO	H	pop(Ph) ₂ CH ⁺	4.42	^g	-782.5
E20 ⁺	4-Me	4-Me	(tol) ₂ CH ⁺	4.82	^g	-789.8
E21 ⁺	4-Me	H	tol(Ph) ₂ CH ⁺	^g	^g	-807.0
E22 ⁺	4-F	4-F	(pfp) ₂ CH ⁺	^g	^g	-834.3
E23 ⁺	4-F	H	pfp(Ph) ₂ CH ⁺	^g	^g	-828.9
E24 ⁺	3-F, 4-Me	3-F, 4-Me	—	^g	^g	-823.9
E25 ⁺	H	H	Ph ₂ CH ⁺	^g	^g	-827.6
E26 ⁺	4-Cl	4-Cl	(pcp) ₂ CH ⁺	^g	^g	-836.1
E27 ⁺	3-F	H	mfp(Ph) ₂ CH ⁺	^g	^g	-844.7
E28 ⁺	4-(CF ₃)	H	tfp(Ph) ₂ CH ⁺	^g	^g	-859.5
E29 ⁺	3,5-F ₂	H	dfp(Ph) ₂ CH ⁺	^g	^g	-863.0
E30 ⁺	3-F	3-F	(mfp) ₂ CH ⁺	^g	^g	-865.0
E31 ⁺	3,5-F ₂	3-F	dfp(mfp) ₂ CH ⁺	^g	^g	-882.2
E32 ⁺	4-(CF ₃)	4-(CF ₃)	(tfm) ₂ CH ⁺	^g	^g	-891.8
E33 ⁺	3,5-F ₂	3,5-F ₂	(dfp) ₂ CH ⁺	^g	^g	-904.1

^aWe use the same numbering as in ref 22 and omit the ferrocenyl(phenyl)methylium ion ($\text{E}12^+$). ^bLewis acidities $\text{LA}_{\text{CH}_2\text{Cl}_2}$ and $\text{LA}_{\text{CH}_3\text{CN}}$ of E^+ as defined by eq 7, this work. ^cMethyl anion affinities of E^+ calculated at the B3LYP/6-311++G(3df,2pd)/B3LYP/6-31G(d,p) level of theory, this work. ^dUnless noted otherwise: data from ref 26 adjusted to the H_{R} acidity scale from ref 14; see section S2 of the Supporting Information for details. ^eNot available. ^fFrom ref 14. ^gNot determined. ^hFrom ref 27.

article to demonstrate the relevance of the data presented in this work, and will elaborate this facet in more detail in subsequent publications.

LEWIS ACIDITY AND BASICITY SCALES

Equilibrium Constants in CH_2Cl_2 at 20 °C. As benzhydrylium ions E^+ are colored, the equilibrium constants K for their reactions with Lewis bases (Scheme 1) can be determined photometrically. We have previously employed this method to determine the equilibrium constants K for some reactions of E^+ with phosphines,²⁸ pyridines,²⁹ isothioureas,³⁰ guanidines,³¹ oxazolines and thiazolines,³² and other Lewis bases in dichloromethane. For the calibrations in this work, we selected the most precise published experimental data and collected them in Table 2. Equilibrium constants, which were

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

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

Table 2. continued

N	Lewis base formula	<i>LB</i> _{CH₂Cl₂}	electrophile		<i>K</i> ^a / M ⁻¹	correlation	
			E ⁺	abbreviation	<i>LA</i> _{CH₂Cl₂}	<i>K_{calc}</i> ^b / M ⁻¹	<i>K_{calc}/K</i>
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 ² ^g	5.81 × 10 ² 0.88
			E8 ⁺	(mor) ₂ CH ⁺	-6.82	4.07 × 10 ³ ^g	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 ⁴ ^f	2.02 × 10 ⁴ 0.90
N22		9.65	E8 ⁺	(mor) ₂ CH ⁺	-6.82	6.38 × 10 ² ^g	6.79 × 10 ² 1.06
			E9 ⁺	(dpa) ₂ CH ⁺	-5.72	7.20 × 10 ³ ^g	8.50 × 10 ³ 1.18
			E10 ⁺	(mfa) ₂ CH ⁺	-5.39	2.27 × 10 ⁴ ^g	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

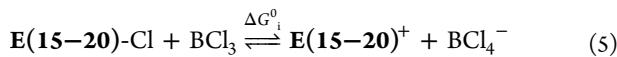
N	Lewis base		E^+	electrophile		K^a / M^{-1}	correlation	
	formula	$LB_{CH_2Cl_2}$		abbreviation	$LA_{CH_2Cl_2}$		K_{calc}^b / M^{-1}	K_{calc}/K
N37	BCl_4^-	-4.04	$E15^+$	(ani) ₂ CH ⁺	0.00	$5.82 \times 10^{-5}^h$	9.06×10^{-5}	1.56
			$E16^+$	ani(pop)CH ⁺	0.90	$1.12 \times 10^{-3}^h$	7.19×10^{-4}	0.64
			$E17^+$	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^j	— 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 ΔG_i^0 (-70 °C) values and $\Delta S_i^0 \approx 0$ 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 °C) and ΔS_i^0 for the ionization of $E20-Cl$ (see footnote j) to calculate the ionization equilibrium constants $1/K$ at 20 °C. ⁱOnly one equilibrium constant was used for the determination of $LA_{CH_2Cl_2}$. ^j $1/K$ (20 °C) was calculated from the thermodynamic parameters of the ionization reaction $E20-Cl + BCl_3 \rightleftharpoons E20^+ + BCl_4^-$: $\Delta H_i^0 = -32.6$ kJ mol⁻¹ (ref 34) and ΔG_i^0 (-70 °C) = -7.0 kJ mol⁻¹ (ref 35) (and thus $\Delta S_i^0 = -126$ J K⁻¹ mol⁻¹).

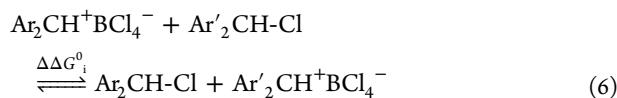
less accurate due to the occurrence of slow subsequent reactions, or which were determined indirectly from the ratio of rate constants $k_{forward}/k_{backward}$ (Scheme 1), are not included in Table 2.

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

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



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



The ionization entropy of $\Delta S_i^0 = -126$ J K⁻¹ mol⁻¹ was then used to convert the ΔG_i^0 (-70 °C) values to 20 °C and to calculate the equilibrium constants $1/K$ for the reactions of eq 5 at 20 °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 °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 employed 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 applicability of eq 7.

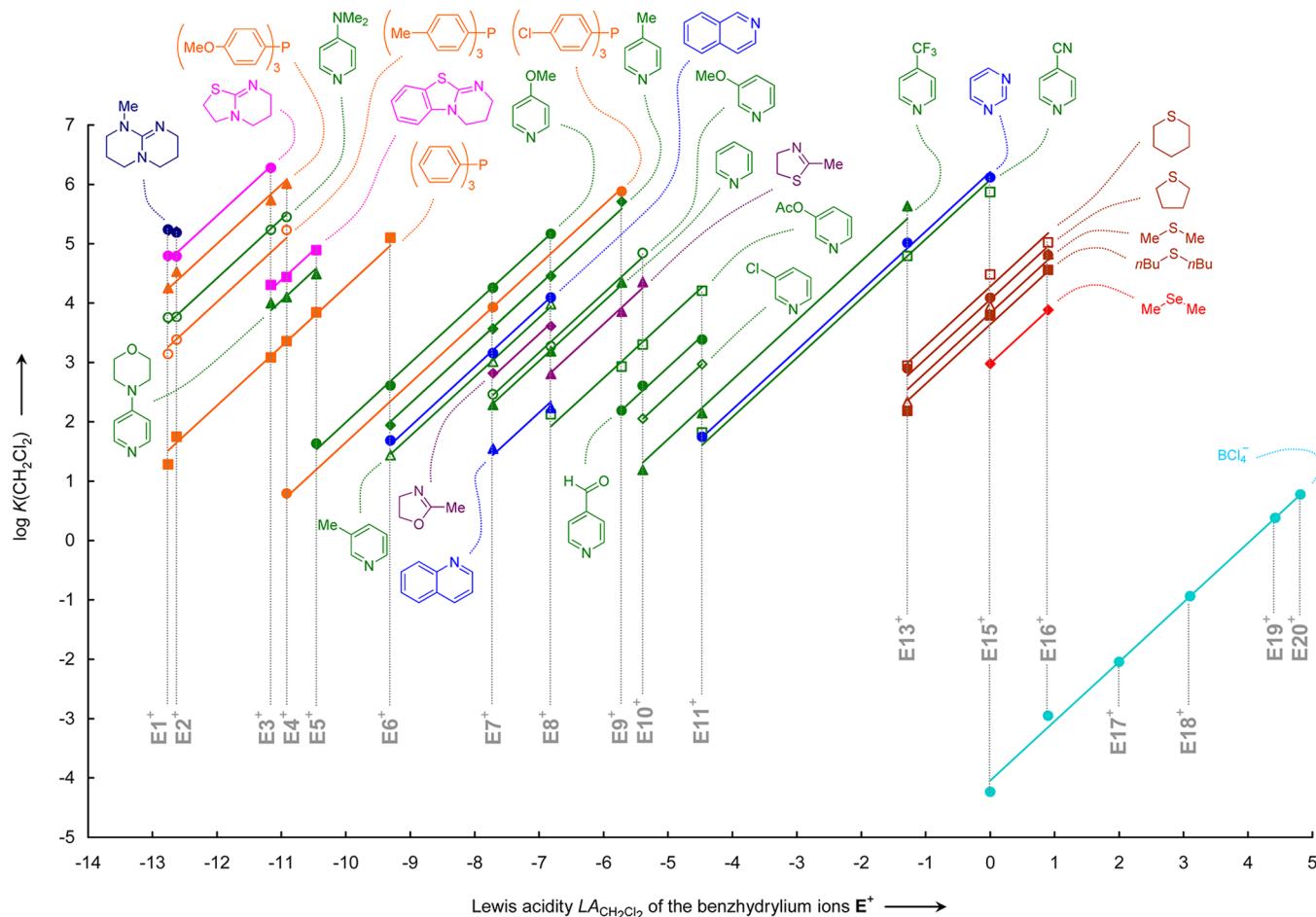


Figure 1. Plot of $\log K$ for reactions of benzhydrylium ions E^+ with Lewis bases in CH_2Cl_2 against the Lewis acidity parameters $\text{LA}_{\text{CH}_2\text{Cl}_2}$ of the benzhydrylium ions. The lines have a slope of unity and were calculated from eq 7. Some correlation lines have been omitted 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 $\log K(\text{CH}_2\text{Cl}_2)$ for the reactions of the
 201 benzhydrylium ions (E^+) with Lewis bases against the $\text{LA}_{\text{CH}_2\text{Cl}_2}$
 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 $\text{LA}_{\text{CH}_2\text{Cl}_2}$ and $\text{LB}_{\text{CH}_2\text{Cl}_2}$ of
 209 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

equilibrium constants for the correlation analysis. Therefore, equilibrium constants for reactions of benzhydrylium ions which are more reactive than E8⁺ are not included in Table 3, because these benzhydrylium ions were found to undergo slow reactions with impurities that remain present in highly purified CH₃CN.

A comparison of Tables 2 and 3 shows that the equilibrium constants K are generally 1.3–9 times (reactions of $\text{E}7^+$, 12–38 times) larger in CH_3CN than in CH_2Cl_2 solution, i.e., the formation of adducts from benzhydrylium ions and neutral Lewis bases is more favorable in CH_3CN than in CH_2Cl_2 . This difference indicates that the onium salts generated by the reaction of the benzhydrylium ions with the neutral Lewis bases (Scheme 1) are better stabilized by the polar solvent CH_3CN than the benzhydrylium ions, in which the charge is highly dispersed. The equilibrium constants for the combinations of the benzhydrylium ions E^+ with the anions N(45–47) are so large in CH_2Cl_2 that their magnitude could not be measured by the photometric method employed in this work.

A closer look at the data is provided by Figure 2, which plots $\log K(\text{CH}_3\text{CN})$ for reactions of benzhydrylium ions E^+ with pyridines and phosphines in CH_3CN (Table 3) against $\log K(\text{CH}_2\text{Cl}_2)$ for the same reactions in CH_2Cl_2 (Table 2). Two observations can be made: (a) the equilibrium constants for the reactions of pyridines (green circles) experience a larger solvent 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 formula	LB_{CH_3CN}	electrophile		K^a / M^{-1}	$K_{\text{calc}}^b / M^{-1}$	K_{calc}/K	
			E^+	abbreviation				
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
N25		9.85	E7⁺	(mor) ₂ CH ⁺	-7.52	9.41×10^2	9.42×10^2	1.00
N26		9.44	E7⁺	(mpa) ₂ CH ⁺	-7.87	3.59×10^1	3.69×10^1	1.03
N29		9.00	E7⁺	(mor) ₂ CH ⁺	-7.52	8.46×10^1	8.24×10^1	0.97
			E8⁺	(mpa) ₂ CH ⁺	-7.87	2.76×10^1	2.99×10^1	1.08

Table 3. continued

N	Lewis base formula	LB _{CH₃CN}	electrophile		experiment <i>K</i> ^a / M ⁻¹	correlation	
			E ⁺	abbreviation		K _{calc} ^b / M ⁻¹	K _{calc} /K
N30		8.59	E7 ⁺	(mpa) ₂ CH ⁺	-7.87	5.68	5.24 0.92
			E8 ⁺	(mor) ₂ CH ⁺	-7.52	1.08 × 10 ¹	1.17 × 10 ¹ 1.08
N38		13.20	E3 ⁺	(ind) ₂ CH ⁺	-11.46	4.68 × 10 ¹ ^c	5.43 × 10 ¹ 1.16
			E4 ⁺	(thq) ₂ CH ⁺	-11.27	8.04 × 10 ¹ ^c	8.51 × 10 ¹ 1.06
			E5 ⁺	(pyr) ₂ CH ⁺	-10.83	2.60 × 10 ²	2.35 × 10 ² 0.90
			E6 ⁺	(dma) ₂ CH ⁺	-9.82	2.66 × 10 ³	2.39 × 10 ³ 0.90
N39		12.76	E4 ⁺	(thq) ₂ CH ⁺	-11.27	3.02 × 10 ¹ ^c	3.13 × 10 ¹ 1.04
			E5 ⁺	(pyr) ₂ CH ⁺	-10.83	9.52 × 10 ¹ ^c	8.64 × 10 ¹ 0.91
			E6 ⁺	(dma) ₂ CH ⁺	-9.82	8.28 × 10 ²	8.81 × 10 ² 1.06
N40		15.48	E4 ⁺	(thq) ₂ CH ⁺	-11.27	1.68 × 10 ⁴ ^c	1.65 × 10 ⁴ 0.98
			E5 ⁺	(pyr) ₂ CH ⁺	-10.83	4.49 × 10 ⁴ ^c	4.56 × 10 ⁴ 1.02
N41		14.49	E4 ⁺	(thq) ₂ CH ⁺	-11.27	1.56 × 10 ³ ^c	1.66 × 10 ³ 1.07
			E5 ⁺	(pyr) ₂ CH ⁺	-10.83	4.89 × 10 ³ ^c	4.59 × 10 ³ 0.94
N42		15.14	E1 ⁺	(lil) ₂ CH ⁺	-12.76	2.44 × 10 ² ^h	2.39 × 10 ² 0.98
			E2 ⁺	(jul) ₂ CH ⁺	-12.61	2.42 × 10 ² ^h	3.63 × 10 ² 1.39
			E3 ⁺	(ind) ₂ CH ⁺	-11.46	5.56 × 10 ³ ^h	4.76 × 10 ³ 0.86
			E4 ⁺	(thq) ₂ CH ⁺	-11.27	8.69 × 10 ³ ^h	7.46 × 10 ³ 0.86
N43		13.49	E3 ⁺	(ind) ₂ CH ⁺	-11.46	9.08 × 10 ¹ ^h	1.07 × 10 ² 1.18
			E4 ⁺	(thq) ₂ CH ⁺	-11.27	1.83 × 10 ² ^h	1.68 × 10 ² 0.92
			E5 ⁺	(pyr) ₂ CH ⁺	-10.83	4.72 × 10 ² ^h	4.63 × 10 ² 0.98
			E6 ⁺	(dma) ₂ CH ⁺	-9.82	4.99 × 10 ³ ^h	4.72 × 10 ³ 0.95
N44		13.77	E3 ⁺	(ind) ₂ CH ⁺	-11.46	1.86 × 10 ² ^h	2.06 × 10 ² 1.11
			E4 ⁺	(thq) ₂ CH ⁺	-11.27	2.60 × 10 ² ^h	3.23 × 10 ² 1.24
			E5 ⁺	(pyr) ₂ CH ⁺	-10.83	9.99 × 10 ² ^h	8.90 × 10 ² 0.89
			E6 ⁺	(dma) ₂ CH ⁺	-9.82	1.11 × 10 ⁴ ^h	9.07 × 10 ³ 0.82
N45		17.45	E1 ⁺	(lil) ₂ CH ⁺	-12.76	6.20 × 10 ⁴ ⁱ	4.87 × 10 ⁴ 0.79
			E2 ⁺	(jul) ₂ CH ⁺	-12.61	5.38 × 10 ⁴ ⁱ	6.84 × 10 ⁴ 1.27
N46		15.41	E1 ⁺	(lil) ₂ CH ⁺	-12.76	5.79 × 10 ² ⁱ	4.44 × 10 ² 0.77
			E2 ⁺	(jul) ₂ CH ⁺	-12.61	5.18 × 10 ² ⁱ	6.24 × 10 ² 1.20
			E3 ⁺	(ind) ₂ CH ⁺	-11.46	1.08 × 10 ⁴ ⁱ	8.84 × 10 ³ 0.82
			E4 ⁺	(thq) ₂ CH ⁺	-11.27	1.13 × 10 ⁴ ⁱ	1.39 × 10 ⁴ 1.23
			E5 ⁺	(pyr) ₂ CH ⁺	-10.83	3.20 × 10 ⁴ ⁱ	3.82 × 10 ⁴ 1.19
			E6 ⁺	(dma) ₂ CH ⁺	-9.82	4.32 × 10 ⁵ ⁱ	3.90 × 10 ⁵ 0.90
N47		13.63	E3 ⁺	(ind) ₂ CH ⁺	-11.46	1.99 × 10 ² ⁱ	1.47 × 10 ² 0.74
			E4 ⁺	(thq) ₂ CH ⁺	-11.27	2.33 × 10 ² ⁱ	2.30 × 10 ² 0.99
			E5 ⁺	(pyr) ₂ CH ⁺	-10.83	5.48 × 10 ² ⁱ	6.35 × 10 ² 1.16
			E6 ⁺	(dma) ₂ CH ⁺	-9.82	5.46 × 10 ³ ⁱ	6.47 × 10 ³ 1.19
N48		11.47	E7 ⁺	(mpa) ₂ CH ⁺	-7.87	3.70 × 10 ³ ^j	3.99 × 10 ³ 1.08
			E8 ⁺	(mor) ₂ CH ⁺	-7.52	9.60 × 10 ³ ^j	8.91 × 10 ³ 0.93

^aPhotometric determination from this work unless indicated otherwise. ^bCalculated from eq 7. ^cFrom ref 37. ^dΔH⁰ and ΔS⁰ 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. ^eΔH⁰ = -53.5 kJ mol⁻¹ and ΔS⁰ = -99.2 J K⁻¹ mol⁻¹. ^fΔH⁰ = -50.7 kJ mol⁻¹ and ΔS⁰ = -88.7 J K⁻¹ mol⁻¹. ^gΔH⁰ = -40.5 kJ mol⁻¹ and ΔS⁰ = -101.4 J K⁻¹ 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-π* 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 CH₃CN. Although Figure 2 indicates that the equilibrium constants for the reactions in CH₃CN correlate with those for the reactions in CH₂Cl₂, we did not make any *a priori* assumptions about the effect of the solvent on the Lewis acids and bases. Instead, we subjected the CH₃CN 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 Δ² as defined in eq 8. As precise equilibrium constants for the reactions of E15⁺ (LA_{CH₃Cl₂} = 0) with Lewis bases could not be determined in CH₃CN (Table 3), we defined LA_{CH₃CN}(E1⁺) = -12.76 (i.e., the same value as obtained for E1⁺ in CH₂Cl₂) 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 CH₃CN and allows us to derive the LA_{CH₃CN} and LB_{CH₃CN} parameters for CH₃CN solution which are listed in Table 3. A graphical illustration of the correlations is given in Figure 3, which plots log K (CH₃CN) for the reactions of benzhydrylium ions with Lewis bases in CH₃CN against the LA_{CH₃CN} parameters of the benzhydrylium ions E⁺ in CH₃CN.

Remarkably, also the benzoate anions N(45–47)³⁹ and thiocyanate anion (N48, reaction at N)⁴⁰ follow the same

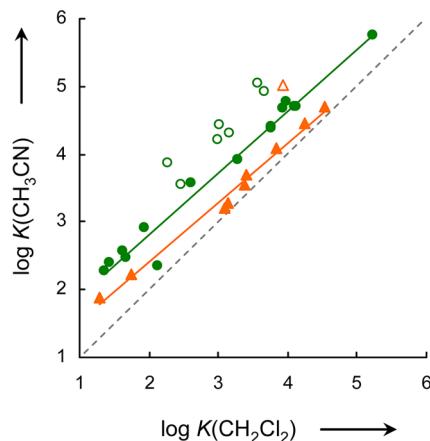


Figure 2. Plot of $\log K(\text{CH}_3\text{CN})$ for reactions of benzhydrylium ions E^+ with pyridines (green circles) and phosphines (orange triangles) in CH_3CN against $\log K(\text{CH}_2\text{Cl}_2)$ for the same reactions in CH_2Cl_2 . Pyridines: $\log K(\text{CH}_3\text{CN}) = 0.913 \log K(\text{CH}_2\text{Cl}_2) + 0.984$, $R^2 = 0.977$. 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.

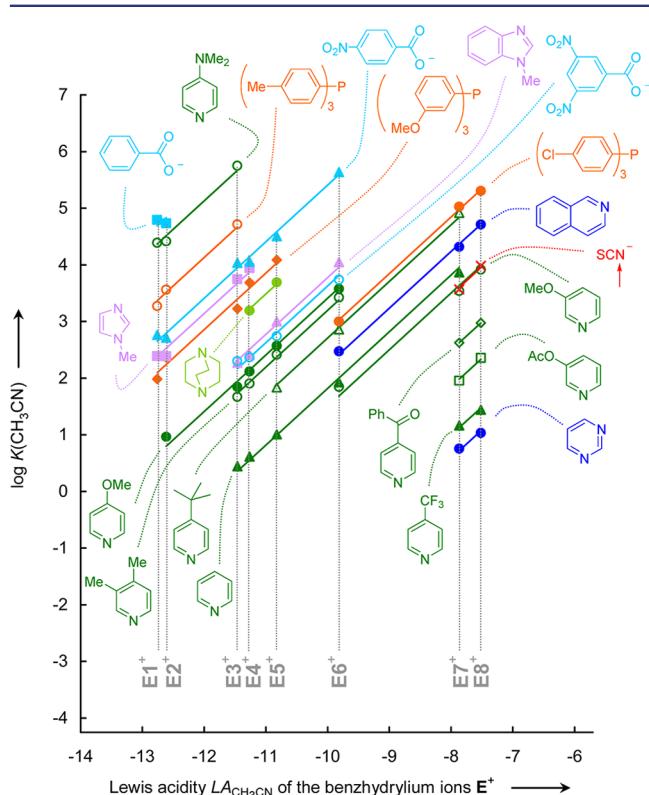


Figure 3. Plot of $\log K(\text{CH}_3\text{CN})$ for reactions of benzhydrylium ions E^+ with Lewis bases in CH_3CN against the Lewis acidity parameters $\text{LA}_{\text{CH}_3\text{CN}}$ of the benzhydrylium ions E^+ calculated from eq 7. Some correlation lines have been omitted for the sake of clarity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

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

Methyl Anion Affinities of the Benzhydrylium Ions in the Gas Phase. In order to investigate the effect of solvation on the relative Lewis acidities of benzhydrylium ions and to extend the Lewis acidity scale, we performed quantum chemical 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 unscaled 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 ($-\Delta G_g^*$)

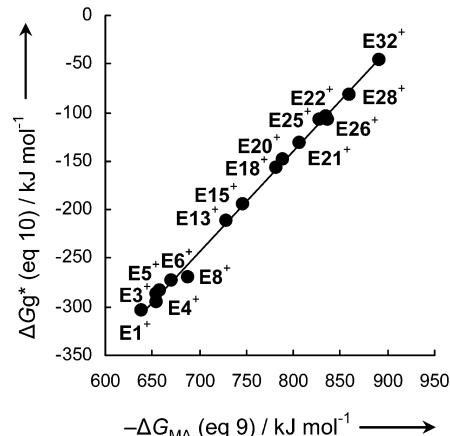


Figure 4. Correlation of the calculated free energies ΔG_g^* (kJ mol^{-1}) for hydride transfer from the diarylmethanes Ar_2CH_2 (E-H) to the benzyl cation in the gas phase (eq 10)⁴² with the calculated methyl anion affinities ΔG_{MA} (kJ mol^{-1}) of the benzhydrylium ions E^+ in the gas phase (eq 9)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

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 extents, in line with previous analyses which also included hydroxide 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 Effects. 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

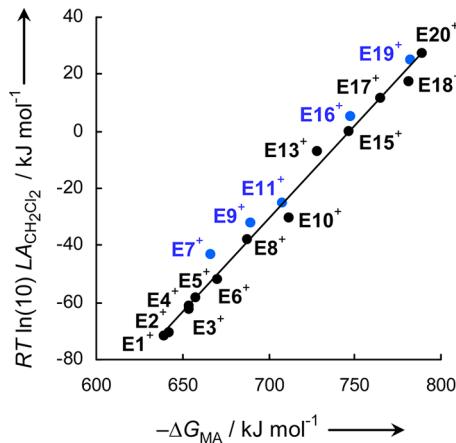


Figure 5. Correlation of the Lewis acidities $LA_{CH_2Cl_2}$ of the benzhydrylium ions E^+ (eq 7) with calculated methyl anion affinities ΔG_{MA} (eq 9) of E^+ ($-RT \ln(10) LA_{CH_2Cl_2} = 0.652\Delta G_{MA} + 487$; $R^2 = 0.987$). Blue symbols: *p*-phenylamino- and *p*-phenoxy-substituted benzhydrylium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

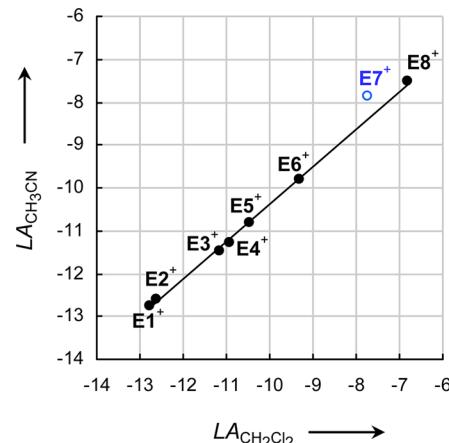


Figure 6. Plot of the LA_{CH_3CN} parameters for benzhydrylium ions in CH_3CN versus their $LA_{CH_2Cl_2}$ parameters in CH_2Cl_2 . The point for $E7^+$ (open blue circle) was not used for the correlation: $LA_{CH_3CN} = 0.878LA_{CH_2Cl_2} - 1.60$; $R^2 = 0.999$.

322 ions in the gas phase. This correlation implies that there is
323 generally no differential solvation of the benzhydrylium ions
324 $E(1-20)^+$; i.e., the solvation energies change linearly with the
325 thermodynamic stabilities of the carbocations, in line with
326 previous conclusions.⁴²⁻⁴⁵

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

332 As mentioned above (Figure 2), the equilibrium constants
333 for the reactions of $E7^+$ with pyridines and phosphines show an
334 unusual solvent dependence. The deviating behavior of $E7^+$ is
335 also evident in Figure 5: Although $E6^+$ and $E7^+$ have similar
336 methyl anion affinities ΔG_{MA} , the *p*-N(Me)(Ph)-substituted
337 benzhydrylium ion $E7^+$ has a considerably higher Lewis acidity
338 $LA_{CH_2Cl_2}$ than the *p*-NMe₂-substituted analogue $E6^+$. Similarly,
339 the other *p*-phenylamino- and *p*-phenoxy-substituted benzhy-
340 drylium ions (blue symbols in Figure 5) also have $LA_{CH_2Cl_2}$
341 values which are about one unit larger than those of
342 carbocations with comparable ΔG_{MA} having only *p*-alkylamino
343 or *p*-alkoxy substituents (compare $E9^+/E8^+$, $E11^+/E10^+$, $E16^+/$
344 $E15^+$, $E19^+/E18^+$).⁴⁶

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

The LB_{CH_3CN} parameters derived from the equilibrium
363 constants in CH_3CN (Table 3) also correlate linearly with
364 the corresponding $LB_{CH_2Cl_2}$ parameters in CH_2Cl_2 (Table 2). In
365 Figure 7, which spans almost 10 orders of magnitude in
366

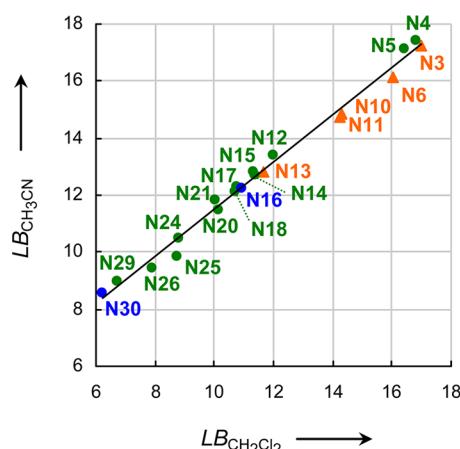


Figure 7. Plot of the LB_{CH_3CN} parameters for pyridines (green circles) and phosphines (orange triangles) in CH_3CN versus their $LB_{CH_2Cl_2}$ parameters in CH_2Cl_2 : $LB_{CH_3CN} = 0.828LB_{CH_2Cl_2} + 3.22$; $R^2 = 0.991$.

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

378 The slopes in Figures 6 and 7 are difficult to interpret, as the
379 effects of the solvent on the Lewis acids and Lewis bases cannot
380 be separated unambiguously. However, by setting $LA_{CH_3CN}(E1^+) =$
381 $LA_{CH_2Cl_2}(E1^+)$, the bulk of the solvent effects is shifted into the
382 LB_{CH_3CN} terms. The larger equilibrium constants observed in
383

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 $\text{LB}_{\text{CH}_3\text{CN}}$ Parameters Determined from Eq 7

N	Lewis base formula	$\text{LB}_{\text{CH}_3\text{CN}}$	electrophile		K^a / M^{-1}	correlation	
			E^+	abbreviation		$K_{\text{calc}}^b / M^{-1}$	K_{calc}/K
N48 (S)		10.27	$E8^+$	(mor) ₂ CH ⁺	-7.52	2.00×10^2 ^c	5.63×10^2 2.82
			$E9^+$	(dpa) ₂ CH ⁺	-6.63 ^d	2.80×10^4 ^c	4.37×10^3 0.16
			$E10^+$	(mfa) ₂ CH ⁺	-6.34 ^d	3.75×10^3 ^c	8.53×10^3 2.27
N49		12.92	$E5^+$	(pyr) ₂ CH ⁺	-10.83	1.3×10^2 ^e	1.23×10^2 0.95
			$E6^+$	(dma) ₂ CH ⁺	-9.82	1.2×10^3 ^e	1.26×10^3 1.05
N50		12.42	$E5^+$	(pyr) ₂ CH ⁺	-10.83	3.3×10^1 ^e	3.89×10^1 1.18
			$E6^+$	(dma) ₂ CH ⁺	-9.82	4.7×10^2 ^e	3.98×10^2 0.85
N51		4.34	$E13^+$	(fur) ₂ CH ⁺	-2.73 ^d	1.9×10^1 ^e	4.11×10^1 2.16
			$E14^+$	fur(anil)CH ⁺	^f	1.1×10^2 ^e	^f
			$E15^+$	(anil) ₂ CH ⁺	-1.60 ^d	1.2×10^3 ^e	5.55×10^2 0.46
N52		3.92 ^g (in CH_2Cl_2)	$E13^+$	(fur) ₂ CH ⁺	-1.29 ^g	3.08×10^2 ^{g,h}	5.15×10^2 1.67
			$E14^+$	fur(anil)CH ⁺	^f	1.40×10^3 ^{g,h}	^f
			$E15^+$	(anil) ₂ CH ⁺	0.00 ^g	1.16×10^4 ^{g,h}	6.94×10^3 0.60
N53		4.27 ^{g,j} (in CH_2Cl_2)	$E13^+$	(fur) ₂ CH ⁺	-1.29 ^g	9.46×10^2 ^{g,h}	ⁱ
			$E14^+$	fur(anil)CH ⁺	^f	7.71×10^3 ^{g,h}	^f
N54		(11) ^j	$E9^+$	(dpa) ₂ CH ⁺	-6.63 ^d	7.5×10^4 ^k	2.28×10^4 0.30
			$E10^+$	(mfa) ₂ CH ⁺	-6.34 ^d	5.9×10^3 ^k	4.43×10^4 7.52
			$E11^+$	(pfa) ₂ CH ⁺	-5.53 ^d	6.5×10^5 ^k	2.85×10^5 0.44
N55		(8) ^{h,j}	$E11^+$	(pfa) ₂ CH ⁺	-5.53 ^d	5.5×10^2 ^l	ⁱ

^aPhotometric determination from laser flash photolysis experiments in CH_3CN unless noted otherwise. ^bCalculated from eq 7. ^cFrom ref 40.

^dExtrapolated from $\text{LA}_{\text{CH}_2\text{Cl}_2}$ parameters using the correlation given in Figure 6. ^eFrom ref 49. ^fThe $\text{LA}_{\text{CH}_2\text{Cl}_2}$ 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 $K = K_{\text{calc}}$ because the $\text{LB}_{\text{CH}_3\text{CN}}$ parameter was calculated from only one equilibrium constant. ^j $\text{LB}_{\text{CH}_3\text{CN}}$ 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 $\text{LB}_{\text{CH}_3\text{CN}}$ 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 carbocations 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 $\text{LB}_{\text{CH}_3\text{CN}}$ 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 $\text{LA}_{\text{CH}_3\text{CN}}$ (Table 1) and $\text{LB}_{\text{CH}_3\text{CN}}$ (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

414 E(9-11)⁺ or $E11^+$, respectively, since benzhydrylium ions of 415 lower Lewis acidity do not show sufficient conversion (adduct 416 formation) whereas the more acidic $E13^+$ reacts almost 417 quantitatively. Since the *N*-phenylamino-substituted benzhy- 418 drylium ions $E9^+$ and $E11^+$ show untypical solvation effects, as 419 described above, the $\text{LB}_{\text{CH}_3\text{CN}}$ values determined in this way are 420 not very reliable. Because of the great importance of the Lewis 421 basicities of halide ions we sought further confirmation of the 422 data for Cl^- and Br^- listed in Table 4 by relating the Lewis 423 basicity of Br^- (N55) to the strengths of neutral Lewis bases. 424

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



427 A major problem of these investigations was the identi- 428 fication of systems which do not show side reactions while 429 having suitable equilibrium constants (see section S5 of the 430 Supporting Information for details). We were able to determine 431 the equilibrium constants K for the reaction of E17-Br with 432 pyrimidine (N30) at different temperatures from -20 °C to 433 +20 °C, from which we obtained the thermodynamic param- 434 eters $\Delta H^\theta = -62.7 \text{ kJ mol}^{-1}$ and $\Delta S^\theta = -210.2 \text{ J mol}^{-1} \text{ K}^{-1}$ 435 (see section S5 of the Supporting Information). The large nega- 436 tive reaction entropy is explained by the increased solvation 437 of the generated ions, which requires strong organization of 438 the solvent. The equilibrium constant $K = 1.6$ shows that the 439 bromide ion (N55) is slightly less Lewis basic than pyrimidine 440 (N30, $\text{LB}_{\text{CH}_3\text{CN}} = 8.59$) in acetonitrile at 20 °C. Further ¹H 441 NMR (CD_3CN) measurements for the reactions of E17-Br 442 with the pyridines N26 and N29 at 20 °C (Table 5) confirm 443

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^d	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 $\Delta H^\circ = -62.7 \text{ kJ mol}^{-1}$ and $\Delta S^\circ = -210.2 \text{ J mol}^{-1} \text{ K}^{-1}$ (see section S5 of the Supporting Information).

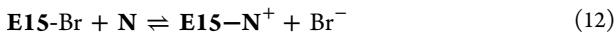
444 the value of $\text{LB}_{\text{CH}_3\text{CN}} \approx 8$ for Br^- (N55) derived from the laser
445 flash photolysis experiment (Table 4).

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 ($10 \mu\text{L}$ 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° , 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° 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° (eq 12) can be expressed by eq 12c.



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

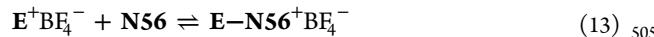
482 As $\Delta H^\circ(\text{eq } 12a)$ is a constant term for all calorimetrically
483 investigated reactions of Table 6, one obtains a linear correla-
484 tion between the enthalpies ΔH° for the reactions of E15-Br

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

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

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

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



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

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

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

541 When $\text{LB}_{\text{CH}_3\text{CN}}$ is expressed in units of kJ mol^{-1} (by
542 multiplication with $-RT \ln(10)$), the slope of the correlation in
543 Figure 8 is 0.83; i.e., the substituent effect on reaction enthalpy
544 ΔH° is attenuated by a compensating entropy effect. More
545 specifically: As the enthalpy term ΔH° becomes more negative,
546

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

Lewis base			$\Delta H^{\theta c} /$	
N	formula	$LB_{CH_2Cl_2}^a$	$LB_{CH_3CN}^b$	kJ mol ⁻¹
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)

Lewis base			$\Delta H^{\theta c} /$	
N	formula	$LB_{CH_2Cl_2}^a$	$LB_{CH_3CN}^b$	kJ mol ⁻¹
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) ^c	−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.

546 17% of the decrease of ΔH^0 is compensated by an increase of
 547 the $-T\Delta S^0$ term, so that only 83% of the change in ΔH^0 is
 548 reflected by changes of ΔG^0 . This means that the formation of
 549 Lewis adducts from stronger Lewis bases (more negative ΔH^0)
 550 is associated with a more negative value of ΔS^0 , i.e., a larger
 551 increase of ordering during the reaction. This implies a weaker
 552 solvation of the stronger Lewis bases and/or that stronger
 553 Lewis bases form Lewis adducts which have higher need for
 554 solvation. Overall, we thus observe a linear correlation between
 555 enthalpy and entropy effects (compensation effect⁵⁵) for the
 556 combinations of Lewis acids and Lewis bases.

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

565 The interpretation of the slopes of these correlations is
 566 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 $\text{LA}_{\text{CH}_2\text{Cl}_2}$ (eq 14) and ΔG_{MA} (eq 15) with pK_R^+ ; see Figure S1.4 in section S1 of the Supporting Information.

$$pK_{R^+} = -1.15 LA_{\text{CH}_2\text{Cl}_2} - 5.28; \quad R^2 = 0.998 \quad (14)$$

$$pK_{R^+} = 0.112\Delta G_{MA} + 79.0; \quad R^2 = 0.968 \quad (15)_{577}$$

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

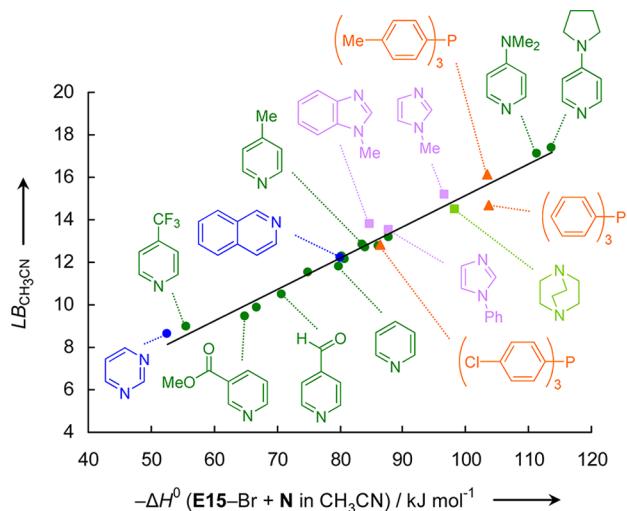


Figure 8. Plot of LB_{CH_3CN} parameters of Lewis bases N versus the enthalpies ΔH^0 for their reactions with E15-Br in CH_3CN at $20\text{ }^\circ\text{C}$ ($LB_{CH_3CN} = -0.148\Delta H^0 + 0.317$; $R^2 = 0.970$).

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 $20\text{ }^\circ\text{C}$

Lewis acid		
E $^+$	abbreviation	$\Delta H^{0a}/kJ mol^{-1}$
E1 $^+$	(lil) $_2$ CH $^+$	-73.2 (± 0.6)
E2 $^+$	(jul) $_2$ CH $^+$	-73.3 (± 0.3)
E3 $^+$	(ind) $_2$ CH $^+$	-77.1 (± 0.3)
E4 $^+$	(thq) $_2$ CH $^+$	-81.4 (± 0.5)
E5 $^+$	(pyr) $_2$ CH $^+$	-81.4 (± 0.5)
E6 $^+$	(dma) $_2$ CH $^+$	-89.9 (± 0.3)
E8 $^+$	(mor) $_2$ CH $^+$	-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.

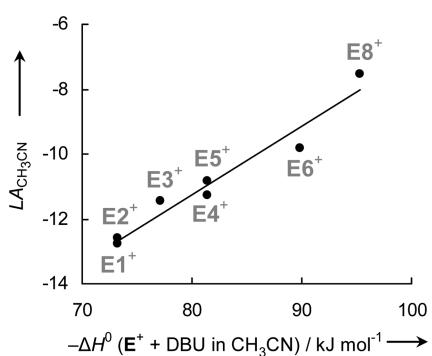


Figure 9. Plot of the LA_{CH_3CN} parameters of the benzhydrylium ions E(1–8) $^+$ versus the enthalpies ΔH^0 for the reactions of E(1–8) $^+$ BF 4^- with 1,8-diazabicycloundec-7-ene (DBU, N56) in CH_3CN at $20\text{ }^\circ\text{C}$ ($LA_{CH_3CN} = -0.211\Delta H^0 - 28.1$; $R^2 = 0.951$).

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

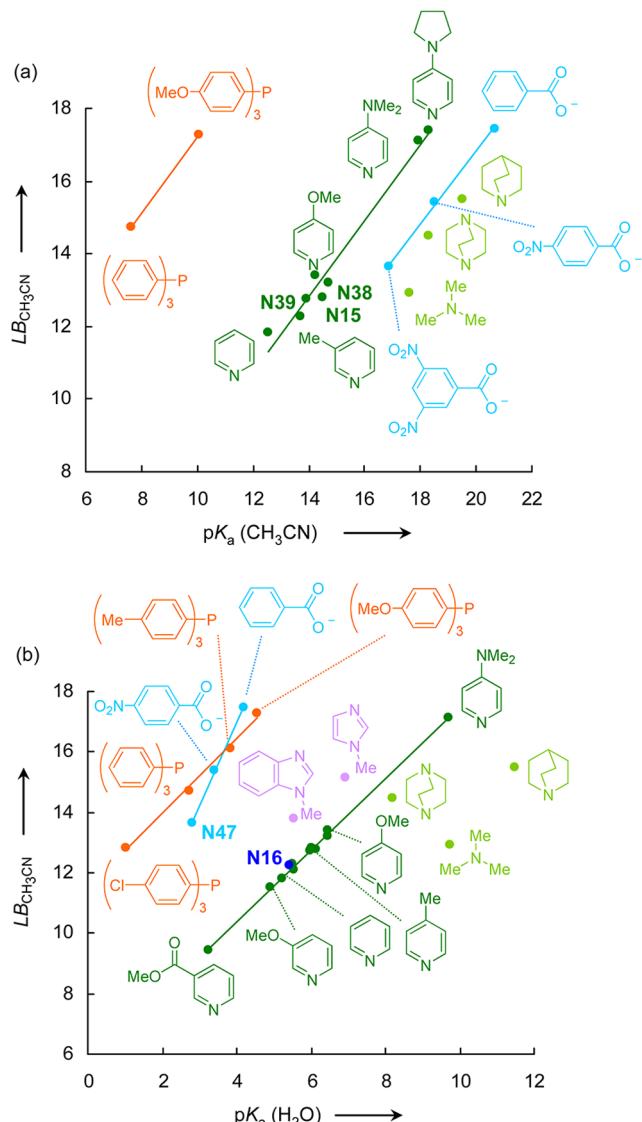


Figure 10. Plot of Lewis basicities LB_{CH_3CN} in CH_3CN (a) and H_2O (b) versus pK_a values of the Lewis bases in CH_3CN (a) and H_2O (b). The pK_a values were taken from refs 7 and 59.

One factor which accounts for the occurrence of separate correlation lines in Figure 10a is the difference in bond dissociation energies.^{56,57} Since the average N–H vs N–C bond energies differ by $\sim 86\text{ kJ mol}^{-1}$ while the P–H and P–C bond energies differ by only $\sim 58\text{ kJ mol}^{-1}$,⁵⁸ one can already explain why phosphines are stronger bases toward Ar₂CH $^+$ than amines of comparable pK_a (the difference of 28 kJ mol^{-1} corresponds to ca. 5 units of LB_{CH_3CN} in Figure 10a). Similarly, the O–H and O–C bond energies differ by $\sim 104\text{ kJ mol}^{-1}$,⁵⁸ which is an even larger difference than that between N–H vs N–C bonds. However, bond energies vary widely depending on the exact structure of the compound,^{56,57} and this may contribute to the large gap (several units of LB_{CH_3CN}) between the correlation lines for pyridines and tertiary amines.

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

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 = Br, Cl, OAc, OBz, 3,5-
617 dinitrobenzoyl, *p*-nitrobenzoyl, OCO_2Me , etc.) in hydroxylc
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 conductometry
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 $\text{E}20^+$ 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 $\text{E}16^+$ and $\text{E}19^+$ 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 recombi-
648 nation 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 $\text{E}18\text{-Cl}$ in aqueous acetonitrile (Figure 13a). The
655 reaction of $\text{E}18^+$ 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 $\text{E}18\text{-Cl} \rightleftharpoons \text{E}18^+ + \text{Cl}^-$ and for all substrates yielding
662 less stabilized carbocations. 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 $\text{E}1\text{-OAc}$ 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

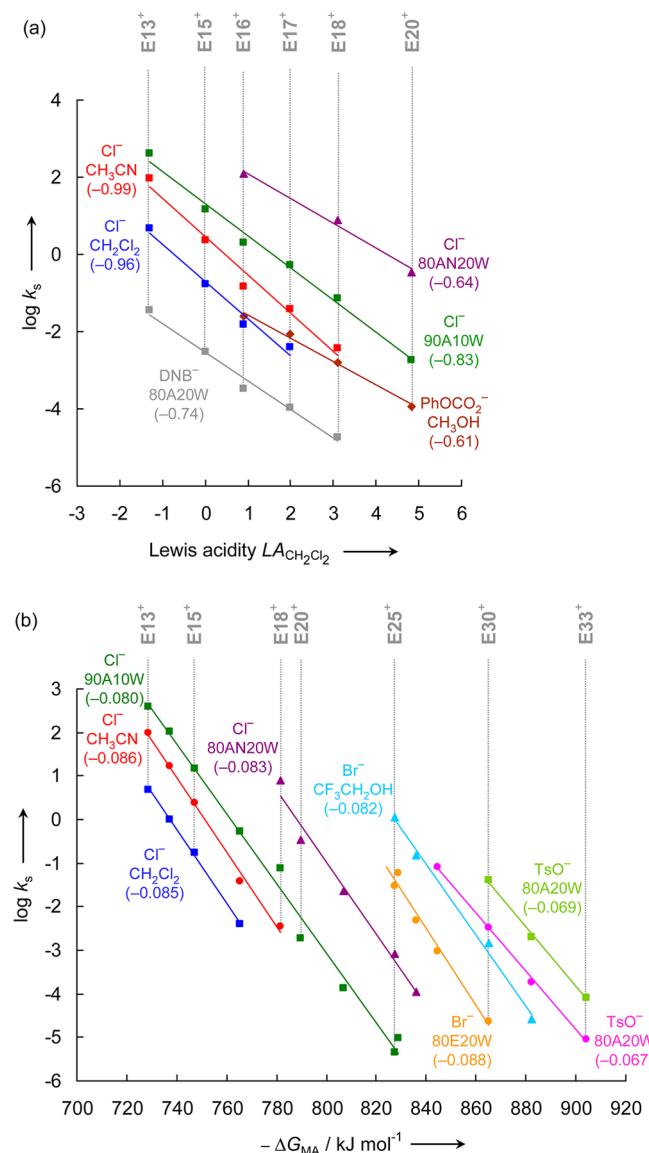


Figure 11. Correlation of $\log k_s$ for solvolysis reactions (25°C) of E(13–33)-X^{23,60} versus the Lewis acidities $\text{LA}_{\text{CH}_2\text{Cl}_2}$ (a) and calculated methyl anion affinities ΔG_{MA} (b) of the benzhydrylium ions E^+ . The slopes of the correlation lines are given in parentheses; data for $\text{E}16^+$ and $\text{E}19^+$ 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.

$\text{E}1\text{-OAc} \rightleftharpoons \text{E}1^+ + \text{AcO}^-$, i.e., there is a significant intrinsic barrier, and the solvolysis rates are not predominantly controlled by the relative free energies of the ionization step ($\text{LA}_{\text{CH}_2\text{Cl}_2}$ of E^+ , Figure 12).

Solvolytic experiments thus provide information about the thermodynamic stabilities of carbocations if the recombination reaction of the carbocation with the leaving group occurs without barrier. In our previous work, we have measured diffusion-controlled or almost diffusion-controlled ($>10^8 \text{ M}^{-1} \text{ s}^{-1}$) rate constants for many combination reactions of E(13–33)⁺ with Cl^- and Br^- in solvolytic media.⁶⁴ In these cases, the Lewis acidities of E^+ can thus be derived indirectly from their solvolysis rate constants k_s . On the other hand, the smaller slopes for X = OTs in Figure 11b might indicate that there is a barrier for the combinations of E^+ with the very weak nucleophile TsO^- so

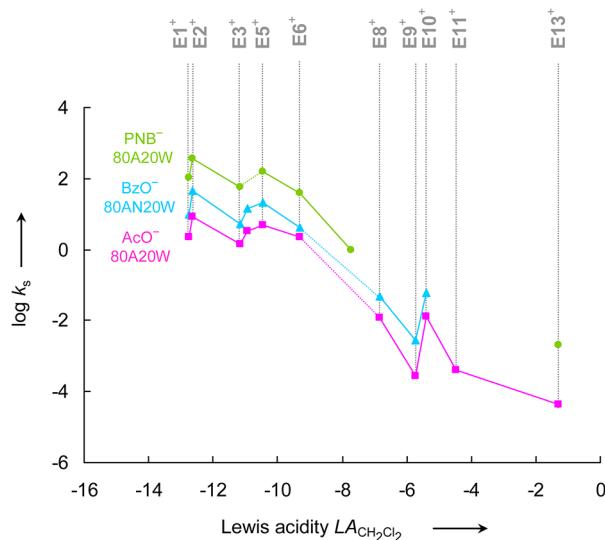


Figure 12. Plot of $\log k_s$ for solvolysis reactions (25°C) of $E(1-13)^+$ ²³ versus the Lewis acidities $LA_{CH_2Cl_2}$ of the benzhydrylium ions E^+ . Abbreviations: PNB^- = *p*-nitrobenzoate; mixtures of solvents are given as (v/v), A = acetone, AN = acetonitrile, W = water.

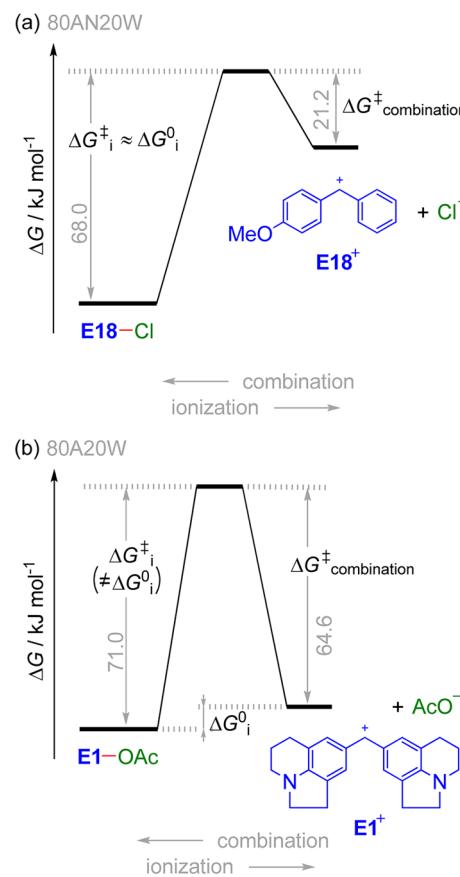


Figure 13. Free energy diagrams for the ionization steps in the solvolyses of $E18-\text{Cl}$ in 80% aqueous acetonitrile (80AN20W)⁶⁶ (a) and $E1-\text{OAc}$ in 80% aqueous acetone (80A20W)⁶⁷ (b). The subsequent reaction of E^+ with the solvent has been omitted for clarity (this reaction is much faster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

that the carbocation character is not fully developed in the transition states of the tosylate solvolyses.⁶⁸

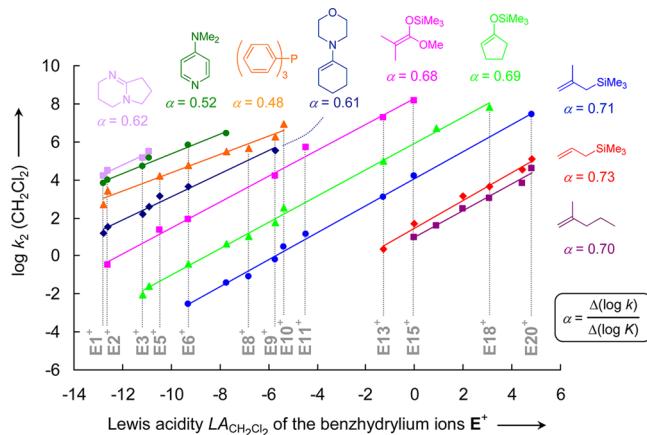


Figure 14. Correlation of $\log k_2$ for the reactions of E^+ with different nucleophiles^{20,22,28,29,31} in CH_2Cl_2 versus the Lewis acidities $LA_{CH_2Cl_2}$ of E^+ (this work).

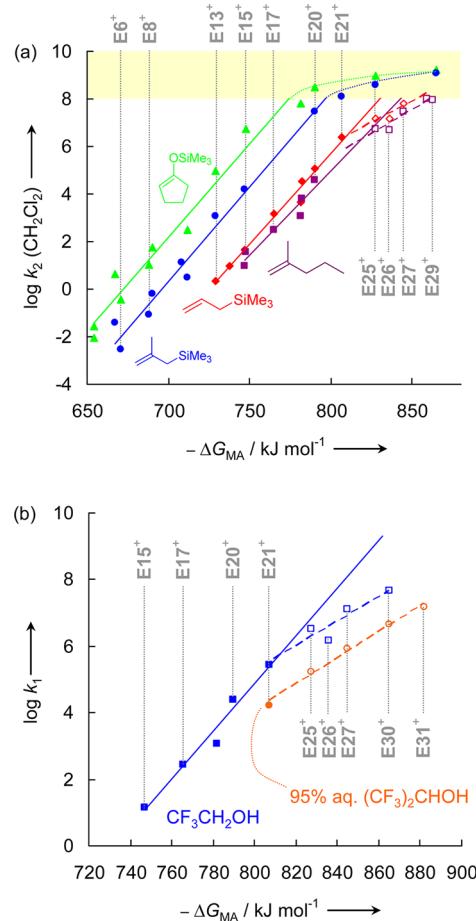


Figure 15. Plots of $\log k_2$ for the reactions of $E(3-30)^+$ with different nucleophiles^{20,22} in CH_2Cl_2 (a) and $\log k_1$ for the reactions of $E(15-31)^+$ with trifluoroethanol^{33,72} and with 95% aqueous hexafluoroisopropanol (*w/w*)⁷⁴ (b) versus the calculated methyl anion affinities ΔG_{MA} (eq 9) of E^+ . Data for the acceptor-substituted benzhydrylium ions $E(25-29)^+$ (empty symbols) and second-order rate constants $>10^8 \text{ M}^{-1} \text{ s}^{-1}$ (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 nucleophiles⁶⁹

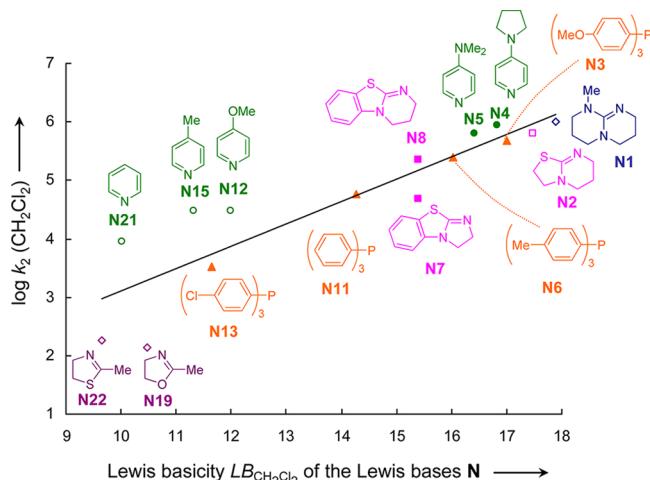


Figure 16. Plot of $\log k_2$ for the reactions of E^+ with different nucleophiles N in CH_3CN ^{28–30} versus the Lewis basicities $LB_{\text{CH}_3\text{CN}}$ of N (this work). Empty symbols: $\log k_2$ calculated from eq 17 and the reactivity parameters published in refs 29–32. The line shows the correlation for all data points ($\log k_2 = 0.38LB_{\text{CH}_2\text{Cl}_2} - 0.74$; $R^2 = 0.814$).

in CH_2Cl_2 ^{20,22,28,29,31} correlate linearly with the Lewis acidities $LA_{\text{CH}_2\text{Cl}_2}$ of E^+ from this work.

The linearity of these correlations over a wide range—from slow reactions with late transition states at the lower end of the correlation lines to very fast, almost diffusion-controlled reactions with early transition states at the top—again show that the Leffler–Hammond $\alpha = \Delta(\log k)/\Delta(\log K)$ cannot be a measure for the position of the transition state.^{25,69,70} According to Marcus theory (eq 16),^{3,24,25,70,71} rate-equilibrium relationships, i.e., $\log k$ vs $\log K$ correlations ($\triangle \Delta G^\ddagger$ vs ΔG^0 correlations) can only be linear if (a) the intrinsic barrier ΔG_0^\ddagger is very high compared with the reaction free enthalpy $\Delta_r G^0$ or if (b) the intrinsic barriers ΔG_0^\ddagger change proportionally with $\Delta_r G^0$. Our previous conclusion⁴³ that in the reactions of $E(1–20)^+$ with π -nucleophiles the intrinsic barriers

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

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

As $LA_{\text{CH}_2\text{Cl}_2}$ parameters for the highly reactive benzhydrylium ions $E(21–33)^+$ are not available, we also plotted $\log k_2$ versus the calculated methyl anion affinities ΔG_{MA} (eq 9) of E^+ . While the donor-substituted benzhydrylium ions $E(1–21)^+$ show good linear correlations (Figure 15), a linear extrapolation of this correlation overestimates the rate constants for the acceptor-substituted benzhydrylium ions $E(26–29)^+$ considerably (Figure 15), although several of these rate constants are still below the limit of $10^8 \text{ M}^{-1} \text{ s}^{-1}$ where the rate-limiting effect of diffusion begins to play a role (yellow-shaded area in Figure 15).²² Moreover, the same behavior is found for the first-order decay reactions with solvents such as trifluoroethanol (Figure 15b),^{33,72} acetone,^{33,73} or hexafluoroisopropanol–water mixtures,⁷⁴ in which diffusion does not have any limiting effect at all.

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

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

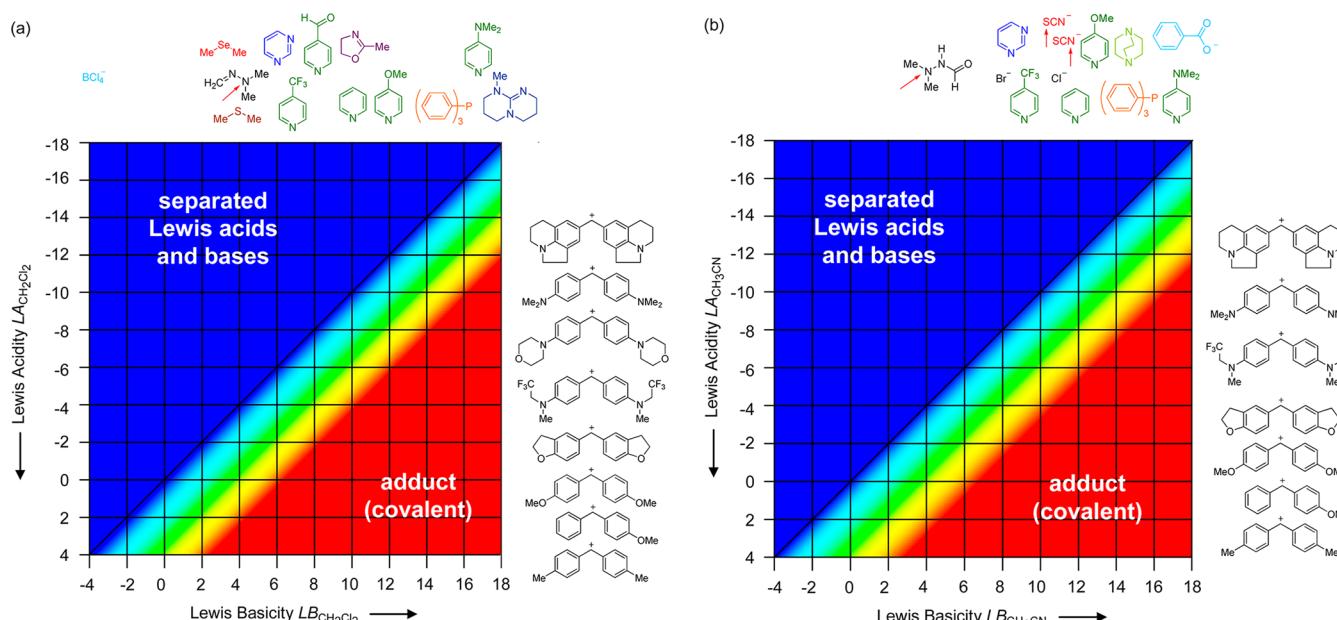


Figure 17. Semiquantitative schemes to estimate equilibria for reactions of Lewis acids (vertical axis) and Lewis bases (horizontal axis) in CH_2Cl_2 (a) and CH_3CN ⁷⁸ (b) at 20 °C. Combinations located in the red area of the figures form Lewis adducts, while combinations located in the blue area do 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.

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

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 $\log K(20^\circ\text{C}) = LA + LB$ (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
 800 considered benzhydrylium ions, i.e., Lewis acids with similar
 801 structures.

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

In contrast, the electrophilic reactivities of all donor-
 822 substituted benzhydrylium ions $E(1–20)^+$ correlate excellently
 823 with the corresponding Lewis acidities, while now the highly
 824 acidic, nonstabilized or destabilized benzhydrylium ions
 825 $E(21–33)^+$ deviate from the linear correlation between rate
 826 and equilibrium constants. These findings explain our previous
 827 observation that only for the narrow group of alkoxy- and alkyl-
 828 substituted benzhydrylium ions $E(13–20)^+$ electrophilicities
 829 (i.e., relative rates of reactions with nucleophiles) are the
 830 inverse of electrofugalities (i.e., relative rates of formation in
 831 S_N1 reactions).²³

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

■ ASSOCIATED CONTENT

■ Supporting Information

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

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Notes

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- 998 (46) Analogous solvent effects were previously noted in our kinetic 1000 studies of the reactions of benzhydrylium ions with nucleophiles: By 1001 treating the electrophilicity parameters E as solvent-independent 1002 parameters in our correlations, we shifted all solvent effects into the 1003 solvent-dependent nucleophile-specific parameters N and s_N .^{20–22}
- 1004 Though this method worked well for the majority of benzhydrylium 1005 ions, phenylamino- and phenoxy-substituted benzhydrylium ions, 1006 particularly $E7^+$ and $E9^+$, always react faster in acetonitrile than 1007 calculated on the basis of their reactivities toward π -nucleophiles in 1008 CH_2Cl_2 .⁴⁷ This behavior can now be explained by a less efficient 1009 ground-state solvation of the N-phenylamino-substituted benzhydry- 1010 lium ions compared to benzhydrylium ions without additional phenyl 1011 groups.
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