

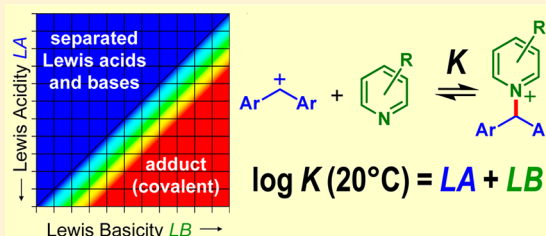
Scales of Lewis Basicities toward C-Centered Lewis Acids (Carbocations)

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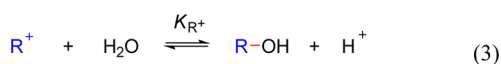
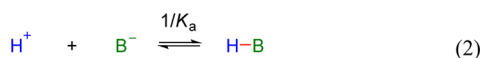
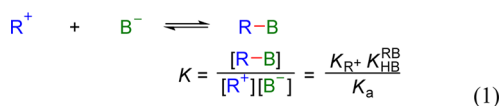
Supporting Information

ABSTRACT: Equilibria for the reactions of benzhydryl cations (Ar_2CH^+) with phosphines, *tert*-amines, pyridines, and related Lewis bases were determined photometrically in CH_2Cl_2 and CH_3CN solution at 20 °C. The measured equilibrium constants can be expressed by the sum of two parameters, defined as the Lewis Acidity (LA) of the benzhydrylium ions and the Lewis basicity (LB) of the phosphines, pyridines, etc. Least-squares minimization of $\log K = \text{LA} + \text{LB}$ with the definition $\text{LA} = 0$ for $(4\text{-MeOC}_6\text{H}_4)_2\text{CH}^+$ gave a Lewis acidity scale for 18 benzhydrylium ions covering 18 orders of magnitude in CH_2Cl_2 as well as Lewis basicities (with respect to C-centered Lewis acids) for 56 bases. The Lewis acidities correlated linearly with the quantum chemically calculated (B3LYP/6-311++G(3df,2pd)//B3LYP/6-31G(d,p) level) methyl anion affinities of the corresponding benzhydrylium ions, which can be used as reference compounds for characterizing a wide variety of Lewis bases. The equilibrium measurements were complemented by isothermal titration calorimetry studies. Rates of $\text{S}_{\text{N}}1$ solvolyses of benzhydryl chlorides, bromides, and tosylates derived from $\text{E}(13\text{--}33)^+$, i.e., from highly reactive carbocations, 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.



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 $\text{p}K_{\text{a}}$ values, play a central role, because $\text{p}K_{\text{a}}$ 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 $\text{p}K_{\text{a}}$ ($-\log K_{\text{a}}$) 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 $\text{p}K_{\text{a}}$.



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

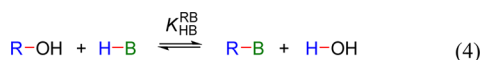
rates of the reactions of a series of B^- with a certain reference electrophile) with the corresponding equilibrium constants and to use the terms hydrogen basicity, carbon basicity, and sulfur basicity for comparing the relative affinities of various bases toward the proton, carbon-centered Lewis acids (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 $1/K_{\text{a}}$ which describes the affinity of B^- toward the proton (eq 2)^{11,12} and Deno's $\text{p}K_{\text{R}^+}$ 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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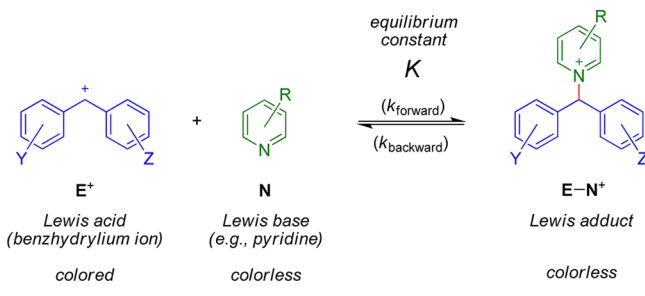


Combination of eqs 2–4 gives access to absolute values of Lewis acid/Lewis base association constants (eq 1).^{12,16,17}

Kessler and Feigel demonstrated for few systems that equilibrium constants for combinations of carbocations with anions B[−] correlate with the pK_R⁺ values of the carbocations and the pK_a values of the conjugate acids HB.¹⁸ Takeuchi and Kitagawa reported analogous relationships for combinations of carbocations with carbanions.¹⁹

However, the calculation of Lewis acid/Lewis base association constants *K* from eq 1 has not frequently been used in practice, probably because of the lack of a sufficient number of suitable pK_R⁺ values and the difficulties to properly handle the influence of solvents on these equilibrium constants. We now report on an alternative, easily applicable method for determining Lewis basicities toward C-centered electrophiles which uses benzhydrylium ions as reference Lewis acids (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



previously used for the construction of comprehensive nucleophilicity^{20–22} and nucleofugality²³ scales where benzhydrylium ions Ar₂CH⁺ (E⁺) were employed as reference electrophiles and reference electrofuges, respectively. As the Lewis acidities of Ar₂CH⁺ (E⁺) can widely be varied by modifying the substituents at the arene rings, strong Lewis bases can be characterized by measuring their coordination equilibria with weakly Lewis-acidic (donor-substituted) benzhydrylium ions, while weak Lewis bases can be characterized by measuring their coordination equilibria with less stabilized more Lewis-acidic benzhydrylium ions. In order to keep the steric demand of the electrophilic reaction center constant, only *m*- and *p*-substituted benzhydrylium ions have been employed for these equilibrium measurements, as for the previous kinetic investigations (Table 1).^{20–23}

By using the method of overlapping correlation lines, we will derive a Lewis acidity scale for benzhydrylium ions in CH₂Cl₂ solution, which can be used for the characterization of a large variety of Lewis bases by photometric measurements of equilibrium constants. We will then show that the Lewis acidities thus obtained correlate well with quantum chemically calculated methyl anion affinities in the gas phase. Since the term “carbon basicity”, as defined by Parker and Hine,^{9,15} is often misunderstood as “reactivities of carbon bases”, we will avoid this term and instead refer to “Lewis basicity with respect to certain Lewis acids”.

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

Table 1. Reference Lewis Acids E(1–33)⁺ and Their Lewis Acidities LA_{CH₂Cl₂} and LA_{CH₃CN}, Calculated Methyl Anion Affinities Δ*G*_{MA}, and p*K*_R⁺ Values

no. ^a	Y		Z	abbreviation	LA ^b		Δ <i>G</i> _{MA} ^c / kJ mol ^{−1}	p <i>K</i> _R ⁺ ^d
	CH ₂ Cl ₂				CH ₃ CN			
E1 ⁺				(lil) ₂ CH ⁺	−12.76	−12.76	−639.8	^e
E2 ⁺				(jul) ₂ CH ⁺	−12.62	−12.61	−642.2	^e
E3 ⁺				(ind) ₂ CH ⁺	−11.16	−11.46	−654.5	^e
E4 ⁺				(thq) ₂ CH ⁺	−10.92	−11.27	−654.0	^e
E5 ⁺	Y = Z = 4-(<i>N</i> -pyrrolidino)			(pyr) ₂ CH ⁺	−10.46	−10.83	−658.3	^e
E6 ⁺	Y = Z = 4-N(Me) ₂			(dma) ₂ CH ⁺	−9.30	−9.82	−670.7	5.61 ^f
E7 ⁺	Y = Z = 4-N(Me)(Ph)			(mpa) ₂ CH ⁺	−7.72	−7.87	−667.1	^e
E8 ⁺	Y = Z = 4-(<i>N</i> -morpholino)			(mor) ₂ CH ⁺	−6.82	−7.52	−688.2	^e
E9 ⁺	Y = Z = 4-N(Ph) ₂			(dpa) ₂ CH ⁺	−5.72	^g	−689.9	^e
E10 ⁺	Y = Z = 4-N(Me)(CH ₂ CF ₃)			(mfa) ₂ CH ⁺	−5.39	^g	−711.9	^e
E11 ⁺	Y = Z = 4-N(Ph)(CH ₂ CF ₃)			(pfa) ₂ CH ⁺	−4.47	^g	−708.5	^e
E13 ⁺				(fur) ₂ CH ⁺	−1.29	^g	−728.8	^e
E14 ⁺				fur(ani)CH ⁺	^g	^g	−737.4	^e
E15 ⁺	4-MeO	4-MeO		(ani) ₂ CH ⁺	0.00	^g	−747.2	−5.65
E16 ⁺	4-MeO	4-PhO		ani(pop)CH ⁺	0.90	^g	−747.6	^e
E17 ⁺	4-MeO	4-Me		ani(tol)CH ⁺	2.00	^g	−765.3	−7.82
E18 ⁺	4-MeO	H		ani(Ph)CH ⁺	3.10	^g	−781.7	−8.77
E19 ⁺	4-PhO	H		pop(Ph)CH ⁺	4.42	^g	−782.5	−10.89
E20 ⁺	4-Me	4-Me		(tol) ₂ CH ⁺	4.82	^g	−789.8	−10.51
E21 ⁺	4-Me	H		tol(Ph)CH ⁺	^g	^g	−807.0	−11.76
E22 ⁺	4-F	4-F		(pfp) ₂ CH ⁺	^g	^g	−834.3	−13.03 ^h
E23 ⁺	4-F	H		pfp(Ph)CH ⁺	^g	^g	−828.9	−12.95
E24 ⁺	3-F, 4-Me	3-F, 4-Me		–	^g	^g	−823.9	^e
E25 ⁺	H	H		Ph ₂ CH ⁺	^g	^g	−827.6	−13.26
E26 ⁺	4-Cl	4-Cl		(pcp) ₂ CH ⁺	^g	^g	−836.1	−13.96 ^f
E27 ⁺	3-F	H		mfp(Ph)CH ⁺	^g	^g	−844.7	^e
E28 ⁺	4-(CF ₃)	H		tfm(Ph)CH ⁺	^g	^g	−859.5	^e
E29 ⁺	3,5-F ₂	H		dfp(Ph)CH ⁺	^g	^g	−863.0	^e
E30 ⁺	3-F	3-F		(mfp) ₂ CH ⁺	^g	^g	−865.0	^e
E31 ⁺	3,5-F ₂	3-F		dfp(mfp)CH ⁺	^g	^g	−882.2	^e
E32 ⁺	4-(CF ₃)	4-(CF ₃)		(tfm) ₂ CH ⁺	^g	^g	−891.8	^e
E33 ⁺	3,5-F ₂	3,5-F ₂		(dfp) ₂ CH ⁺	^g	^g	−904.1	^e

^aWe use the same numbering as in ref 22 and omit the ferrocenyl(phenyl)methyl ion (E12⁺). ^bLewis acidities LA_{CH₂Cl₂} and LA_{CH₃CN} 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 CH₂Cl₂ 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 $20^\circ C$ and Comparison with Equilibrium Constants K_{calc} (M^{-1}) Calculated from Eq 7



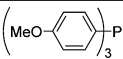
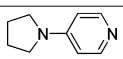
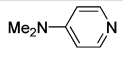
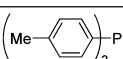
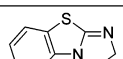
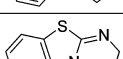
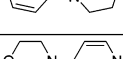
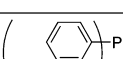
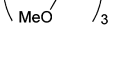
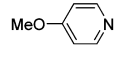
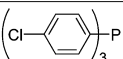
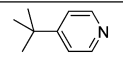
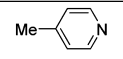
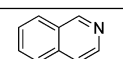
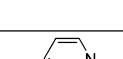
N	Lewis base		electrophile		experiment		correlation	
	formula	$LB_{CH_2Cl_2}$	E^+	abbreviation	$LA_{CH_2Cl_2}$	K^a / M^{-1}	K_{calc}^b / M^{-1}	K_{calc}/K
N1		17.90	$E1^+$	(lil) ₂ CH ⁺	-12.76	1.73×10^5 ^c	1.40×10^5	0.81
			$E2^+$	(jul) ₂ CH ⁺	-12.62	1.54×10^5 ^c	1.90×10^5	1.23
N2		17.47	$E1^+$	(lil) ₂ CH ⁺	-12.76	6.27×10^4 ^d	5.16×10^4	0.82
			$E2^+$	(jul) ₂ CH ⁺	-12.62	6.16×10^4 ^d	7.01×10^4	1.14
			$E3^+$	(ind) ₂ CH ⁺	-11.16	1.90×10^6 ^d	2.03×10^6	1.07
N3		17.00	$E1^+$	(lil) ₂ CH ⁺	-12.76	1.79×10^4 ^e	1.74×10^4	0.97
			$E2^+$	(jul) ₂ CH ⁺	-12.62	3.38×10^4 ^e	2.37×10^4	0.70
			$E3^+$	(ind) ₂ CH ⁺	-11.16	5.45×10^5 ^e	6.85×10^5	1.26
			$E4^+$	(thq) ₂ CH ⁺	-10.92	1.03×10^6 ^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	5.70×10^3 ^f	4.57×10^3	0.80
			$E2^+$	(jul) ₂ CH ⁺	-12.62	5.85×10^3 ^f	6.20×10^3	1.06
			$E3^+$	(ind) ₂ CH ⁺	-11.16	1.71×10^5 ^f	1.79×10^5	1.05
			$E4^+$	(thq) ₂ CH ⁺	-10.92	2.81×10^5 ^f	3.15×10^5	1.12
N6		16.02	$E1^+$	(lil) ₂ CH ⁺	-12.76	1.38×10^3 ^e	1.82×10^3	1.32
			$E2^+$	(jul) ₂ CH ⁺	-12.62	2.41×10^3 ^e	2.47×10^3	1.02
			$E4^+$	(thq) ₂ CH ⁺	-10.92	1.69×10^5 ^e	1.25×10^5	0.74
N7		15.40	$E3^+$	(ind) ₂ CH ⁺	-11.16	2.00×10^4 ^d	1.71×10^4	0.85
			$E4^+$	(thq) ₂ CH ⁺	-10.92	2.56×10^4 ^d	3.00×10^4	1.17
N8		15.39	$E3^+$	(ind) ₂ CH ⁺	-11.16	2.02×10^4 ^d	1.69×10^4	0.84
			$E4^+$	(thq) ₂ CH ⁺	-10.92	2.75×10^4 ^d	2.96×10^4	1.08
			$E5^+$	(pyr) ₂ CH ⁺	-10.46	7.73×10^4 ^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	1.91×10^1 ^e	3.27×10^1	1.71
			$E2^+$	(jul) ₂ CH ⁺	-12.62	5.57×10^1 ^e	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	2.27×10^3 ^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	1.26×10^5 ^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	8.52×10^3 ^e	8.65×10^3	1.02
			$E9^+$	(dpa) ₂ CH ⁺	-5.72	7.58×10^5 ^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	5.07×10^5 ^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

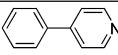





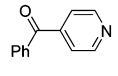












N	Lewis base		electrophile			experiment		correlation	
	formula	$LB_{CH_2Cl_2}$	E^+	abbreviation	$LA_{CH_2Cl_2}$	K^a / M^{-1}	K_{calc}^b / M^{-1}	K_{calc}/K	
N18		10.71	$E6^+$	(dma) ₂ CH ⁺	-9.30	2.29×10^1	2.55×10^1	1.11	
			$E7^+$	(mpa) ₂ CH ⁺	-7.72	9.77×10^2	9.87×10^2	1.01	
			$E8^+$	(mor) ₂ CH ⁺	-6.82	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

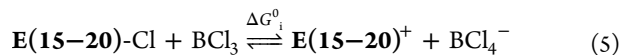
N	Lewis base		electrophile			experiment	correlation	
	formula	$LB_{CH_2Cl_2}$	E^+	abbreviation	$LA_{CH_2Cl_2}$	K^a / M^{-1}	K_{calc}^b / M^{-1}	K_{calc}/K
N37	BCl_4^-	-4.04	$E15^+$	(ani) ₂ CH ⁺	0.00	$5.82 \times 10^{-5}^h$	9.06×10^{-5}	1.56
			$E16^+$	ani(pop)CH ⁺	0.90	$1.12 \times 10^{-3}^h$	7.19×10^{-4}	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 $E(15-20)\text{-Cl} + BCl_3 \rightleftharpoons E(15-20)^+ + BCl_4^-$.³⁴ These values were combined with ΔG_i^0 ($-70^\circ C$) and ΔS_i^0 for the ionization of $E20\text{-Cl}$ (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 $E20\text{-Cl} + BCl_3 \rightleftharpoons E20^+ + BCl_4^-$: $\Delta H_i^0 = -32.6 \text{ kJ mol}^{-1}$ (ref 34) and ΔG_i^0 ($-70^\circ C$) = -7.0 kJ mol^{-1} (ref 35) (and thus $\Delta S_i^0 = -126 \text{ J K}^{-1} \text{ mol}^{-1}$).

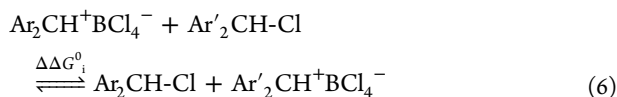
less accurate due to the occurrence of slow subsequent reactions, or which were determined indirectly from the ratio of rate constants $k_{forward}/k_{backward}$ (Scheme 1), are not included in Table 2.

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 $20^\circ C$ 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 ($20^\circ C$) 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 $-70^\circ C$.³⁴



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

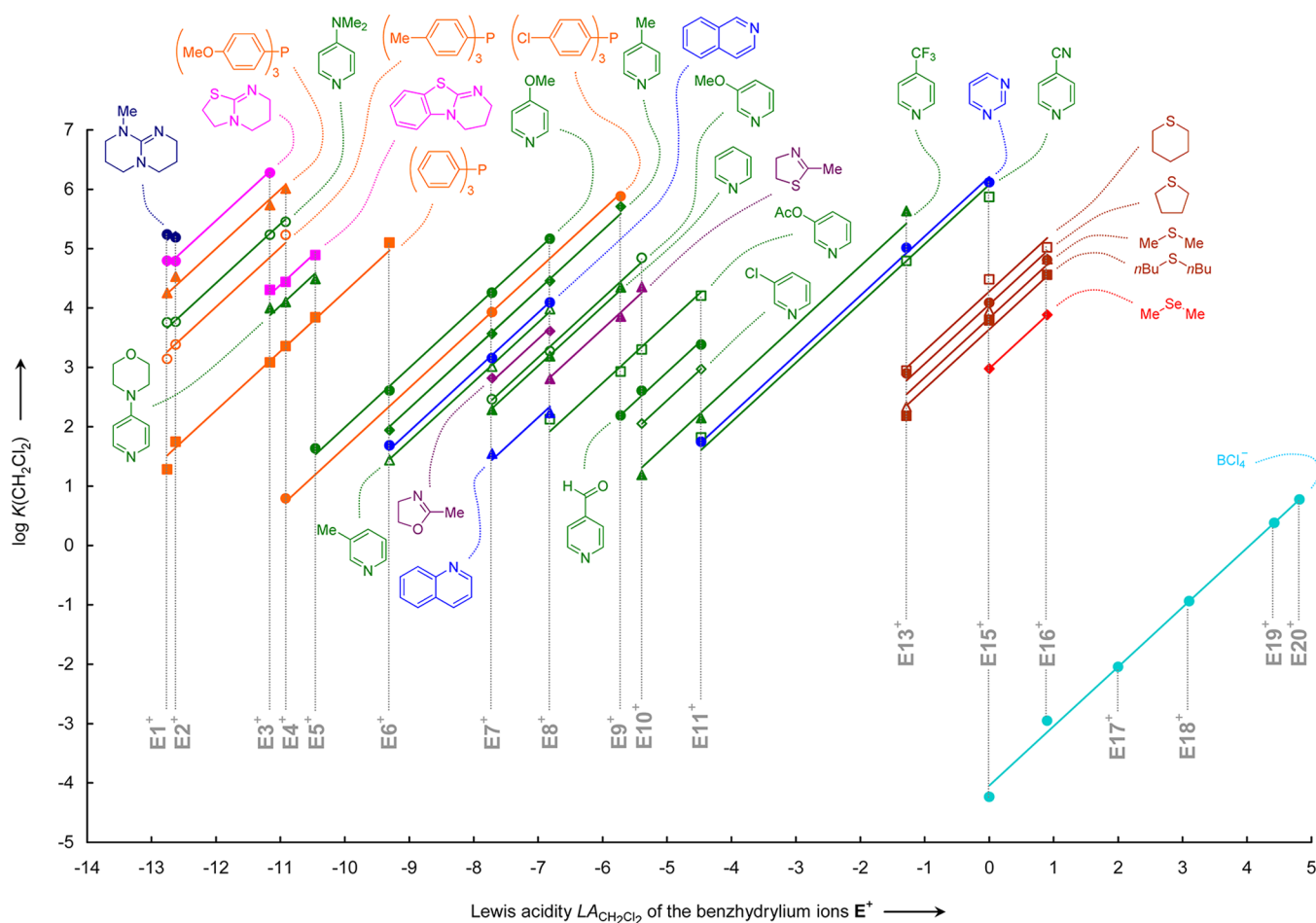


Figure 1. Plot of $\log K$ for reactions of benzhydrylium ions E^+ with Lewis bases in CH_2Cl_2 against the Lewis acidity parameters $LA_{CH_2Cl_2}$ of the benzhydrylium ions. The lines have a slope of unity and were calculated from eq 7. Some correlation lines have been omitted for the sake of clarity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

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

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

Equilibrium Constants in CH_3CN at 20 °C. In order to study the role of the solvent, we have also investigated the reactions of $E(1–8)^+$ with Lewis bases in CH_3CN solution. Table 3 lists 96 equilibrium constants, 56 of which have been determined in this work, while the others have previously been 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 CH_3CN .

A comparison of Tables 2 and 3 shows that the equilibrium constants K are generally 1.3–9 times (reactions of $E7^+$, 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 $\log K(CH_3CN)$ for reactions of benzhydrylium ions E^+ with pyridines and phosphines in CH_3CN (Table 3) against $\log K(CH_2Cl_2)$ 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

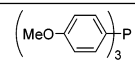
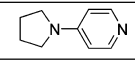
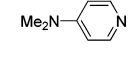
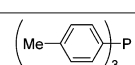
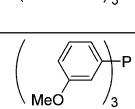
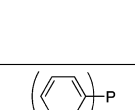
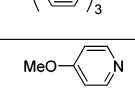
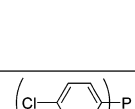
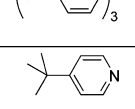
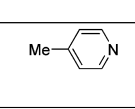
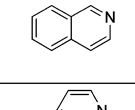
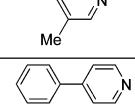
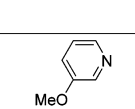
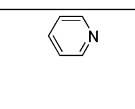
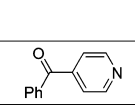
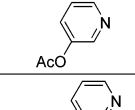
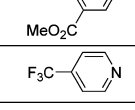




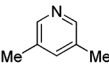





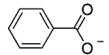
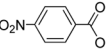
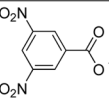
N	Lewis base		electrophile		experiment		correlation	
	formula	LB_{CH_3CN}	E^+	abbreviation	LA_{CH_3CN}	K^a / M^{-1}	K_{calc}^b / M^{-1}	K_{calc}/K
N3		17.26	$E1^+$	(lil) ₂ CH ⁺	-12.76	2.78×10^4	3.15×10^4	1.13
			$E2^+$	(jul) ₂ CH ⁺	-12.61	5.00×10^4	4.42×10^4	0.88
N4		17.39	$E1^+$	(lil) ₂ CH ⁺	-12.76	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^{4i}	8.84×10^3	0.82	
			$E4^+$	(thq) $_2CH^+$	-11.27	1.13×10^{4i}	1.39×10^4	1.23	
			$E5^+$	(pyr) $_2CH^+$	-10.83	3.20×10^{4i}	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	SCN ⁻	11.47	$E7^+$	(mpa) $_2CH^+$	-7.87	3.70×10^{3j}	3.99×10^3	1.08	
			(N)	$E8^+$	(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

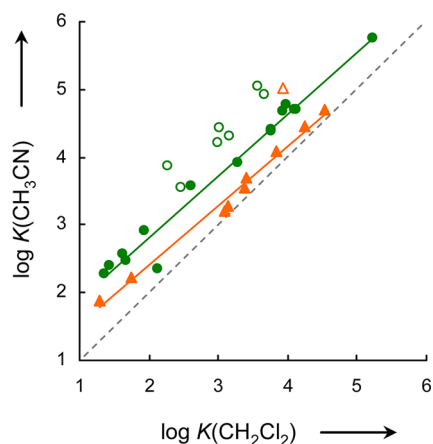


Figure 2. Plot of $\log K(\text{CH}_3\text{CN})$ for reactions of benzhydrylium ions E^+ with pyridines (green circles) and phosphines (orange triangles) in CH_3CN against $\log K(\text{CH}_2\text{Cl}_2)$ for the same reactions in CH_2Cl_2 . Pyridines: $\log K(\text{CH}_3\text{CN}) = 0.913 \log K(\text{CH}_2\text{Cl}_2)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

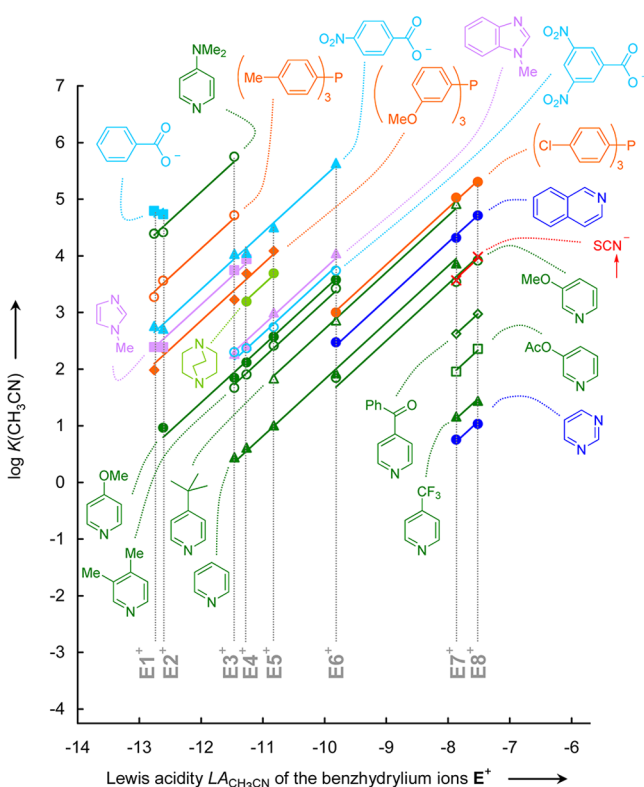


Figure 3. Plot of $\log K(\text{CH}_3\text{CN})$ for reactions of benzhydrylium ions E^+ with Lewis bases in CH_3CN against the Lewis acidity parameters $\text{LA}_{\text{CH}_3\text{CN}}$ of the benzhydrylium ions in CH_3CN calculated from eq 7. Some correlation lines have been omitted for the sake of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

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 ($-\Delta G_{\text{g}}^*$)

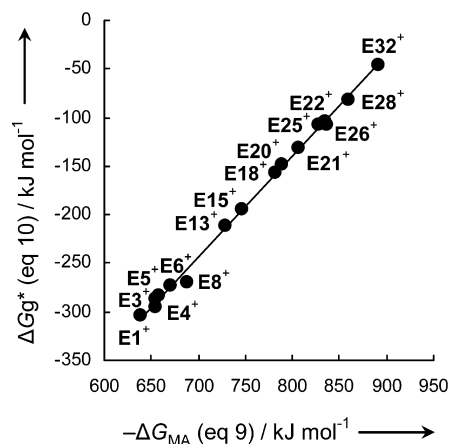


Figure 4. Correlation of the calculated free energies ΔG_{g}^* (kJ mol^{-1}) for hydride transfer from the diarylmethanes Ar_2CH_2 (E-H) to the benzyl cation in the gas phase (eq 10)⁴² with the calculated methyl anion affinities ΔG_{MA} (kJ mol^{-1}) of the benzhydrylium ions E^+ in the gas phase (eq 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 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

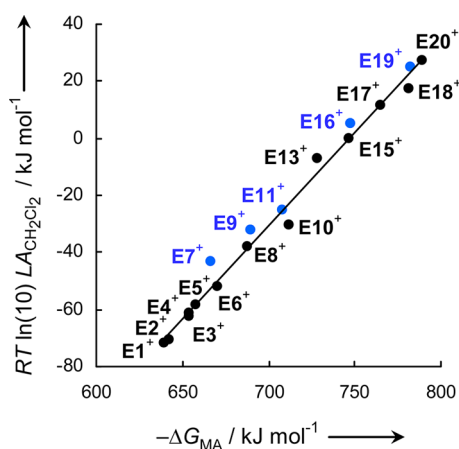


Figure 5. Correlation of the Lewis acidities $LA_{CH_2Cl_2}$ of the benzhydrylium ions E^+ (eq 7) with calculated methyl anion affinities ΔG_{MA} (eq 9) of E^+ ($-RT \ln(10) LA_{CH_2Cl_2} = 0.652\Delta G_{MA} + 487$; $R^2 = 0.987$). Blue symbols: *p*-phenylamino- and *p*-phenoxy-substituted benzhydrylium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

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 the 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*- NMe_2 -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.

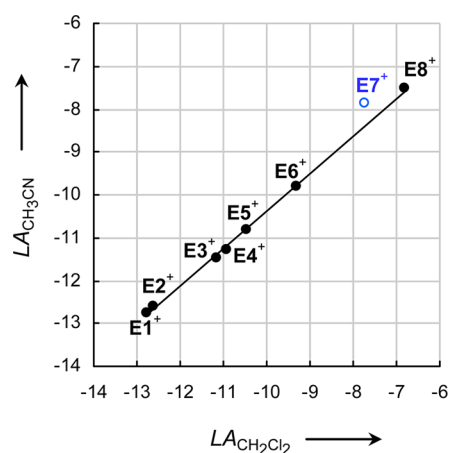


Figure 6. Plot of the LA_{CH_3CN} parameters for benzhydrylium ions in CH_3CN versus their $LA_{CH_2Cl_2}$ parameters in CH_2Cl_2 . The point for $E7^+$ (open blue circle) was not used for the correlation: $LA_{CH_3CN} = 0.878LA_{CH_2Cl_2} - 1.60$; $R^2 = 0.999$.

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

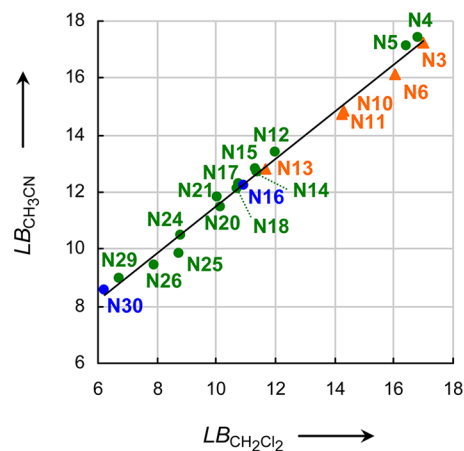

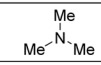
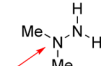
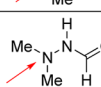
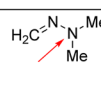
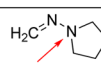


Figure 7. Plot of the LB_{CH_3CN} parameters for pyridines (green circles) and phosphines (orange triangles) in CH_3CN versus their $LB_{CH_2Cl_2}$ parameters in CH_2Cl_2 : $LB_{CH_3CN} = 0.828LB_{CH_2Cl_2} + 3.22$; $R^2 = 0.991$.

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) ₂ CH ⁺	-7.52	2.00×10^{2c}	5.63×10^2	2.82
			$E9^+$	(dpa) ₂ CH ⁺	-6.63 ^d	2.80×10^{4c}	4.37×10^3	0.16
			$E10^+$	(mfa) ₂ CH ⁺	-6.34 ^d	3.75×10^{3c}	8.53×10^3	2.27
N49		12.92	$E5^+$	(pyr) ₂ CH ⁺	-10.83	1.3×10^{2e}	1.23×10^2	0.95
N50		12.42	$E6^+$	(dma) ₂ CH ⁺	-9.82	1.2×10^{3e}	1.26×10^3	1.05
			$E5^+$	(pyr) ₂ CH ⁺	-10.83	3.3×10^{1e}	3.89×10^1	1.18
N51		4.34	$E13^+$	(fur) ₂ CH ⁺	-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) ₂ CH ⁺	-1.60 ^d	1.2×10^{3e}	5.55×10^2	0.46
N52		3.92 ^g (in CH_2Cl_2)	$E13^+$	(fur) ₂ CH ⁺	-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) ₂ CH ⁺	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) ₂ CH ⁺	-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) ₂ CH ⁺	-6.63 ^d	7.5×10^{4k}	2.28×10^4	0.30
			$E10^+$	(mfa) ₂ CH ⁺	-6.34 ^d	5.9×10^{3k}	4.43×10^4	7.52
			$E11^+$	(pfa) ₂ CH ⁺	-5.53 ^d	6.5×10^{5k}	2.85×10^5	0.44
N55	Br ⁻	(8) ^{h,j}	$E11^+$	(pfa) ₂ CH ⁺	-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.

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

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

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

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

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

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



A major problem of these investigations was the identification of systems which do not show side reactions while having suitable equilibrium constants (see section S5 of the Supporting Information for details). We were able to determine the equilibrium constants K for the reaction of $E17-Br$ with pyrimidine (N30) at different temperatures from -20 °C to +20 °C, from which we obtained 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). The large negative reaction entropy is explained by the increased solvation of the generated ions, which requires strong organization of the solvent. The equilibrium constant $K = 1.6$ shows that the bromide ion (N55) is slightly less Lewis basic than pyrimidine (N30, $LB_{CH_3CN} = 8.59$) in acetonitrile at 20 °C. Further ¹H NMR (CD_3CN) measurements for the reactions of $E17-Br$ 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^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 $\Delta H^0 = -62.7 \text{ kJ mol}^{-1}$ and $\Delta S^0 = -210.2 \text{ J mol}^{-1} \text{ K}^{-1}$ (see section S5 of the Supporting Information).

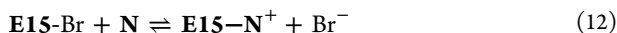
the value of $\text{LB}_{\text{CH}_3\text{CN}} \approx 8$ for Br^- (N55) derived from the laser flash photolysis experiment (Table 4).

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

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

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

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



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

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

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

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

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

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



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

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

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

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

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 CH₃CN do not follow a common correlation with their pK_a values in CH₃CN. 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

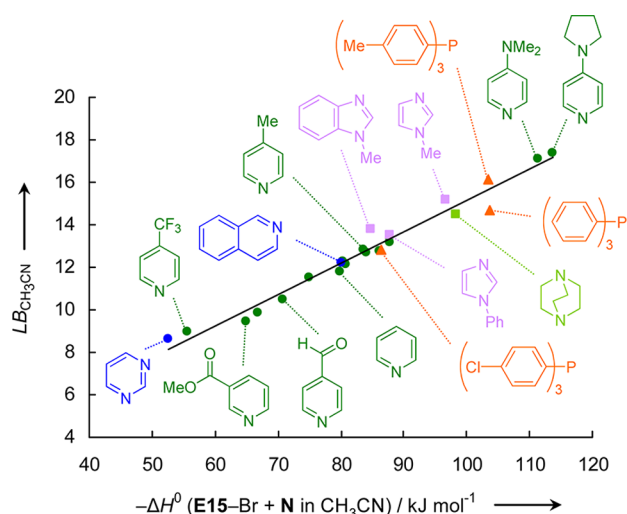


Figure 8. Plot of LB_{CH_3CN} parameters of Lewis bases N versus the enthalpies ΔH^0 for their reactions with E15-Br in CH_3CN at 20 °C ($LB_{CH_3CN} = -0.148\Delta H^0 + 0.317$; $R^2 = 0.970$).

Table 7. Reaction Enthalpies ΔH^0 (kJ mol⁻¹) for the Reactions of the Benzhydrylium Tetrafluoroborates E(1–8)⁺BF₄⁻ with 1,8-Diazabicycloundec-7-ene (DBU, N56) in CH_3CN at 20 °C

Lewis acid		ΔH^{0a} / kJ mol ⁻¹
E ⁺	abbreviation	
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.

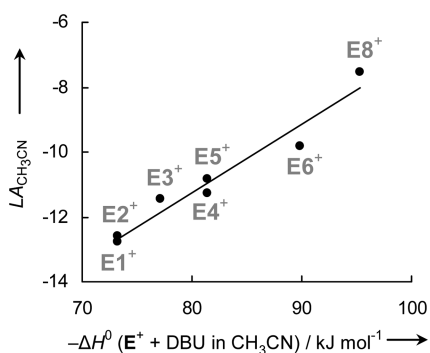


Figure 9. Plot of the LA_{CH_3CN} parameters of the benzhydrylium ions E(1–8)⁺ versus the enthalpies ΔH^0 for the reactions of E(1–8)⁺BF₄⁻ with 1,8-diazabicycloundec-7-ene (DBU, N56) in CH_3CN at 20 °C ($LA_{CH_3CN} = -0.211\Delta H^0 - 28.1$; $R^2 = 0.951$).

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

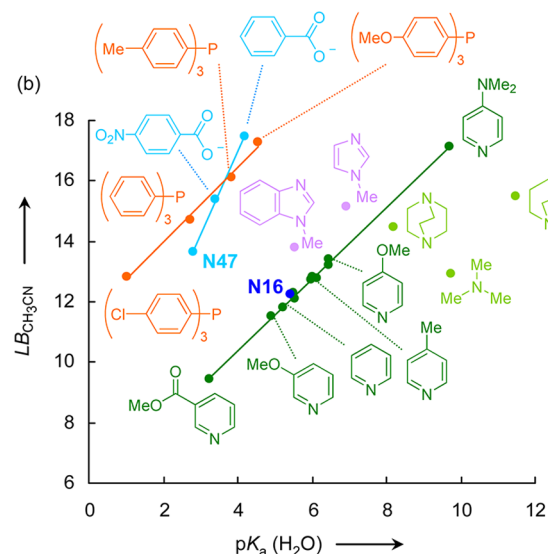
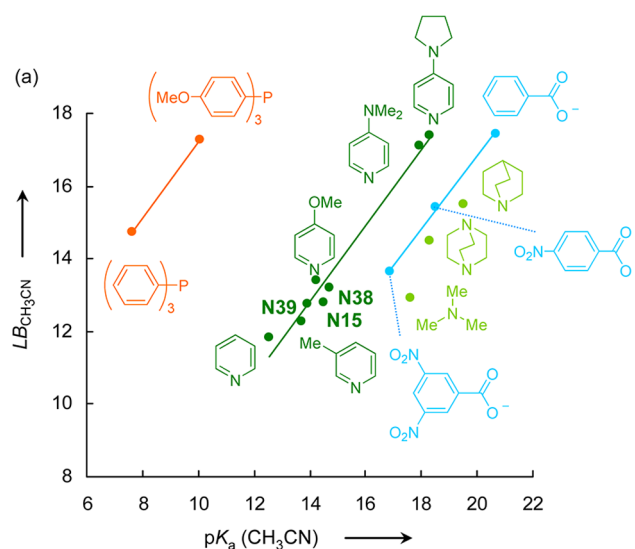


Figure 10. Plot of Lewis basicities LB_{CH_3CN} in CH_3CN versus pK_a values of the Lewis bases in CH_3CN (a) and H_2O (b). The pK_a values were taken from refs 7 and 59.

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 ~ 86 kJ mol⁻¹ while the P–H and P–C bond energies differ by only ~ 58 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 ~ 104 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).

RELATIONSHIPS BETWEEN KINETIC AND THERMODYNAMIC PARAMETERS

Heterolysis Rate Constants (S_N1 Solvolyses). In previous work, we have compiled rate constants k_s (corresponding to k_{backward} in Scheme 1) for solvolysis reactions of benzhydryl derivatives $E(1-33)-X$ ($X = \text{Br}, \text{Cl}, \text{OAc}, \text{OBz}, 3,5\text{-dinitrobenzoyl}, p\text{-nitrobenzoyl}, \text{OCO}_2\text{Me}$, etc.) in hydroxylic solvents.²³ Rate constants k_s for heterolysis reactions of benzhydryl halides in aprotic solvents like CH_2Cl_2 and CH_3CN have subsequently been determined by conductimetry in the presence of amines or triphenylphosphine, which trap the intermediate ion pairs and suppress ion recombination.^{60,61}

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

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

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

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

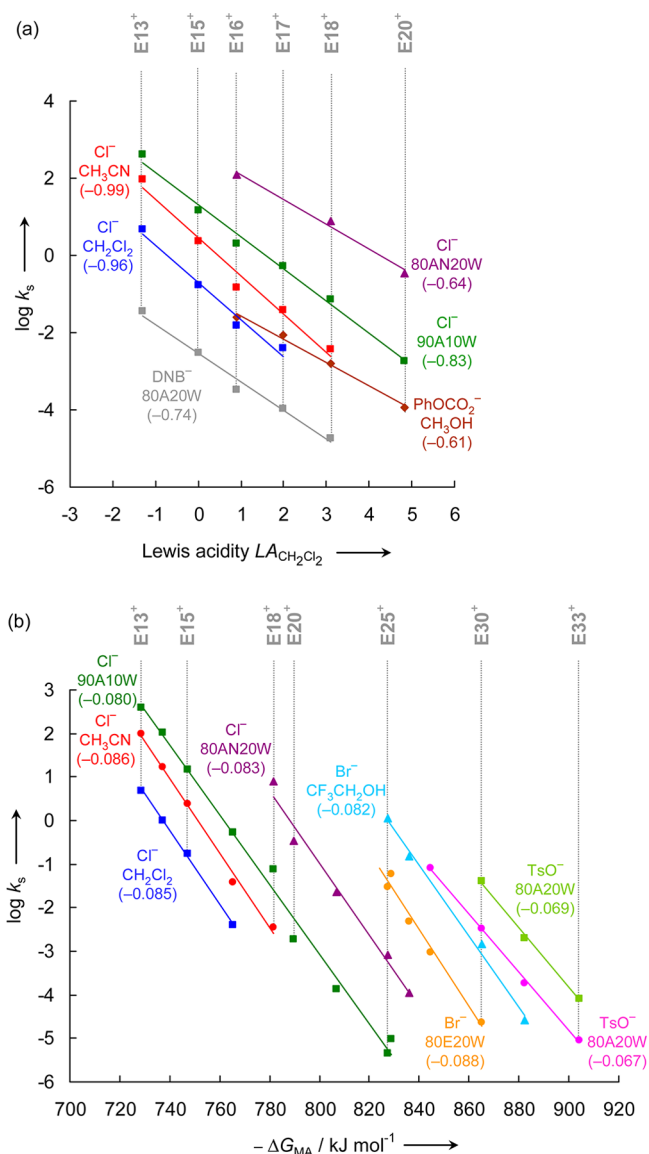


Figure 11. Correlation of $\log k_s$ for solvolysis reactions (25 °C) of $E(13-33)-X$ ^{23,60} versus the Lewis acidities $LA_{\text{CH}_2\text{Cl}_2}$ (a) and calculated methyl anion affinities ΔG_{MA} (b) of the benzhydrylium ions E^+ . The slopes of the correlation lines are given in parentheses; 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 barrier, and the solvolysis rates are not predominantly controlled by the relative free energies of the ionization step ($LA_{\text{CH}_2\text{Cl}_2}$ of E^+ , Figure 12).

Solvolysis 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 $X = \text{OTs}$ in Figure 11b might indicate that there is a barrier for the combinations of E^+ with the very weak nucleophile TsO^- so

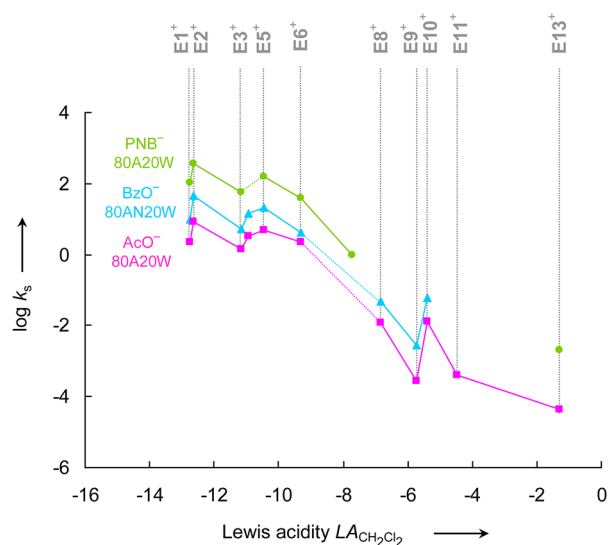


Figure 12. Plot of $\log k_s$ for solvolysis reactions (25 °C) of $E(1-13)-X^{23}$ versus the Lewis acidities $LA_{CH_2Cl_2}$ of the benzhydrylium ions E^+ . Abbreviations: PNB^- = *p*-nitrobenzoate; mixtures of solvents are given as (v/v), A = acetone, AN = acetonitrile, W = water.

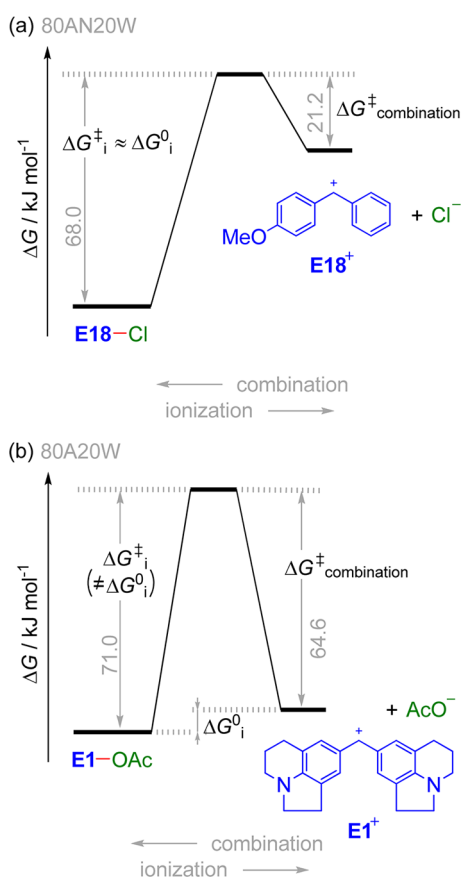


Figure 13. Free energy diagrams for the ionization steps in the solvolyses of $E18-Cl$ in 80% aqueous acetonitrile (80AN20W)⁶⁶ (a) and $E1-OAc$ in 80% aqueous acetone (80A20W)⁶⁷ (b). The subsequent reaction of E^+ with the solvent has been omitted for clarity (this reaction is much faster than the ionization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

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

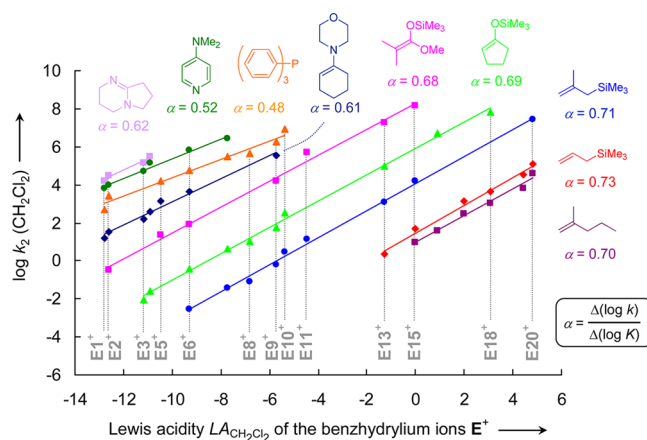


Figure 14. Correlation of $\log k_2$ for the reactions of E^+ with different nucleophiles^{20,22,28,29,31} in CH_2Cl_2 versus the Lewis acidities $LA_{CH_2Cl_2}$ of E^+ (this work).

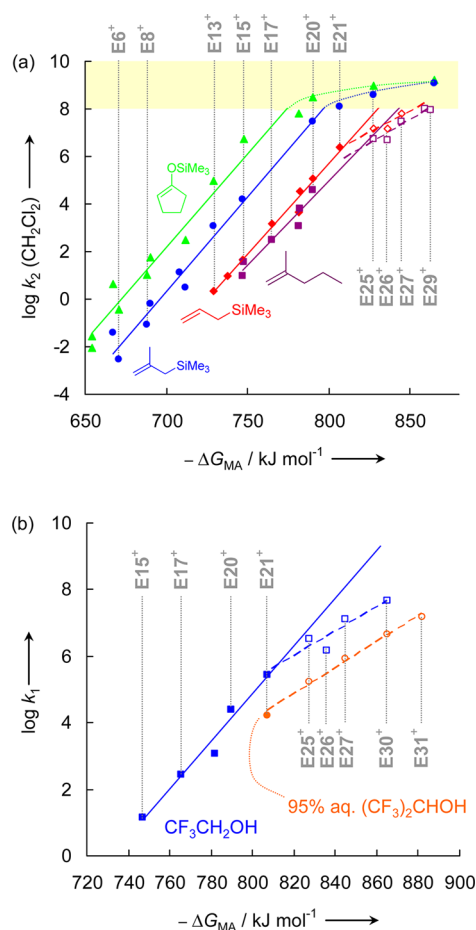


Figure 15. Plots of $\log k_2$ for the reactions of $E(3-30)^+$ with different nucleophiles^{20,22} in CH_2Cl_2 (a) and $\log k_1$ for the reactions of $E(15-31)^+$ with trifluoroethanol^{33,72} and with 95% aqueous hexafluoroisopropanol (w/w)⁷⁴ (b) versus the calculated methyl anion affinities ΔG_{MA} (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

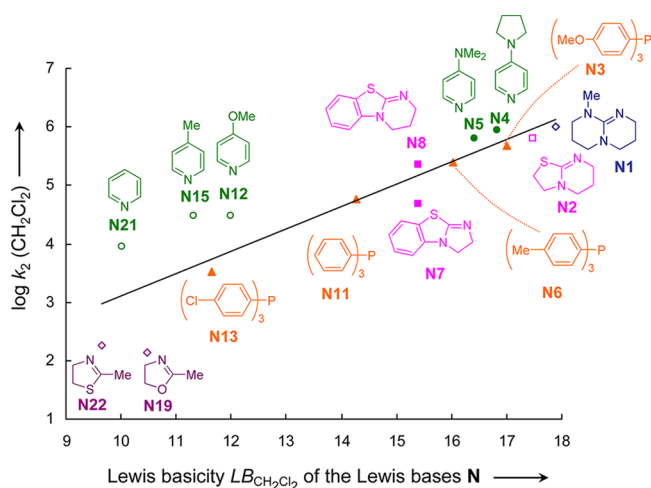


Figure 16. Plot of $\log k_2$ for the reactions of $E6^+$ with different nucleophiles N in CH_3CN ^{28–30} versus the Lewis basicities $LB_{CH_2Cl_2}$ of N (this work). Empty symbols: $\log k_2$ calculated from eq 17 and the reactivity parameters published in refs 29–32. The line shows the correlation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

in CH_2Cl_2 ^{20,22,28,29,31} correlate linearly with the Lewis acidities $LA_{CH_2Cl_2}$ 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 ($\Delta\Delta G^\ddagger$ 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.

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

As $LA_{CH_2Cl_2}$ 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 $10^8 M^{-1} s^{-1}$ 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} acetonitrile,^{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; the

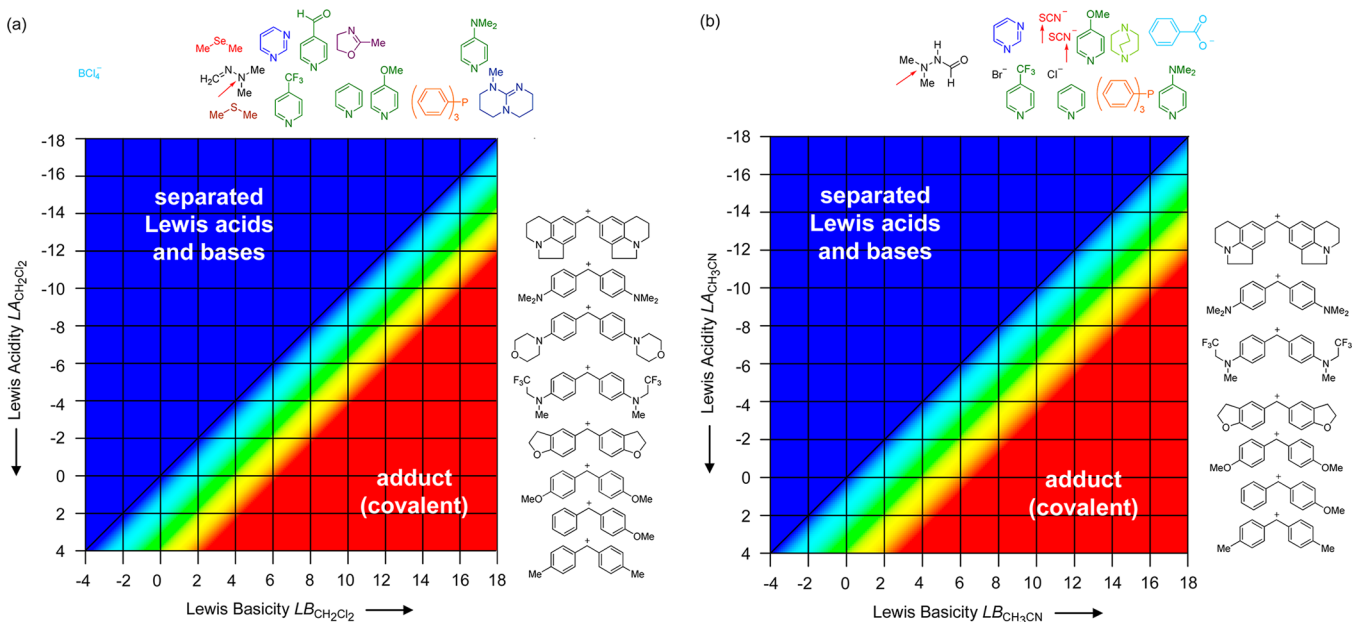


Figure 17. Semiquantitative schemes to estimate equilibria for reactions of Lewis acids (vertical axis) and Lewis bases (horizontal axis) in CH_2Cl_2 (a) and CH_3CN ⁷⁸ (b) at 20 °C. Combinations located in the red area of the figures form Lewis adducts, while combinations located in the blue area do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

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

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

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

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

CONCLUSION

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

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

As expected, the Lewis acidities LA are tightly correlated with pK_R^+ , while the Lewis basicities LB only correlate with the corresponding Brønsted basicities within groups of structurally 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 measurements) 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 counterpart 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

The authors declare no competing financial interest.

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