dichloromethane, and 11 mmol of *N*-chlorourethane in 30 mL of CH_2Cl_2 was gradually added at −50 °C. The mixture was stirred at −50 to −70 °C for 2 h. The solvent was distilled off, the residue was dissolved in ether, and the inorganic salts were filtered off. The mixture of products was separated by column chromatography (Al_2O_3, $CHCl_3$): yield of **5** 53%; mp 50–53 °C (ether-*n*-hexane). Anal. Calcd for $C_8H_{15}NO_2S$: C, 50.77; H, 7.40. Found: C, 50.46; H, 7.25.

Thiane 1-(*N*-acetyl)imide (**6**)[34] was prepared by the following method. Thiane (50 mmol) was dissolved in 200 mL of anhydrous CH_2Cl_2. To the stirred solution a suspension of 55 mmol of *N*-bromoacetamide in 100 mL of CH_2Cl_2 was gradually added at −70 °C. After addition was complete stirring was continued for 2 h and the equivalent amount of triethylamine was then slowly added. The mixture was gradually brought to room temperature, and the solvent and unreacted triethylamine were distilled off at 10^{-3} torr, keeping the temperature as low as possible (20 °C). The residue was suspended in ether, and the ether was dried and concentrated. The remaining oil was fractionated by column chromatography (Al_2O_3, $CHCl_3$) and the product was recrystallized repeatedly from ether: yield 4%; mp 98–101 °C. Anal. Calcd for $C_7H_{13}NO_2$: C, 52.80; H, 8.23. Found: C, 52.76; H, 8.41.

cis-1-Thiadecalin 1β-oxide (**32**) was prepared as follows. To a solution of 60 mmol of *cis*-1-thiadecalin in 100 mL of anhydrous CH_2Cl_2 was added 57 mmol of *m*-chloroperbenzoic acid in 120 mL of CH_2Cl_2 at 0 °C. When addition was complete the mixture was stirred at room temperature overnight. The solution was extracted with dilute aqueous NaOH, and the extract was washed with CH_2Cl_2. The dichloromethane solutions were united and the solvent was distilled off. The residue was distributed between petroleum ether and water. The aqueous phase was extracted with CH_2Cl_2, and the extract was dried and the solvent distilled off. The residue was distilled in a Kugelrohr distillation unit (150 °C (3 torr)). The distillate crystallized. GC analysis showed two compounds in a ratio of 79:21. The product was recrystallized from ether–petroleum ether and the major component was obtained in pure form. NMR analysis showed it to be **32**; the mother liquor contained **32** and *cis*-1-thiadecalin 1α-oxide in equal amounts: yield of **32** 56%; mp 60–62 °C. Anal. Calcd for $C_9H_{16}SO$: C, 62.74; H, 9.36. Found: C, 62.60; H, 9.41.

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Registry No. **1**, 59335-75-0; **3**, 62936-65-6; **4**, 13553-73-6; **5**, 70528-34-6; **6**, 70528-35-7; **7**, 59335-79-4; **9**, 67512-77-0; **10**, 70528-36-8; **11**, 31815-16-4; **12**, 70528-37-9; **12** picrate, 70528-38-0; **13**, 70528-39-1; **14**, 70528-40-4; **15**, 70528-41-5; **15** picrate, 70528-42-6; **16**, 70528-43-7; **17**, 70528-44-8; **18**, 70528-45-9; **19**, 70528-46-0; **20**, 70528-47-1; **21**, 70528-48-2; **22**, 70528-49-3; **23**, 70528-50-6; **24**, 70528-51-7; **25**, 56158-05-5; **26**, 70528-52-8; **27**, 70528-53-9; **28**, 62936-66-7; **29**, 58484-97-2; **30**, 70528-54-0; **31**, 70562-06-0; **32**, 59335-76-1; **33**, 67530-04-5; **34**, 70528-55-1; *cis*-1-thiadecalin 1α-oxide, 70561-54-5; *cis*-1-thiadecalin-1α-(*N*-phenyl)imide, 70561-55-6; *cis*-1-thiadecalin, 57259-80-0; thiane, 1613-51-0; aniline, 62-53-3; *p*-anisidine, 104-94-9; *p*-toluidine, 106-49-0; 4-fluoroaniline, 371-40-4; 4-cyanoaniline, 873-74-5; 4-nitroaniline, 100-01-6; *o*-toluidine, 95-53-4; 2,6-dimethylaniline, 87-62-7; 2,6-dimethyl-4-chloroaniline, 24596-18-7; *o*-fluoroaniline, 348-54-9; 2,6-difluoroaniline, 5509-65-9; *p*-chloroaniline, 106-47-8; 4-chlorothiane, 32358-87-5; 1,4-dithiane, 505-29-3; 1,4-oxathiane, 15980-15-1; 5-methyl-1,3-dithiane, 38761-25-0; *N*-bromobenzamide, 19964-97-7; 4,4-dimethylthiane, 40324-30-9; 1,3-dithiane, 505-23-7; *N*-chlorourethane, 16844-21-6; *N*-bromoacetamide, 79-15-2.

Quantitative Separation of Electronic and Steric Substituent Effects in Reactions between Aliphatic Amines and Electron Acceptors[1]

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The effects of three N substituents on reactivities of aliphatic amines were analyzed by means of free-energy-related substituent constants and regression analysis. In hydrogen-bond formation with $CHCl_3$ and charge-transfer-complex formation with I_2, electronic and steric effects of three N substituents were quantitatively separated by means of the equation $\log K = \rho^*\sum\sigma^* + a_1E_s^c(R_1) + a_2E_s^c(R_2) + a_3E_s^c(R_3) + c$, where K is the equilibrium constant, ρ^*, a_1, a_2, and a_3 are susceptibility constants, and c is the intercept. $\sum\sigma^*$ is the sum of the Taft σ^* values of three N substituents. $E_s^c(R_1)$, $E_s^c(R_2)$, and $E_s^c(R_3)$ are, respectively, the Hancock corrected steric constants of N-substituents R_1, R_2, and R_3, where $E_s^c(R_1) \geq E_s^c(R_2) \geq E_s^c(R_3)$. Examination of literature data seems to suggest a general applicability of the present procedure to various reactivities of aliphatic amines.

Aliphatic amines react with various lone pair electron acceptors. The reactivities are generally governed by polar and steric factors of three N substituents. Free-energy-related substituent parameters have been used to carry out a number of analyses for such reaction systems as the acid dissociation of ammonium ions,[2] gas-phase association with BMe_3,[3] Menschutkin reaction with EtI,[4] and others.[5-9] However, these works primarily correlated the reactivity with the total polar effect of three N substituents by using $\sum\sigma^*$, the summation of the Taft σ^* values, for sterically "unhindered" amines. The deviation of the data for the "hindered" amines from the apparent correlation for the "unhindered" compounds was only qualitatively attributed to the steric effect of bulky N substituents.

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Table I. Hydrogen-Bond Formation with $CHCl_3$ in Cyclohexane and the Charge-Transfer Complexation with I_2 in *n*-Heptane of Aliphatic Noncyclic Amines

		log *K*(HB)		log *K*(CT)				log *K*(HB)		log *K*(CT)	
no.	substituents	obsd[a]	calcd[b]	obsd[c]	calcd[d]	no.	substituents	obsd[a]	calcd[b]	obsd[c]	calcd[d]
1	H_3			1.83[i]	2.00	21	Me_2, *t*-Bu	−0.27[h]	−0.47	3.87	3.81
2	H_2, Me			2.72[i]	2.95	22	Me_2, c-Hex	−0.26[h]	−0.32	4.14	3.97
3	H_2, Et			2.86[i]	3.00	23	Me, Et_2	−0.31[g]	−0.24		
4	H_2, *n*-Bu	−0.21	−0.21	3.09[i]	2.92	24	Me, Et, *t*-Bu	−0.52[g]	−0.57		
5	H_2, *i*-Bu			2.77	2.64	25	Me, $n\text{-Pr}_2$	−0.59[g]	−0.41		
6	H_2, *sec*-Bu			2.84	2.61	26	Me, $i\text{-Pr}_2$	−0.55[g]	−0.59		
7	H_2, *n*-Hex	−0.18	−0.20			27	Me, $i\text{-Bu}_2$	−1.58	−1.26	1.59	2.02
8	H_2, c-Hex	−0.15	−0.35			28	Me, *sec*-Bu_2	−0.77[g]	−0.98		
9	H_2, Bz[e]	−0.49[f]	−0.39			29	Me, c-Hex_2	−0.63	−0.83	3.37	3.03
10	H, Me_2			3.83[i]	3.77	30	Et_3	−0.43[h]	−0.57	3.79[j]	3.72
11	H, Et_2			3.85[i]	3.70	31	Et_2, *n*-Pr	−0.60[g]	−0.63		
12	H, $n\text{-Pr}_2$			3.70	3.37	32	Et_2, *n*-Bu	−0.59[g]	−0.63		
13	H, $i\text{-Pr}_2$			2.97	3.15	33	$n\text{-Pr}_3$	−0.89[h]	−1.03	3.20[j]	2.89
14	H, $n\text{-Bu}_2$	−0.31	−0.33			34	$n\text{-Pr}_2$, *i*-Bu	−1.41	−1.31	2.21	2.27
15	H, $i\text{-Bu}_2$	−0.59	−0.67			35	$n\text{-Pr}_2$, *sec*-Bu	−1.24	−1.20	2.15	2.60
16	Me_3			4.08[i]	4.28	36	*n*-Pr, $i\text{-Pr}_2$	−1.31	−1.21	2.43	2.67
17	Me_2, *n*-Pr	−0.34[g]	−0.18			37	*n*-Pr, $i\text{-Bu}_2$			1.27	1.04
18	Me_2, *n*-Bu	−0.35[h]	−0.18	3.99	4.25	38	$n\text{-Bu}_3$	−1.03	−1.36	3.20[i]	2.89
19	Me_2, *i*-Bu	−0.65[h]	−0.46			39	*n*-Bu, c-Hex_2	−1.51	−1.47		
20	Me_2, *sec*-Bu	−0.46[h]	−0.40	3.76	3.94	40	*i*-$Pent_3$	−0.84	−0.94		

[a] Unless otherwise noted, data from this laboratory; the standard error (SE) of the *K* value is less than 3.5%. [b] By eq 12. [c] Unless otherwise noted, data from this laboratory; SE of the *K* value is less than 7.5%. [d] By eq 13. [e] Bz = benzyl. [f] SE of the *K* value is ±6.8%. [g] From ref 8. [h] Data of Wong and Ng[8] are as follows: **18**, −0.33; **19**, −0.62; **20**, −0.44; **21**, −0.26; **22**, −0.24; **30**, −0.42; **33**, −0.89. [i] From ref 6. [j] The standard deviation of the *K* value is less than 2%. Data of Yada et al.[6] are as follows: **30**, 3.80; **33**, 3.14.

Table II. Hydrogen-Bond Formation with $CHCl_3$ in Cyclohexane and the Charge-Transfer Complexation with I_2 in *n*-Heptane of Aliphatic Cyclic Amines

no.	substituents	log *K*(HB)[a]	log *K*(CT)[b]	no.	substituents	log *K*(HB)[a]	log *K*(CT)[b]
41	H, $(CH_2)_4$[c]	−0.12	3.97[g]	47	Me, $(CH_2)_5$	−0.23	
42	H, $(CH_2)_5$[d]	−0.20	3.97[h]	48	$(CH_2)_5$, Et	−0.32	3.97[g]
43	Me, $(CH_2)_4$	−0.20[f]		49	$(CH_2)_5$, *i*-Pr	−0.52	3.47[g]
44	$(CH_2)_4$, *i*-Pr	−0.21	4.38[g]	50	$(CH_2)_5$, *i*-Bu	−1.25	2.49
45	$(CH_2)_4$, *n*-Bu	−0.34	4.35[g]	51	$(CH_2)_5$, *sec*-Bu	−0.88	2.89
46	$(CH_2)_4$, *i*-Bu	−0.70	3.22	52	$CH(C_2H_4)_3$[e]	−0.04	5.36[i]

[a] The standard error (SE) of the *K* value is less than 3.5%. [b] Unless otherwise noted, data from this laboratory; the SE of the *K* value is less than 5.5%. [c] Tetramethylene ligand in pyrrolidine. [d] Pentamethylene ligand in piperidine. [e] Tridentate quinuclidine skeleton. [f] The value of Wong and Ng[8] is −0.16. [g] The standard deviation (SD) of the *K* value is less than 10%. [h] From ref 6. [i] SD of the *K* value is ±27%.

Recently, we showed that the total steric effect of the type of substituents, $CR_1R_2R_3$, on the reaction center in the transition state of ester hydrolysis is analyzable by the steric effects of the component α substituents R_1, R_2, and R_3.[10a] In terms of the Hancock steric constants, the situation is represented as eq 1, where $E_s^c(R_1) \geq E_s^c(R_2)$

$$E_s^c(CR_1R_2R_3) = a_1E_s^c(R_1) + a_2E_s^c(R_2) + a_3E_s^c(R_3) + c \quad (1)$$

$$E_s^c = E_s - 0.306(3 - n_H) \quad (2)$$

$\geq E_s^c(R_3)$, a_1, a_2, and a_3 are susceptibility coefficients, and c is a constant. The Hancock steric constant, E_s^c, is the constant corrected for hyperconjugation effect of α-hydrogen atoms[11] which is related to the Taft E_s constant[3] by eq 2, where n_H is the number of α-hydrogen atoms. The Taft E_s constant was found to be much poorer in correlating the steric effect in the ester hydrolysis in terms of those of the component α substituents.[10a]

Since the total steric effect of the three N substituents of aliphatic amines against lone pair electron acceptors has been suggested to be similar to, if not identical with, that of three component α substituents of alkyl groups on the ester reactions,[12] we attempted to separate polar and steric effects of N substituents of amines $NR_1R_2R_3$ by means of eq 3, where K is the rate or equilibrium constant and

$$\log K = \rho^*\textstyle\sum\sigma^* + \sum_{i=1}^{3} a_iE_s^c(R_i) + c \quad (3)$$

$E_s^c(R_1) \geq E_s^c(R_2) \geq E_s^c(R_3)$. In this work, we analyzed the effect of N substituents on equilibria for hydrogen-bond

Table III. Equilibrium Constant *K* for Quinuclidine-I_2 System in *n*-Heptane Evaluated by Eq 9[a]

$10^4[B]_0$, mol/L	absorbance	$10^{-5}K$
0	0.005[b]	
0.243	0.481	1.61[d]
0.389	0.697	2.76[d]
0.486	0.742	2.62[d]
2.92	0.838	
4.86	0.846	
24.3	0.865[c]	
38.9	0.868[c]	
97.2	0.862[c]	

[a] $[A]_0 = 3.00 \times 10^{-5}$ mol/L; *E* was measured at 280 nm. [b] E_A. [c] Average of these three values 0.865 ($=E_{max}$). [d] Average of these three values 2.33 ± 0.63.

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Table IV. Substituent Parameters Used for Correlations

substituent	σ^*[a]	E_s^c[b]	substituent	σ^*[a]	E_s^c[b]
H	0.490	0.32	*n*-Hept	−0.166[g]	−0.75[n]
Me	0.000	0.00	c-HexCH$_2$	−0.06	−1.29
Et	−0.100	−0.38	*n*-Oct	−0.148[g]	−0.64
n-Pr	−0.115	−0.67	*n*-Non	−0.152[g]	−0.64[o]
i-Pr	−0.190	−1.08	*n*-Dec	−0.152[h]	−0.64[o]
n-Bu	−0.130	−0.70	allyl	0.15[i]	−0.38[p]
i-Bu	−0.125	−1.24	NCCH$_2$	1.300	−1.25[q]
sec-Bu	−0.210	−1.74	NCCH$_2$CH$_2$	0.49[j]	−1.21[m]
t-Bu	−0.300	−2.46	Bz[c]	0.215	−0.69
n-Pent	−0.162[g]	−0.71	BzCH$_2$	0.080	−0.69
i-Pent	−0.162[g]	−0.66	BzCH$_2$CH$_2$	0.02	−0.76
neo-Pent	−0.165	−2.05	(CH$_2$)$_4$[d]	−0.26[k]	−0.19[r]
n-Hex	−0.165[g]	−0.75[m]	(CH$_2$)$_5$[e]	−0.14[k]	−0.38[r]
c-Hex	−0.15	−1.40	CH(C$_2$H$_4$)$_3$[f]	−0.29[l]	0.00[r]

[a] From ref 3 unless otherwise noted. [b] Calculated from E_s value by eq 2. Unless otherwise noted, E_s values are taken from ref 3. [c] Bz = benzyl. [d] Tetramethylene ligand in pyrrolidine. [e] Pentamethylene ligand in piperidine. [f] Tridentate quinuclidine skeleton. [g] From A. B. Hoefelmeyer and C. K. Hancock, *J. Am. Chem. Soc.*, 77, 4746 (1955). [h] Taken as that of *n*-Non group. [i] From I. Sestáková, V. Horák, and P. Zuman, *Collect. Czech. Chem. Commun.*, 31, 3889 (1966). [j] From V. E. Bel'skii, L. A. Kudryavtseva, and B. E. Ivanov, *Zh. Obshch. Khim.*, 42, 2427 (1972); *J. Gen. Chem. USSR (Engl. Transl.)*, 42, 2421 (1972). [k] From ref 2. [l] Estimated from the log K_A value of quinuclidine[23] by using eq 21. [m] The E_s value is taken from F. L. Lambert, *J. Org. Chem.*, 31, 4184 (1966). [n] Taken as that of *n*-Hex group. [o] Taken as that of *n*-Oct group. [p] Taken as that of Et group. [q] The E_s value is taken from W. A. Pavelich and R. W. Taft, Jr., *J. Am. Chem. Soc.*, 79, 4935 (1957). [r] Per unit ligand; see text.

Table V. Correlations According to Eq 3 for HB and CT Equilibrium Constants[a]

$$\log K = \rho^*\Sigma\sigma^* + a_1E_s^c(R_1) + a_2E_s^c(R_2) + a_3E_s^c(R_3) + c$$

reacn system	ρ^*	a_1	a_2	a_3	c	n[b]	s[c]	r[d]	F[e]	eq no.
HB	−0.409[g]	0.931	0.412	0.146[h]	−0.205	29	0.222	0.867	18.1	10
	(±0.328)	(±0.355)	(±0.185)	(±0.171)	(±0.228)					
CT	−2.439	2.035	1.208	0.512	4.345	24	0.438	0.876	15.6	11
	(±0.709)	(±0.755)	(±0.472)	(±0.337)	(±0.478)					
HB[f]	−0.499	1.013	0.419	0.209	−0.101	29	0.145	0.946	50.6	12
	(±0.210)	(±0.229)	(±0.108)	(±0.098)	(±0.138)					
CT[f]	−2.265	1.878	0.908	0.469	4.283	24	0.266	0.956	50.3	13
	(±0.385)	(±0.451)	(±0.215)	(±0.181)	(±0.251)					

[a] In this and following tables, the values of ρ^*, a_1, a_2, and a_3 are justified by the t test at better than the 99.5% level of significance, unless otherwise noted. The figures in parentheses are the 95% confidence intervals. [b] The number of data used in the correlation. [c] Standard deviation. [d] Multiple correlation coefficient. [e] F value of the correlation. [f] E_s^c value of the *i*-Bu group in tertiary amines is taken as that of neo-Pent group. [g] Justified at a level between 99 and 97.5%. [h] Justified at a level between 95 and 90%.

formation with $CHCl_3$ and charge-transfer complexation with I_2 of a number of aliphatic amines.

Experimental Section

Materials. Primary and secondary amines were obtained commercially. Most of the tertiary amines were synthesized from appropriate primary and secondary amines either by the alkylation with alkyl bromides in ethanol[13] or by the reductive methylation with formic acid–formaldehyde[14] according to the reported procedures. Quinuclidine was liberated from the commercially available hydrochloride with concentrated aqueous NaOH and extracted with ether. After the ether solution was dried and evaporated, quinuclidine was purified by sublimation. Other amines, mostly stored as hydrochlorides, were liberated with aqueous NaOH, dried with NaOH or KOH pellets, and distilled under atmospheric or reduced pressure over Na metal. All measurements were performed immediately after the purification. $CHCl_3$ was washed with concentrated H_2SO_4, 2 N aqueous NaOH, and water until the washing was neutral. After the $CHCl_3$ was dried, a fraction boiling at 61 °C was collected. I_2 was purified by sublimation under a N_2 atmosphere at 60–90 °C. Cyclohexane and *n*-heptane were of spectroscopic grade.

Previously unknown amines are *n*-Pr$_2$-*i*-BuN (bp 167–169 °C), *n*-Pr$_2$-*sec*-BuN (bp 173–174 °C, mp of HCl salt 60–78 °C), and *n*-Pr-*i*-Bu$_2$N (bp 176–177 °C). These were confirmed by elemental analyses for C, H, and N of either the free bases or the hydrochlorides. The purity was also checked for each of the amines by ^{1}H NMR and/or GLC analyses.

Table VI. Squared Correlation Matrices of Variables for the HB Equilibrium

	eq 10			eq 12		
	$\Sigma\sigma^*$	$E_s^c(R_1)$	$E_s^c(R_2)$	$\Sigma\sigma^*$	$E_s^c(R_1)$	$E_s^c(R_2)$
$E_s^c(R_1)$	0.500	1		0.500	1	
$E_s^c(R_2)$	0.347	0.140	1	0.306	0.106	1
$E_s^c(R_3)$	0.050	0.005	0.021	0.058	0.000	0.043

Table VII. Squared Correlation Matrices of Variables for the CT Equilibrium

	eq 11			eq 13		
	$\Sigma\sigma^*$	$E_s^c(R_1)$	$E_s^c(R_2)$	$\Sigma\sigma^*$	$E_s^c(R_1)$	$E_s^c(R_2)$
$E_s^c(R_1)$	0.596	1		0.596	1	
$E_s^c(R_2)$	0.500	0.314	1	0.416	0.270	1
$E_s^c(R_3)$	0.243	0.066	0.067	0.289	0.126	0.200

Hydrogen-Bonding (HB) Equilibrium. The HB equilibrium constant between H donor (AH) and H acceptor (B) can be determined by measuring the ^{1}H NMR chemical shift of the AH signal in an inert solvent. According to Mathur and co-workers,[15] the 1:1 equilibrium constant K is calculated by eq 4 under

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$$\frac{1}{\nu - \nu_M} = \frac{1}{K(\nu_c - \nu_M)} \frac{1}{[B]_0} + \frac{1}{\nu_c - \nu_M} \quad (4)$$

conditions where the initial molar concentration of AH, $[AH]_0$, is kept constant and that of B, $[B]_0$, is varied in a range where $[B]_0 >> [AH]_0$. In this work, AH is $CHCl_3$ and B represents aliphatic amine. ν is the observed frequency of the reaction mixture, and ν_M and ν_c are, respectively, the characteristic frequency of the free and complexed $CHCl_3$. From the plot of $1/(\nu - \nu_M)$ vs. $1/[B]_0$, the equilibrium constant K and the value of $(\nu_c - \nu_M)$ are determined.

For benzylamine, where the benzene ring behaves as another H-acceptor site, the counterpart of eq 4 is formulated as eq 5.

$$\frac{1}{\nu - \nu_M} = \frac{1}{K(\nu_c - \nu_M) + K'(\nu_c' - \nu_M)} \frac{1}{[B]_0} + \frac{K + K'}{K(\nu_c - \nu_M) + K'(\nu_c' - \nu_M)} \quad (5)$$

K' and ν_c' are, respectively, the 1:1 equilibrium constant of the H-bond formation with the benzene ring and the characteristic frequency of the complexed $CHCl_3$. Since $[B]_0 >> [AH]_0$, we neglected the dual complexation of $CHCl_3$ with benzylamine. From the plot of $1/(\nu - \nu_M)$ vs. $1/[B]_0$, we can derive the value of $K + K'$. For the K' value, we used the value observed between toluene-d_8 and $CHCl_3$ as a first approximation which was determined from the plot according to eq 4.

In practice, the concentration of $CHCl_3$ was kept constant either at 0.025 or at 0.05 M in cyclohexane. The concentration of amines was varied in a range of either 0.4–2.0 or 0.8–4.0 M, respectively. The chemical shift (Hz) of the CH signal, ν, which is the weighted average of ν_M and ν_c, was measured at 35 °C with respect to that of cyclohexane used as the internal standard by using a Hitachi R-22 NMR spectrometer. The frequency of the CH signal in the absence of amine, ν_M, was measured in each set of experiments.

Charge-Transfer (CT) Complexation. According to Benesi and Hildebrand,[16] the equilibrium constant K for the 1:1 complex formation between electron donor (B) and acceptor (A) in an inert solvent can be determined by using eq 6 under conditions similar

$$\frac{1}{E - E_A} = \frac{1}{K(\epsilon_{AB} - \epsilon_A)[A]_0} \frac{1}{[B]_0} + \frac{1}{(\epsilon_{AB} - \epsilon_A)[A]_0} \quad (6)$$

$$K = \frac{[B]_0(E_A - E') + [B]_0'(E - E_A)}{[B]_0[B]_0'(E' - E)} \quad (7)$$

to those used to derive eq 4 such as $[A]_0$ = constant and $[B]_0 >> [A]_0$. In this work, A is I_2 and B represents aliphatic amine. In eq 6, ϵ_{AB} and ϵ_A are, respectively, the molar extinction coefficients of the CT complex and the free I_2 molecule at an appropriate wavelength in the UV region where amines and the solvent exhibit no absorption. E and E_A are, respectively, the observed absorbances of the reaction system with and without addition of amines. From the plot of $1/(E - E_A)$ vs. $1/[B]_0$ for various concentrations of amines (the Benesi–Hildebrand plot) which shows a straight line, the values of K and $\epsilon_{AB} - \epsilon_A$ can be derived. The K value can be also determined by using eq 7 when the absorbances E and E' are measured with only two different amine concentrations $[B]_0$ and $[B]_0'$, respectively.[17]

If the equilibrium constant is so high that the E value does not vary appreciably under conditions of $[B]_0 >> [A]_0$, eq 6 and 7 are not applicable to estimate the K value. When the initial concentration of the amine, $[B]_0$, is sufficiently high, all of the I_2 molecules initially present in the reaction mixture are in the complexed form. Under these conditions, $[A]_0 = [AB]$ so that the absorbance reached a maximum which is expressed by $E_{max} = [A]_0\epsilon_{AB}$. If we vary $[B]_0$ in the same order as $[A]_0$, which is fixed, the equilibrium constant is calculated by means of eq 8 which is transformed to eq 9 by substituting such relationships as $[A]_0 = [AB] + [A]$, $E = \epsilon_A[A] + \epsilon_{AB}[AB]$, $\epsilon_A = E_A/[A]_0$, and $\epsilon_{AB} = E_{max}/[A]_0$.

$$K = \frac{[AB]}{([B]_0 - [AB])([A]_0 - [AB])} \quad (8)$$

$$K = \frac{(E - E_A)(E_{max} - E_A)}{E_{max} - E} \frac{1}{[B]_0(E_{max} - E_A) - [A]_0(E - E_A)} \quad (9)$$

For most of the present determinations, the initial I_2 concentration was kept constant at about 3×10^{-5} M and the amine concentration was varied in a range of 10^{-3}–10^{-2} M in *n*-heptane. The K value was determined with eq 6 at the λ_{max} of the CT complex, AB, which is located in ranges of 245–250, 255–270, and 270–295 nm for primary, secondary, and tertiary amines, respectively. For $(CH_2)_4NH$, Et_3N, *n*-Pr_3N, and $(CH_2)_5N$-*i*-Pr, only two $[B]_0$ values were used to measure the spectra. Therefore, the K value was determined by averaging the values calculated by eq 7 at three different wavelengths near the λ_{max}.

For $(CH_2)_4N$-*i*-Pr, $(CH_2)_4N$-*n*-Bu, $(CH_2)_5NEt$, and $CH(C_2H_4)_3N$, the K value was determined by using eq 9 with a fixed $[A]_0$ value around 3×10^{-5} M. The E_{max} value was determined with $[B]_0$ in the order of 10^{-4}–10^{-3} M. The E value was measured with at least three different $[B]_0$ values on the order of 10^{-5} M, and the calculated K values were averaged.

In each of the measurements, the absorbance reached a stable state a few minutes after preparation of the reaction mixture and remained unchanged for about 30 min. We took the stable absorbance value as E. The absorbance without addition of the amines was taken as E_A. To avoid undesirable ionic reaction, we took extra care to maintain the reaction system under anhydrous conditions as far as possible. For all of the measurements, turbidity or decolorization due to the ionic reaction was not observed.[17] All the determinations were performed at 20 °C by using a Hitachi 124 spectrophotometer.

Results

The HB equilibrium constants for noncyclic and cyclic amines are shown in Tables I and II, respectively. The plot according to eq 4 or 5 for each of the amines was entirely linear indicating that the self-association of $CHCl_3$ as well as of primary and secondary amines is negligible under the present experimental conditions.

For eight tertiary amines (**18–22, 30, 33, 43**), the constants agree within the experimental precision with those determined by Wong and Ng[8] under the same experimental conditions. Their values for eight other compounds, (**17, 23–26, 28, 31, 32**) are also included in Table I and used in the analysis.

For benzylamine, the plot according to eq 5 gave the $K + K'$ value 0.503 ± 0.022. Approximating the K' value to the association constant with toluene-d_8, 0.177 ± 0.006, we estimated the K value as the difference. We also determined the association constant with benzene-d_6 and bromobenzene-d_5 by using eq 4 as 0.131 ± 0.007 and 0.102 ± 0.062, respectively. The higher the electron withdrawal of the substituent, the lower the association constant. Thus, the association constant with the benzene ring π-electron systems seems to be primarily governed by the electron-withdrawing property of substituents. The electronic effect of the CH_2NH_2 substituent in benzylamine is not significantly different from that of Me in toluene; e.g., the Taft σ_I and σ_R^0 values[18,19] may be used to obtain $\sigma_m^0(CH_2NH_2) = -0.08$ and $\sigma_p^0(CH_2NH_2) = -0.15$, while $\sigma_m^0(Me) = -0.07$[20] and $\sigma_p^0(Me) = -0.12$.[21] Since the association constants with the benzene ring systems are considerably lower than that with the NH_2 lone-pair electrons, the estimate for the K value, when taken in log units, does not seem to be so susceptible to the uncertainty in the K' value.

(16) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).
(17) S. Nagakura, *J. Am. Chem. Soc.*, **80**, 520 (1958).
(18) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 709 (1963).
(19) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Am. Chem. Soc.*, **85**, 3146 (1963).
(20) R. W. Taft, *J. Phys. Chem.*, **64**, 1805 (1960).
(21) Y. Yukawa, Y. Tsuno, and M. Sawada, *Bull. Chem. Soc. Jpn.*, **39**, 2274 (1966).

Table VIII. Correlations According to the Equation

$$\log K = \rho^* \Sigma \sigma^* + a \Sigma E_s^c + c$$

reacn	ρ^*	a	c	n	s	r	F	eq no.
HB[a]		0.291 (±0.116)	−0.152 (±0.231)	29	0.298	0.704	26.6	14
CT	−1.712 (±0.888)	0.846 (±0.403)	4.375 (±0.673)	24	0.622	0.694	9.7	15
HB[a,b]		0.297 (±0.088)	−0.109 (±0.190)	29	0.253	0.798	47.4	16
CT[b]	−1.687 (±0.571)	0.737 (±0.213)	4.355 (±0.420)	24	0.462	0.845	26.2	17

[a] The ρ^* value is significant only at 50% level. [b] The E_s^c of *i*-Bu group in tertiary amines is taken as that of neo-Pent group.

Table IX. Correlations According to Eq 18

reacn	ρ^*	a_1	a_2	c	n	s	r	F	eq no.
HB[a,b]			−0.296 (±0.076)	−0.398	29	0.229	0.838	63.7	19
CT[c]	−1.767 (±0.552)	0.437 (±0.289)	−0.619 (±0.219)	4.263 (±0.420)	24	0.385	0.900	28.5	20

[a] ρ^* and a_1 values are significant only at 50% level. [b] a_3 value is significant at 75% level. [c] a_3 value is significant at 50% level.

The CT-complex formation constants of noncyclic and cyclic amines are shown in Tables I and II, respectively. The constants determined for some compounds (**30, 33**) agree within experimental precision with those determined by Yada and co-workers[6] under the same experimental conditions. Thus, their values for nine compounds (**1–4, 10, 11, 16, 38, 42**) are included in Tables I and II and employed in the analysis. The plot according to eq 6 for 17 amines (**5, 6, 12, 13, 18, 20–22, 27, 29, 34–37, 46, 50,** and **51**) was sensibly linear indicating that the assumptions leading to the equation are entirely satisified and no side reaction is significant. For four amines (**30, 33, 41, 49**), where the K value was derived from eq 7, the values determined at different wavelengths coincide with each other within experimental precision. For the other four amines (**44, 45, 48, 52**), the E_{max} and E_A values were first determined. The K values derived from eq 9 with at least three different $[B]_0$ values agree with each other. As an example, the data for quinuclidine are shown in Table III.

Regression Analysis of Log *K* with Substituent Parameters. The correlations according to eq 3 by means of substituent parameters listed in Table IV and multiple regression analysis for the HB and CT equilibrium constants are shown in Table V. Equations 10 and 11 are derived from the data in Table I for noncyclic amines where E_s^c values of N substituents are known. Although the quality of the correlations is not as high as one would like, it is not extremely poor. Inspecting the correlations closer, we found that the calculated values for tertiary amines having at least one *i*-Bu group are considerably higher than the observed values. When we analyzed the $E_s^c(CR_1R_2R_3)$ values according to eq 1 previously,[10a] some of the component substituents should be considered as being conformationally restricted so that their effective steric effect is not expressible by their original E_s^c constants, in particular, in cases where three-component substituents are congested. Quite similarly in this work, the conformation of the *i*-Bu group would be so limited that it exerts a higher steric effect than that represented by the original E_s^c value. The β-Me branch of the *i*-Bu group may be forced to orient forward so as to exaggerate its steric effect. In other words, the higher steric effect may be due to a type of the six-number effect[10b] operative specifically in tertiary amines. The number of atoms in the six position from the electron-accepting atom is largest in the *i*-Bu group among N substituents in Table I. Assuming that the "effective" steric effect of the *i*-Bu group in tertiary amines mimicks that of the neopentyl group, the calculations were repeated to give eq 12 and 13. Quality of correlations of eq 12 and 13 is much improved over that for eq 10 and 11, respectively.

For this type of multiple regression, independent variables should be independent from each other as far as possible. As shown in Tables VI and VII, the degrees of independence among variables, especially among steric parameters, are reasonably high in warranting the above procedure.

The analyses with the use of $\sum E_s^c(R_n)$ instead of $\sum a_n E_s^c(R_n)$ show only poorer correlations as shown in eq 14 and 15 in Table VIII. They are again much improved by using the E_s^c value of the neopenyl group for the *i*-Bu group in tertiary amines as in eq 16 and 17, although the correlations are still poorer than those for eq 12 and 13. The use of E_s values instead of E_s^c also resulted in poorer correlations.

When three-component substituents are severely crowded, they may buttress each other to force hybridization changes at nitrogen relative to uncrowded cases. Thus, $\sum \sigma^*$ would become a deficient measure of their electronic effects. If this type of "growing" buttressing effect is taken into account, then the correlations may be improved over those based on eq 3. One way to test this hypothesis could be to use eq 18 for the analysis. Using

$$\log K = \rho^* \sum \sigma^* + a_1 \sum E_s^c(R_i) + a_2 \sum_{i \neq j} E_s^c(R_i) E_s^c(R_j) + a_3 E_s^c(R_1) E_s^c(R_2) E_s^c(R_3) + c \quad (18)$$

the original E_s^c values for substituents, we derived eq 19 and 20 in Table IX for HB and CT equilibrium constant, respectively. The quality of correlations seems improved over eq 10 and 11. However, the collinearities among variables, as shown in Table X, are higher so that the physicochemical meaning of each term is less warranted. Moreover, eq 12 and 13 are still better correlated than eq 19 and 20.

Discussion

The above analyses indicate that the overall effect of three N substituents of aliphatic amines on lone-pair acceptors is quantitatively factored into electronic and

Table X. Squared Correlation Matrices of Variables for Correlations According to Eq 18

	eq 19			eq 20		
	$\Sigma\sigma^*$	ΣE_s^c	$\Sigma E_s^c E_s^c$ [a]	$\Sigma\sigma^*$	ΣE_s^c	$\Sigma E_s^c E_s^c$ [a]
ΣE_s^c	0.521	1		0.710	1	
$\Sigma E_s^c E_s^c$ [a]	0.387	0.761	1	0.416	0.562	1
$E_s^c E_s^c E_s^c$ [b]	0.095	0.203	0.472	0.180	0.319	0.588

[a] $\Sigma E_s^c(R_i)E_s^c(R_j)$ $(i \neq j)$. [b] $E_s^c(R_1)E_s^c(R_2)E_s^c(R_3)$.

Table XI. Estimation of E_s^c Values for Cyclic Polydentate Ligands

	N substituent[a]			E_s^c [d] calcd		
ligand	R	$E_s^c(R)$ [b]	$\Sigma\sigma^*$ [c]	eq 12	eq 13	av[e]
$(CH_2)_4<$	H	0.32	0.23	−0.36	−0.29	−0.25 ± 0.10
	Me	0.00	−0.26	−0.36		
	i-Pr	−1.08	−0.45	−0.08	−0.15	
	n-Bu	−0.70	−0.39	−0.20	−0.17	
	i-Bu	−2.05[f]	−0.39	−0.26	−0.35	
$(CH_2)_5<$	H	0.32	0.35	−0.39	−0.09	−0.35 ± 0.15
	Me	0.00	−0.14	−0.32		
	Et	−0.38	−0.24	−0.18	−0.24	
	i-Pr	−1.08	−0.33	−0.25	−0.38	
	i-Bu	−2.05[f]	−0.27	−0.60	−0.52	
	sec-Bu	−1.74	−0.35	−0.41	−0.49	
$CH(C_2H_4)_3<$			−0.29[g]	−0.05	0.13	0.04 ± 0.13

[a] Bonded to heterocyclic nitrogen in pyrrolidine and piperidine derivatives. [b] Calculated from E_s value by eq 2. E_s values are taken from ref 3. [c] Sum of σ^* values of polydentate ligand and N substituent. Unless otherwise noted, σ^* values are taken from ref 2 and 3. [d] Per unit ligand. [e] Average of all the calculated E_s^c values shown in left two columns. [f] Taken as that of neo-Pent group; see text. [g] Estimated from log K_A value of quinuclidine[23] by using eq 21.

steric effects of component substituents according to eq 3.

The negative ρ^* value in eq 12 and 13 shows that the more the electron-donating ability of N substituents, the greater the association reactivity of amines. In both eq 12 and 13, the susceptibility constant of the steric terms decreases in the order of $a_1 > a_2 > a_3$. The association reactions with $CHCl_3$ as well as with I_2 of amines are most sensitive to the steric effect of R_1 and least to that of R_3. It is interesting to note that the ratio of a_1, a_2, and a_3 is nearly equivalent to 4.5:2:1 in eq 12 and 13. The relative significance of the steric effects of component substituents seems to be almost identical in the HB and CT reactions.

The above result could mean that the electron-acceptor molecule may locate closer to the less bulky substituents so that the atoms participating in the association, i.e., N–H–C in HB association and N–I–I in CT-complex formation, are not collinear. Another possibility is that the lone-pair electrons of the amine N do not strictly locate in the tetrahedral direction with the substituents but are most deviated from the R_3 substituent and least from the R_1 substituent. A further possibility may be that the total steric effect of N substituents is inherently expressible as the weighted sum of those of the component substituents without distortion of the geometry of either lone-pair electrons or the association complex. Further investigations are required in order to definitely clarify the ultimate origin of these empirical relationships.

The $E_s(R)$[3] as well as the $E_s^c(R)$[11] values are ultimately derived from the acid-hydrolysis rate constant of RCOOEt where R should be monodentate. Thus, the E_s^c values for bidentate (in pyrrolidine and piperidine) and tridentate (in quinuclidine) ligands cannot be estimated from the ester reactivity. However, we can estimate the E_s^c values of cyclic polydentate ligands by assigning the order of the magnitude per unit ligand relative to the E_s^c values for *N*-alkyl substituents and by substituting the observed log *K* values for cyclic secondary and tertiary amines into eq 12 and 13 along with the known E_s^c values of N substituents. From the preliminary examinations, we assumed their relative magnitudes as $E_s^c(H) > E_s^c[{}^1/_3(C_2H_4)_3CH] = E_s^c(Me) > E_s^c[{}^1/_2(CH_2)_4] > E_s^c(Et) = E_s^c[{}^1/_2(CH_2)_5] > E_s^c(n\text{-}Pr)$. We considered that each of the polydentate ligands comprises two or three equivalent units. In N-substituted piperidines, the N lone-pair electrons are known to orient either equatorially or axially.[22] In H-bonded and CT-complexed N-substituted piperidines, the conformation of the N substituents is considered to be governed by their bulkiness relative to the complexed lone-pair electrons. As a first approximation, we did not differentiate the effect of conformational variation on the complex formation since it is difficult to estimate the relative bulkiness.

The E_s^c values are calculated as shown in Table XI. The $\sum\sigma^*$ values used for these ligands were estimated by using eq 21 with log K_A of tertiary ammonium ions having

$$\log K_A = 3.30\sum\sigma^* - 9.61 \qquad (21)$$

heterocyclic components.[2] The log K_A value of quinuclidine is −10.58.[23] For the *N*-*i*-Bu derivatives of pyrrolidine and piperidine, the E_s^c value of the *i*-Bu substituent was taken as that of the neopentyl group in a manner similar to that for the noncyclic tertiary amines. Although the E_s^c values estimated for each of the cyclic ligand units are scattered to some extent with variation of N substituents, the scatter is not very large. The averaged E_s^c values of the unit ligands are compared with those of monodentate alkyl groups in Table IV. It is shown that $E_s^c(Et) < E_s^c[{}^1/_2(CH_2)_4] < E_s^c(Me)$, $E_s^c[{}^1/_2(CH_2)_5] \simeq E_s^c(Et)$, and $E_s^c[{}^1/_3(C_2H_4)_3CH] \simeq E_s^c(Me)$. We assigned the E_s^c value for each of the unit ligands by simulating them to those of existing E_s^c values as far as possible, as $E_s^c[{}^1/_2(CH_2)_4] = {}^1/_2[E_s^c(Me) + E_s^c(Et)] = -0.19$, $E_s^c[{}^1/_2(CH_2)_5] = E_s^c(Et) = -0.38$ and $E_s^c[{}^1/_3(C_2H_4)_3CH] = E_s^c(Me) = 0$ (Table IV).

(22) M. Tsuda and Y. Kawazoe, *Chem. Pharm. Bull.*, **16**, 702 (1968).
(23) B. M. Wepster, *Recl. Trav. Chim., Pays-Bas*, 71, 1171 (1952).

Table XII. Correlations for Various Reactivity Data of Aliphatic Amines

$$\log K = \rho^*\Sigma\sigma^* + a_1E_S^c(R_1) + a_2E_S^c(R_2) + a_3E_S^c(R_3) + bn_H + c$$

reacn system	log K	ρ^*	a_1	a_2	a_3	b	c	n	s	r	F	eq no.
HB formation in CCl_4, 27 °C	log K	0.473	0.637	0.321			1.969	31	0.090	0.931	58.6	22
$R_1R_2R_3N$ + HOPh	(L/mol)	(±0.121)	(±0.123)	(±0.090)			(±0.066)					
assocn in gas phase, 100 °C	log K	4.878	14.585	4.879	1.461		0.001	17	0.569	0.876	9.9	23
$R_1R_2R_3N$ + BMe_3	(atm^{-1})	(±2.087)	(±5.655)	(±2.578)	(±0.594)		(±0.755)					
Menshutkin reacn in Me_2CO,	log K	0.801	1.701		0.843[a]		−2.546	13	0.388	0.967	43.3	24
35 °C, $R_1R_2R_3N$ + EtI	(L/mol s)	(±0.438)	(±0.834)		(±0.500)		(±0.502)					
acid dissocn of conjugate	log K_A	3.603		−0.335[a]		−1.427	−9.545	29	0.168	0.962	103.2	25
cation of primary and	(mol/L)	(±0.465)		(±0.097)		(±0.250)	(±0.414)					
secondary amines												

[a] The coefficient of the combined steric term $[E_S^c(R_2) + E_S^c(R_3)]$.

Table XIII. Hydrogen-Bond Formation of Aliphatic Amines with Phenol

	log K			log K	
substituents	obsd[a]	calcd[b]	substituents	obsd[a]	calcd[b]
H_2, n-Pr	1.91	1.86	H, i-Pr_2	1.75	1.77
H_2, i-Pr	2.01	1.90	H, n-Bu_2	1.93	1.84
H_2, n-Bu	1.96	1.87	H, t-Bu_2	1.62	1.66
H_2, i-Bu	1.87	1.87	H, n-$Pent_2$	1.93	1.86
H_2, sec-Bu	1.93	1.91	H, Bz_2	1.35	1.52
H_2, t-Bu	1.96	1.95	Me_2, c-Hex	1.96	2.04
H_2, n-Pent	1.90	1.89	Et_3	1.82	1.75
H_2, i-Pent	1.88	1.89	n-Pr_3	1.51	1.49
H_2, n-Hex	1.87	1.89	n-Bu_3	1.47	1.48
H_2, n-Hept	1.85	1.89	n-$Pent_3$	1.51	1.52
H_2, n-Oct	1.93	1.88	i-$Pent_3$	1.58	1.57
H_2, n-Non	1.90	1.88	n-Oct_3	1.58	1.56
H_2, n-Dec	1.91	1.88	$(allyl)_3$	1.29	1.39
H_2, Bz	1.63	1.71	Me_2, Bz	1.55	1.86
H, Et_2	1.98	1.91	Bz_3	1.12	1.00
H, n-Pr_2	1.89	1.83			

[a] From D. Clotman and Th. Zeegers-Huyskens, *Spectrochim. Acta, Part A*, **23**, 1627 (1967). [b] By eq 22.

Table XIV. Association of Aliphatic Amines with Trimethylboron

	log K			log K	
substituents	obsd[a]	calcd[b]	substituents	obsd[a]	calcd[b]
H_3	−0.66	−0.47	H_2, n-Hex	1.41	1.18
H_2, Me	1.44	1.45	H, Me_2	1.67	2.28
H_2, Et	1.15	1.38	H, Et_2	−0.09	0.85
H_2, n-Pr	1.22	1.01	Me_3	0.33	0.00
H_2, i-Pr	0.43	0.80	Me_2, n-Bu	−1.01[c]	−0.39
H_2, n-Bu	1.33	1.06	H, $(CH_2)_4$	2.46	2.34
H_2, sec-Bu	0.43	−0.07	H, $(CH_2)_5$	1.68	0.55
H_2, t-Bu	−0.98	−0.68	$CH(C_2H_4)_3$	1.71	1.42
H_2, n-Pent	1.38	1.19			

[a] Unless otherwise noted, from H. C. Brown, D. H. McDaniel, and O. Häfliger, "Determination of Organic Structures by Physical Methods", Vol. 1, E. A. Braude and F. C. Nachod, Eds., Academic Press, New York, N.Y., 1955, p 634. [b] By eq 23. [c] From H. C. Brown and R. B. Johannesen, *J. Am. Chem. Soc.*, 75, 16 (1953).

Table XV. Menschutkin Reaction Rate of Aliphatic Amines with Ethyl Iodide

	log K	
substituents	obsd[a]	calcd[b]
H_2, n-Pr	−2.89	−2.99
H_2, n-Bu	−2.90	−3.00
H, Et_2	−3.32	−2.87
H, n-Pr_2	−3.46	−3.34
H, n-Bu_2	−3.45	−3.37
H, $(NCCH_2)_2$	−6.64	−6.58
H, $(NCCH_2CH_2)_2$	−5.16	−5.71
Me_3	−2.19	−2.55
Et_3	−3.76	−3.59
n-Pr_3	−4.33	−4.53
n-Bu_3	−4.25	−4.60
Et_2, $NCCH_2$	−6.13	−5.45
Et_2, $NCCH_2CH_2$	−5.13	−5.01

[a] From ref 4. [b] By eq 24.

In examining the applicability of the present procedure, we attempted to analyze various reactivity data for aliphatic amines published in the literature. Unfortunately, not many published data are suitable for this type of correlation because of certain collinearities among steric and electronic substituent parameters. A few examples are shown in Table XII as eq 22–25, using data listed in Tables XIII–XVI, respectively. In Tables XIV and XVI, cyclic amines are included. Although the number of

Table XVI. log K_A Values of Conjugate Cations of Aliphatic Primary and Secondary Amines

substituents	log K_A obsd[a]	log K_A calcd[b]	substituents	log K_A obsd[a]	log K_A calcd[b]
H_2, Me	−10.62	−10.40	H, Me_2	−10.64	−10.64
H_2, Et	−10.63	−10.63	H, Et_2	−10.98	−11.10
H_2, *n*-Pr	−10.53	−10.57	H, *n*-Pr_2	−11.00	−11.01
H_2, *i*-Pr	−10.63	−10.72	H, *i*-Pr_2	−11.05	−11.28
H_2, *n*-Bu	−10.59	−10.64	H, *n*-Bu_2	−11.25	−11.10
H_2, *i*-Bu	−10.43	−10.42	H, *i*-Bu_2	−10.50	−10.70
H_2, *sec*-Bu	−10.56	−10.58	H, *sec*-Bu_2	−11.01	−10.98
H_2, *t*-Bu	−10.45	−10.66	H, c-Hex, *t*-Bu	−11.23	−10.96
H_2, neo-Pent	−10.21	−10.29	H, Me, allyl	−10.11	−9.97
H_2, c-Hex	−10.64	−10.47	H, $(allyl)_2$	−9.29	−9.30
H_2, c-$HexCH_2$	−10.49	−10.19	H, Me, Bz	−9.58	−9.61
H_2, allyl	−9.49	−9.73	H, Et, Bz	−9.68	−9.84
H_2, Bz	−9.34	−9.38	H, $(CH_2)_4$	−11.27	−11.44
H_2, $BzCH_2$	−9.83	−9.88	H, $(CH_2)_5$	−11.22	−10.88
H_2, $BzCH_2CH_2$	−10.20	−10.07			

[a] From ref 2. [b] By eq 25.

Table XVII. Squared Correlation Matrices of Variables in Eq 22 and 23

	eq 22			eq 23		
	$\Sigma\sigma^*$	$E_s^c(R_1)$	$E_s^c(R_2)$	$\Sigma\sigma^*$	$E_s^c(R_1)$	$E_s^c(R_2)$
$E_s^c(R_1)$	0.550	1		0.580	1	
$E_s^c(R_2)$	0.476	0.230	1	0.465	0.061	1
$E_s^c(R_3)$	0.020	0.073	0.038	0.014[a]	0.057[a]	0.121[a]

[a] The $E_s^c(R_3)$ term is insignificant in eq 23.

compounds included in the various sets for correlation is still short for this type of multiple regression analysis[24] and although the quality of the correlations is still not high, the overall results seem to support the present procedure. The collinearity among variables is indicated in Tables XVII–XVIII.

The ρ^* value in eq 22 which is quite close to that in eq 12 is reasonable since they are derived from similar hydrogen bonding equilibrium data sets. The $E_s^c(R_3)$ term is not significant in eq 22. This may be due to the fact that the benzene ring of phenol is situated furthest from R_3 substituents in the hydrogen-bonded complex. The ρ^* value for B–N complexation in eq 23 is large because this is a strong(est) bond. Thus, the distance between associating partners is close resulting in large a_i values. In each of eq 24 and 25, the magnitudes of the a_2 and a_3 values are close to each other. The $E_s^c(R_2)$ and $E_s^c(R_3)$ terms are combined to reduce the number of independent variables.

Equation 25 does not include log K_A values of tertiary ammonium ions which are correlated very nicely without the $E_s^c(R_i)$ term as eq 21.[2] Since R_1 (=H) is invariable in the set of primary and secondary ammonium ions, the $E_s^c(R_1)$ term does not appear in eq 25. As suggested by Hall,[2] the steric effect of substituents operates significantly only in primary and secondary ammonium ions where more than one ^+N–H hydrogen atoms are capable of associating with water. n_H is the number of hydrogen atoms in ammonium ions which accounts for the stabilization effect due to the hydration which is proportional to the number of hydration sites.[25]

Taft and co-workers have shown that linear free-energy relationships hold for hydrogen-bonded-complex formation of various hydrogen donors.[26] The relationships follow eq 26, where K is the HB equilibrium constant with a series

$$\log K = m(pK_{HB}) + c \qquad (26)$$

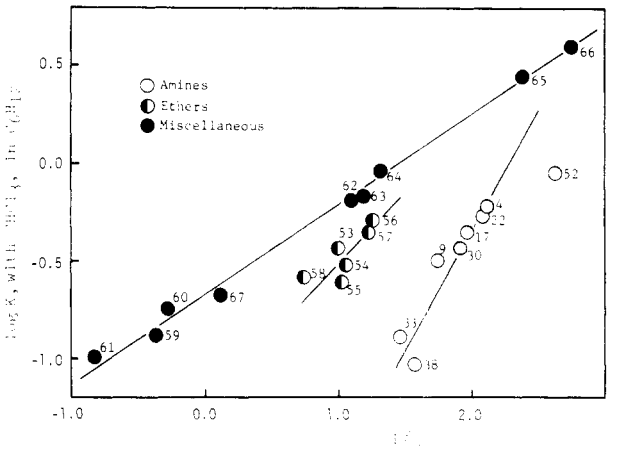

Figure 1. Hydrogen bonding equilibrium constant, log K, of various H acceptors with $CHCl_3$ plotted against the Taft pK_{HB} value.

of H acceptors for a number of OH reference acids in inert solvents and pK_{HB} is the log of the corresponding constant for *p*-fluorophenol adduct in CCl_4 at 25 °C. The constants m and c are characteristic of the H donor, temperature, and the solvent. Similar correlations are found between log K values for phenol adduct and those for $CHCl_3$ adduct in CCl_4 by Gramstad and Vikane of a number of phosphoryl, carbonyl, and sulfonyl H acceptors.[27] In Figure 1, the log K values for various H acceptors with $CHCl_3$ in cyclohexane at 35 °C shown in Table XIX are plotted against the available Taft pK_{HB} values. The log K values except for those of most of aliphatic amines, benzene, and substituted benzenes are taken from the literature.[8,28] While the log K values for monosubstituted benzenes, carbonyl and phosphoryl compounds, and thioethers are correlated linearly, those for ethers and amines fall on the separate lines. The lower two lines, especially the amine family line, are not parallel with the upper line. The deviation of the ether and amine points from the upper line as well as the scatter along the lower family lines correspond to the steric requirements of substituents. For the aromatic π and the terminal double-bonded oxygen bases and the sulfur lone-pair electrons, the steric requirement for the complex formation with $CHCl_3$ is similar to that for the association with *p*-fluorophenol. For ethers and amines, however, this is not the case. Thus, the pK_{HB}

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(28) G. R. Wiley and S. I. Miller, *J. Am. Chem. Soc.*, **94**, 3287 (1972).

Table XVIII. Squared Correlation Matrices of Variables in Eq 24 and 25

	eq 24				eq 25			
	$\Sigma\sigma^*$	$E_s^c(R_1)$	$E_s^c(R_2)$	$E_s^c(R_3)$	$\Sigma\sigma^*$	$E_s^c(R_2)$	$E_s^c(R_3)$	$\Sigma E_s^{c\,a}$
$E_s^c(R_1)$	0.266	1						
$E_s^c(R_2)$	0.168[b]	0.000[b]	1		0.758[b]	1		
$E_s^c(R_3)$	0.476[b]	0.000[b]	0.243[b]	1	0.033[b]	0.047[b]	1	
$\Sigma E_s^{c\,a}$	0.377	0.000	0.805[b]	0.675[b]	0.430	0.570[b]	0.643[b]	1
n_H					0.674	0.608[b]	0.037[b]	0.120

[a] $E_s^c(R_2) + E_s^c(R_3)$. [b] These combinations of variables are not used in correlations.

Table XIX. Hydrogen Bonding Equilibrium Constant, log K, of Various H Acceptors with $CHCl_3$ in Cyclohexane at 35 °C and the Taft pK_{HB} Value

no.[a]	H acceptor	log K[b]	pK_{HB}[c]
	Amines		
4	n-$BuNH_2$	−0.21	2.11
9	$BzNH_2$	−0.49	1.75
17	Me_2-n-PrN	−0.34[d]	1.98
22	Me_2-c-HexN	−0.26	2.08[i]
30	Et_3N	−0.43	1.91
33	n-Pr_3N	−0.89	1.45
38	n-Bu_3N	−1.03	1.57
52	$CH(C_2H_4)_3N$	−0.04	2.63[i]
	Ethers		
53	Et_2O	−0.43[d]	1.01[i]
54	i-Pr_2O	−0.52[d]	1.05
55	n-Bu_2O	−0.61[e]	1.02
56	$(CH_2)_4O$	−0.29[d]	1.26
57	$(CH_2)_5O$	−0.35[d]	1.23
58	$O(C_2H_4)_2O$	−0.59[f,g]	0.73[g,i]
	Miscellaneous		
59	C_6H_6	−0.88[h]	−0.36[j]
60	C_6H_5Me	−0.75[h]	−0.29[j]
61	C_6H_5Br	−0.99[h]	−0.84[j]
62	MeCOOEt	−0.19[f]	1.09[i]
63	Me_2CO	−0.17[f]	1.18
64	$(CH_2)_5CO$	−0.04[f]	1.32[i]
65	$CH_2(CH_2)_2CONMe$	0.45[f]	2.37
66	$(EtO)_3PO$	0.61[f]	2.73
67	Et_2S	−0.68[f]	0.11

[a] The compound number of amines is the same as in Tables I and II. [b] Unless otherwise noted, data from this laboratory. [c] Unless otherwise noted, from ref 26. [d] At 34 °C, from ref 8. [e] At 28 °C, from ref 28. [f] The values estimated from those at 28 °C by using the ΔH° and ΔS° values in ref 28. [g] Statistical factor of 2 has been applied. [h] For the corresponding deuterium compound. [i] From L. Joris, J. Mitsky, and R. W. Taft, *J. Am. Chem. Soc.*, 94, 3438 (1972). [j] From T. Fujita, T. Nishioka, and M. Nakajima, *J. Med. Chem.*, **20**, 1071 (1977).

value for ethers and amines, in particular, that for amines, should not be regarded as a direct index for the HB equilibrium with such CH reference acids as $CHCl_3$. In $CHCl_3$, the steric effect of Cl_3C moiety on the H acceptor is more significant than that of RO moiety in OH reference acids, as evident by comparison of eq 12 and 22.

Bogatkov and co-workers[12] have analyzed a number of existing reactivity data for aliphatic amines. They used the two-parameter equation

$$\log K = \rho^*\Sigma\sigma^* + aE_N + \text{constant} \qquad (27)$$

where E_N is the constant for the total steric effect of N substituents defined as $E_N(R_1R_2R_3N) = E_s(R_1R_2R_3C)$. The most difficult problem in applying this procedure is to know the corresponding $E_s(R_1R_2R_3C)$ values for all of amines included in each of the data sets. This is not always possible, in particular, for tertiary amines where various combinations of substituents are involved. Thus, although they have found acceptable correlations for 18 reaction series, some of the compounds for which the corresponding $E_s(R_1R_2R_3C)$ value is not available were not included in correlations. Our procedure does not require such prior knowledge of $E_s(R_1R_2R_3C)$ values. One disadvantage in applying our procedure is that it should include many more compounds in a set to obtain meaningful correlations since the number of independent variables is usually four (one for electronic and three for steric). Nevertheless, we believe the versatility of our procedure which is not limited to the type of reactions where $E_N(R_1R_2R_3N)$ can be approximated by $E_s(R_1R_2R_3C)$. Work performed quite recently in this laboratory indicates that the procedure, where the total steric effect is analyzed in terms of the effect of component substituents, is indeed applicable to the interaction between ammonium ions, $R_1R_2R_3R_4N^+$, and a counteranion. The result will be published elsewhere.

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Registry No. **1**·I_2, 15457-69-9; **2**·I_2, 65756-34-5; **3**·I_2, 13347-61-0; **4**, 109-73-9; **4**·I_2, 7094-39-5; **5**·I_2, 37053-94-4; **6**·I_2, 36951-63-0; **7**, 111-26-2; **8**, 108-91-8; **9**, 100-46-9; **10**·I_2, 22396-67-4; **11**·I_2, 13347-62-1; **12**·I_2, 70623-51-7; **13**·I_2, 70623-52-8; **14**, 111-92-2; **15**, 110-96-3; **16**·I_2, 6982-28-1; **17**, 926-63-6; **18**, 927-62-8; **18**·I_2, 70623-53-9; **19**, 7239-24-9; **20**, 921-04-0; **20**·I_2, 70623-54-0; **21**, 918-02-5; **21**·I_2, 70623-55-1; **22**, 98-94-2; **22**·I_2, 70623-56-2; **23**, 616-39-7; **24**, 52841-28-8; **25**, 3405-42-3; **26**, 10342-97-9; **27**, 10471-20-2; **27**·I_2, 70623-57-3; **28**, 26819-66-9; **29**, 7560-83-0; **29**·I_2, 70623-58-4; **30**, 121-44-8; **30**·I_2, 2071-89-8; **31**, 4458-31-5; **32**, 4444-68-2; **33**, 102-69-2; **33**·I_2, 40651-41-0; **34**, 60021-92-3; **34**·I_2, 70623-59-5; **35**, 60021-91-2; **35**·I_2, 70623-60-8; **36**, 5792-46-1; **36**·I_2, 70623-61-9; **37**·I_2, 70623-62-0; **38**, 102-82-9; **38**·I_2, 70623-63-1; **39**, 27942-54-7; **40**, 645-41-0; **41**, 123-75-1; **41**·I_2, 70623-64-2; **42**, 110-89-4; **43**, 120-94-5; **44**, 17544-07-9; **44**·I_2, 70623-65-3; **45**, 767-10-2; **45**·I_2, 70623-66-4; **46**, 39198-81-7; **46**·I_2, 70623-67-5; **47**, 626-67-5; **48**, 766-09-6; **48**·I_2, 70623-68-6; **49**, 766-79-0; **49**·I_2, 70623-69-7; **50**, 10315-89-6; **50**·I_2, 70623-70-0; **51**, 25991-45-1; **51**·I_2, 70623-71-1; **52**, 100-76-5; **52**·I_2, 23290-15-5; propylamine, 107-10-8; isopropylamine, 75-31-0; isobutylamine, 78-81-9; *sec*-butylamine, 13952-84-6; *tert*-butylamine, 75-64-9; pentylamine, 110-58-7; isopentylamine, 107-85-7; heptylamine, 111-68-2; octylamine, 111-86-4; nonylamine, 112-20-9; decylamine, 2016-57-1; diethylamine, 109-89-7; dipropylamine, 142-84-7; dipropylamine, 108-18-9; dipentylamine, 2050-92-2; dibenzylamine, 103-49-1; tripentylamine, 621-77-2; trioctylamine, 1116-76-3; triallylamine, 102-70-5; *N,N*-dimethylbenzylamine, 103-83-3; tribenzylamine, 620-40-6; ammonia, 7664-41-7; methylamine, 74-89-5; ethylamine, 75-04-7; dimethylamine, 124-40-3; trimethylamine, 75-50-3; $NR_1R_2R_3$ (R_1 = H, R_2 = R_3 = $(NCCH_2)$), 628-87-5; $NR_1R_2R_3$ (R_1 = H, R_2 = R_3 = $(NCCH_2CH_2)$), 111-94-4; $NR_1R_2R_3$ (R_1 = R_2 = Et, R_3 = $(NCCH_2)$), 3010-02-4; $NR_1R_2R_3$ (R_1 = R_2 = Et, R_3 = $(NCCH_2CH_2)$), 5351-04-2; $NR_1R_2R_3$ (R_1 = R_2 = H, R_3 = *neo*-pentyl), 5813-64-9; $NR_1R_2R_3$ (R_1 = R_2 = H, R_3 = c-Hex CH_2), 3218-02-8; $NR_1R_2R_3$ (R_1 = R_2 = H, R_3 = allyl), 107-11-9; $NR_1R_2R_3$ (R_1 = R_2 = H, R_3 = $BzCH_2$), 64-04-0; $NR_1R_2R_3$ (R_1 = R_2 = H, R_3 = $BzCH_2CH_2$), 2038-57-5; $NR_1R_2R_3$ (R_1 = H, R_2 = R_3 = *sec*-Bu), 626-23-3; $NR_1R_2R_3$ (R_1 = H, R_2 = c-Hex, R_3 = *tert*-Bu), 51609-06-4; $NR_1R_2R_3$ (R_1 = H, R_2 = Me, R_3 = allyl), 627-37-2; $NR_1R_2R_3$ (R_1 = H, R_2 = R_3 = allyl), 124-02-7; $NR_1R_2R_3$ (R_1 = H, R_2 = Me, R_3 = Bz), 103-67-3; $NR_1R_2R_3$ (R_1 = H, R_2 = Et, R_3 = Bz), 14321-27-8.