mercuric acetate and 60 ml. of 5% aqueous acetic acid was converted to 1.75 g. of perchlorate **8**, m.p. 233.5–235.5°, infrared maximum 1670 cm.$^{-1}$ (C=N$^+$) (in KBr pellet) and ultraviolet maxima at 264 mμ (ε 1200) and 272 (1200). A mixture melting point of this material with the perchlorate **6** was depressed (m.p. 202–205°).

Anal. Calcd. for $C_{17}H_{22}ClNO_4$: C, 60.08; H, 6.53; N, 4.12. Found: C, 59.78; H, 6.28; N, 4.36.

A portion of the perchlorate **9** was converted to the corresponding enamine using sodium hydroxide. Distillation of the product through a Hickmann apparatus and trituration of the distillate with a drop of ethanol gave material with m.p. 74.5–76.5° and infrared maximum at 1650 cm.$^{-1}$ (C=C) (in chloroform).

3-Methoxy-2-picoline.—To a stirred solution of 26 g. of diazomethane in 2 l. of ether cooled to 5° was added dropwise over a 30-min. period 60 g. of 3-hydroxy-2-picoline in 500 ml. of butanol. With continued stirring overnight, the temperature of the solution was allowed to rise to room temperature. The solution was distilled through a short Vigreux column and gave 31 g. of 3-methoxy-2-picoline, b.p. 84.5–85.5° (17 mm.), n^{28}D 1.5128, ultraviolet maxima at 221 mμ (ε 7150) and 279 (5400), and picrate derivative m.p. 166–168° (lit.[13] m.p. 167–168°). The residue from the distillation was crystallized from an acetonitrile–hexane mixture and gave 13.0 g. of unchanged 3-hydroxy-2-picoline, m.p. 167–169° (lit.[15] m.p. 170–171°).

Ethyl 3-Methoxy-2-pyridylacetate.—To a solution of phenyllithium prepared from 5.0 g. of lithium wire, 400 ml. of ether, and 56.3 g. of bromobenzene was added with stirring 44.0 g. of 3-methoxy-2-picoline over a 45-min. period. The red solution was treated with excess Dry Ice. The mixture was allowed to stand overnight and the ether was then removed *in vacuo*. Absolute ethanol (300 ml.) was added to the solid and, while the mixture was cooled in an ice bath, a saturated solution of ethanolic hydrogen chloride was added dropwise with stirring until the mixture was strongly acidic. The mixture was allowed to stand for 10 hr. at room temperature when most of the ethanol was removed *in vacuo* and 400 ml. of chloroform was added. The chloroform solution was stirred with a paste of 110 g. of potassium carbonate and 65 ml. of water for 30 min., then filtered. The filtrate was washed with water, concentrated, and distilled to give 17.7 g. of 3-methoxy-2-picoline, b.p. 85–87° (18 mm.), and 20.8 g. of ethyl 3-methoxy-2-pyridylacetate, b.p. 94.0–94.5° (0.5 mm.), n^{21}D 1.5038, and infrared maximum at 1730 cm.$^{-1}$ (ester C=O).

Anal. Calcd. for $C_{10}H_{13}NO_3$: C, 61.52; H, 6.71; N, 7.18. Found: C, 61.40; H, 6.77; N, 7.34.

The **picrate** derivative was obtained from ethanol and melted at 156–158°.

Anal. Calcd. for $C_{16}H_{16}N_4O_{10}$: C, 45.29; H, 3.80; N, 13.21. Found: C, 45.32; H, 4.01; N, 13.24.

2-Hydroxyethyl-3-methoxypyridine.—To a stirred solution of 800 ml. of ether and 8.3 g. of lithium aluminum hydride was added dropwise 37.0 g. of ethyl 3-methoxy-2-pyridylacetate. After 1 hr., 8.3 ml. of water was added cautiously followed by 8.3 ml. of 15% sodium hydroxide solution and 25 ml. of water. The ether solution was filtered, dried, and concentrated giving 27.5 g. of product with m.p. 76–80° and infrared maximum at 3340 cm.$^{-1}$ (associated O–H). The analytical sample was recrystallized from hexane–ethyl acetate, m.p. 79–80°.

Anal. Calcd. for $C_8H_{11}NO_2$: C, 62.72; H, 7.24; N, 9.15. Found: C, 62.96; H, 7.37; N, 9.28.

The **picrate** derivative was prepared in ethanol and had m.p. 146–149°.

Anal. Calcd. for $C_{14}H_{14}N_4O_9$: C, 43.98; H, 3.69; N, 14.66. Found: C, 44.03; H, 3.61; N, 14.90.

3-Methoxy-2-vinylpyridine (12).—To 150 ml. of 50% sodium hydroxide solution heated to reflux was added dropwise a solution of 6.5 g. of 2-hydroxyethyl-3-methoxypyridine in 25 ml. of water. The product steam distilled from the reaction mixture. The distillate was extracted with ether and the ether extract was dried over sodium hydroxide. Distillation of the solution gave 3.5 g. of 3-methoxy-2-vinylpyridine, b.p. 60–62° (0.5 mm.), n^{23}D 1.5600, and ultraviolet maxima at 237 mμ (ε 9850) and 308 (7000).

Anal. Calcd. for C_8H_9NO: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.30; H, 6.96; N, 10.58.

The **picrate** derivative was obtained from ethanol, m.p. 139–141° (softened at 132°).

Anal. Calcd. for $C_{14}H_{12}N_4O_8$: C, 46.16; H, 3.32; N, 15.38. Found: C, 46.25; H, 3.30; N, 15.34.

Acknowledgment.—The author is indebted to Dr. N. A. Nelson for his helpful suggestions and constant interest and encouragement.

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Studies on the Base Strengths of N,N-Disubstituted Amides

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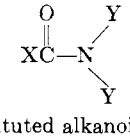
The carbonyl stretching vibration frequencies were determined for a series of N,N-disubstituted alkanoic acid amides and closely related compounds in dilute solution in isooctane ($\gamma_{C=O(iso)}$) and in chloroform ($\gamma_{C=O(HCCl_3)}$). pK_a values were determined by potentiometric titration in dilute nitromethane solution using perchloric acid as titrant. A linear relationship was found between $\gamma_{C=O(iso)}$ and $\Sigma\sigma^*$, where σ^*-values for X were the Taft polar factors, and σ^*-values for NY_2 were empirically estimated. A linear relation was also observed between pK_a and σ^* for the N,N-disubstituted formamides and acetamides but not for the N,N-disubstituted propionamides. With chloroform as the electron acceptor, relative base strengths were measured by $\Delta\gamma_{C=O}/\gamma_{C=O(iso)}$, where $\Delta\gamma_{C=O}$ was $\gamma_{C=O(iso)} - \gamma_{C=O(HCCl_3)}$. In this case, an increase in $\Delta\gamma_{C=O}/\gamma_{C=O(iso)}$ with increase in $\Sigma\sigma^*$ was observed only for the formamides. Using published data for log K_{assn} with phenol as the acid, $\Sigma\sigma^*$-log K_{assn} relationships were obtained which were intermediate to those using perchloric acid and chloroform. These results permitted an analysis of the variable steric effects in the free base and in the associated complexes. The order of steric requirements was found to be perchloric acid < phenol < chloroform. Evidence is presented that relief of steric strains in these complexes occurs through twisting about the C–N bond.

We have been concerned with various Lewis bases in nonaqueous systems and how the base strength relates to structure. Toward this end, spectroscopic and potentiometric titration measurements were made on



N,N-Disubstituted alkanoic acid amides

a series of N,N-disubstituted alkanoic acid amides and closely related compounds in dilute solution, using perchloric acid and chloroform as electron acceptors. The relative base strengths were compared with literature values using phenol and also iodine as electron acceptors.

The general approach and results are presented in the next section and in Tables I–III. This is followed by a discussion of the base strength parameters and an

TABLE I

PHYSICAL CONSTANTS OF N,N-DISUBSTITUTED AMIDES

	N,N-Disubstituted amides	B.p. (mm.), °C.	Density at 25°	Refractive index, $n^{25}D$	$\Sigma\sigma^*$ [a]	Log K_{assn} (phenol, 20°)
(1)	N,N-Dimethylformamide	55 (20)[b]	0.94	1.4279[c]	+0.49	1.90[d]
(2)	N,N-Diethylformamide	79 (20), 67 (14)[e]	0.90	1.4321[f]	+0.41[g]	1.87[h]
(3)	N,N-Dimethylacetamide	65 (20)	0.94	1.4351	0	2.21[h]
(4)	N,N-Diethylacetamide	86 (24)[i]	0.90	1.4369[j]	−0.20	2.20[d]
(5)	N,N-Di-*n*-propylacetamide	101 (16)[k]	0.88	1.4410[l]	−0.23	
(6)	N,N-Diisopropylacetamide	87–88 (17)[m]	0.88	1.4378	−0.38	
(7)	N,N-Dimethylpropionamide	77 (22)	0.92	1.4376	−0.10	2.11[h]
(8)	N,N-Diethylpropionamide	91.5–92 (22)[n]	0.89	1.4390	−0.30	2.13[d]
(9)	N,N-Di-*n*-butylpropionamide	125 (13)[o]	0.87	1.4450	−0.36	
(10)	N,N-Diisobutylpropionamide	110 (12)[p]	0.87	1.4436	−0.35	
(11)	N-Acetylpiperidine	109 (18)[q]	1.00	1.4790	−0.18	2.13[d]
(12)	N-Formylpyrrolidine	96 (14)	1.02	1.4770	+0.39[r]	
(13)	N,N-Diethylbutyramide	52 (0.5)[d]			−0.32	2.09[d]
(14)	N-Propionylpiperidine	50 (4)[d]			−0.28	2.09[d]
(15)	N-Butyrylpiperidine	70 (1)[d]			−0.30	2.11[d]

[a] Where $\Sigma\sigma^* = \Sigma$ Taft σ^*-values for X and 2Y in all cases except 1, 2, and 12, where $\Sigma\sigma^* = \sigma_X{}^* + 0.42\Sigma(2\sigma_Y{}^*)$. $\sigma_Y{}^*$-values for 11 and 12 from ref. 17. [b] 153° (760), product information bulletin on dimethylformamide, Du Pont Industrial and Biochemicals Department. [c] 1.4269, footnote *b*. [d] Ref. 1. [e] 69° (15), Eastman Chemical Catalog; 59° (6), ref. 1. [f] 1.4296, J. H. Robson and J. Reinhard, *J. Am. Chem. Soc.*, **77**, 498 (1955). [g] $\Sigma\sigma^*$ uncorrected +0.29. [h] Calculated from K_{assn}, ΔH data at 25°, ref. 13. [i] 88.5–91° (31), footnote *f*. [j] 1.4333, footnote *f*. [k] 94.5° (12), footnote *f*. [l] 1.4411, footnote *f*. [m] 71–73° (6), footnote *e*. [n] 55° (2), ref. 1. [o] 115–116° (6), footnote *e*. [p] 99–100° (4), footnote *e*. [q] 60° (0.4), ref. 1. [r] $\Sigma\sigma^*$ uncorrected +0.23.

TABLE II

SPECTROSCOPIC DATA ON N,N-DISUBSTITUTED AMIDES

	N,N-Disubstituted amides	$\gamma_{C=O(iso)}$, cm.$^{-1}$	$\gamma_{C=O(HCCl_3)}$, cm.$^{-1}$	$10^3\Delta\gamma/\gamma$ [a]	—Relative frequency shifts— Acetophenone reference[b]	Dimethylformamide reference[c]
(1)	N,N-Dimethylformamide	1697[d,e]	1673[f]	14.2[g]	0.58[h]	1.00
(2)	N,N-Diethylformamide	1693	1663	17.7	0.46	0.80
(3)	N,N-Dimethylacetamide	1674	1633	24.4	0.34	0.58
(4)	N,N-Diethylacetamide	1665[i,j]	1627[k]	22.8	0.36[l]	0.62
(5)	N,N-Di-*n*-propylacetamide	1663	1627	21.6	0.38	0.66
(6)	N,N-Diisopropylacetamide	1660	1625	21.1	0.39	0.67
(7)	N,N-Dimethylpropionamide	1675	1633	25.1	0.33	0.58
(8)	N,N-Diethylpropionamide	1664[m]	1625	23.4	0.35	0.61
(9)	N,N-Di-*n*-butylpropionamide	1662	1624	22.8	0.36	0.62
(10)	N,N-Diisobutylpropionamide	1661	1624	22.3	0.37	0.64
(11)	N-Acetylpiperidine	1666[n]	1625	24.6	0.33	0.58
(12)	N-Formylpyrrolidine	1693	1660	19.5	0.42	0.73
(13)	N,N-Diethylbutyramide	1657[o]				
(14)	N-Propionylpiperidine	1659[o]				
(15)	N-Butyrylpiperidine	1658[o]				

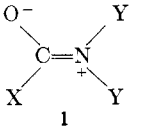
[a] $\gamma_{C=O(iso)} - \gamma_{C=O(HCCl_3)}/\gamma_{C=O(iso)}$. [b] $[\Delta\gamma/\gamma_{(acetophenone)}]/[\Delta\gamma/\gamma_{(amide)}]$. [c] $[\Delta\gamma/\gamma_{(DMF)}]/[\Delta\gamma/\gamma_{(amide)}]$. [d] 1696 cm.$^{-1}$, L. J. Bellamy and R. L. Williams, *Trans. Faraday Soc.*, **55**, 14 (1959). Hexane was solvent. [e] 1699 cm.$^{-1}$ as estimated by addition of 7 cm.$^{-1}$ to $\gamma_{C=O(CCl_4)}$-value, as reported in ref. 1. [f] 1673 cm.$^{-1}$, footnote *d*. [g] 13.6 as calculated from footnotes *d* and *f*. [h] 0.60 as calculated from footnotes *d* and *f*. [i] 1667, ref. 14. [j] 1664, estimated as in footnote *e*. [k] 1628, ref. 14. [l] 0.35, calculated from footnotes *i* and *k*. [m] 1664, as estimated in footnote *e*. [n] 1664, estimated as in footnote *e*. [o] Estimated as in footnote *e*.

analysis of the variable steric effects present in these systems.

Results

I. Polarity Measurements on the Free Base.—For an analysis of structural effects in the associated complexes, it was of value to examine initially the free base, to demonstrate a polarity parameter, and to determine the effects of structural variations on polarity.

It is generally recognized that (1) the N,N-disubstituted amides exist essentially in a planar configuration, (2) that the polar resonance structure makes an important contribution to the ground state (structure **1**), and (3) that the acid–base interactions occur through the nonbonding electrons on the oxygen atom.[1-6]



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The electron density on the oxygen atom is directly related to the polar effects of the substituents on the carbonyl group. Therefore, two parameters related to the polar contributions of the substituents were compared: (1) the carbonyl stretching vibration frequency

(1) T. Gramstad and W. E. Fuglevick, *Acta Chem. Scand.*, **16**, 1369 (1962).

(2) R. M. Moriarity, *J. Org. Chem.*, **28**, 1296 (1963).

(3) J. C. Woodbrey and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 13 (1962), and earlier references.

(4) D. Cook, *ibid.*, **80**, 49 (1958).

(5) G. Fraenkel and C. Franconi, *ibid.*, **82**, 4478 (1960).

(6) (a) C. D. Schmulback and R. S. Drago, *ibid.*, **82**, 4484 (1960); (b) A. R. Katrisky and R. A. Y. Jones, *Chem. Ind.* (London), 722 (1961); (c) J. T. Edward, H. S. Chang, K. Yates, and R. Stewart, *Can. J. Chem.*, **38**, 1518 (1960).

TABLE III

POTENTIOMETRIC TITRATION DATA ON VARIOUS AMIDES, UREAS, AND AMINES WITH PERCHLORIC ACID AS TITRANT IN DILUTE NITROMETHANE

	Base	E.m.f. at half neutralization, v.	ΔHNP (Δe.m.f. at half neutralization), v.[a]	$pK_{a(H_2O)}$ Calcd.	$pK_{a(H_2O)}$ Lit.	K_a[b]
(0)	N,N′-Diphenylguanidine	+0.010	0.00	+10.0	+10.0[c]	1×10^{-10}
(1)	N,N-Dimethylformamide	0.930	+0.917	−0.70	−0.01[d]	5.02
(2)	N,N-Diethylformamide	0.925	0.909	−0.50		3.17
(3)	N,N-Dimethylacetamide	0.870	0.851	+0.10		0.80
(4)	N,N-Diethylacetamide	0.865	0.843	+0.20		0.63
(5)	N,N-Di-*n*-propylacetamide	0.885	0.854	+0.10		0.80
(6)	N,N-Diisopropylacetamide	0.860	0.826	+0.50		0.32
(7)	N,N-Dimethylpropionamide	0.895	0.870	−0.10		1.26
(8)	N,N-Diethylpropionamide	0.890	0.862	0		1.00
(9)	N,N-Di-*n*-butylpropionamide	0.890	0.853	+0.10		0.80
(10)	N,N-Diisobutylpropionamide	0.905	0.870	−0.10		1.26
(11)	N-Acetylpiperidine	0.875	0.829	+0.40		0.40
(12)	N-Formylpyrrolidine	0.920	0.868	−0.10		1.26
(13)	Tetramethylurea	0.875	0.83	+0.40		0.40
(14)	N-Methyl-2-pyrrolidone	0.895	0.846	+0.20	−0.2[e]	0.63
(15)	Repeat of N,N′-diphenylguanidine (0)	0.050	0.00	+10.0	+10.0[c]	1×10^{-10}
(17)	Pyridine	0.455	0.461	+4.70	+5.30[c]	2×10^{-9}
(18)	Triethylamine			+10.70	+10.75[f]	2×10^{-11}
(19)	New sample of N,N′-diphenylguanidine	0.010	0.00	+10.0	+10.0[c]	1×10^{-10}
(20)	Acetamide	0.865	0.855	+0.10	−0.48[c] +0.11[d]	3.02
(21)	Urea	0.830	0.820	+0.50	+0.50[g]	0.32

[a] HNP = half-neutralization potential. Corrected for change in e.m.f. of reference solution (N,N′-diphenylguanidine in nitromethane), *i.e.*, 15 *vs.* 0. [b] The inverse of the base strength of the amide, expressed as the ionization constant of the conjugate acid BH^+ in the equilibrium $BH^+ \rightleftarrows B + H^+$; that is, $K_a = [B][H^+]/[BH^+]$. [c] W. F. Hall, *J. Am. Chem. Soc.*, **52**, 5115 (1930). [d] R. Huisgen and H. Brade, *Ber.*, **90**, 1432 (1957). [e] Ref. 12. [f] Lange's "Handbook of Chemistry," 7th Ed., Handbook Publishers, Inc., Sandusky, Ohio, 1949, p. 1410. [g] H. Le Marie and H. J. Lucas, *J. Am. Chem. Soc.*, **73**, 5193 (1951).

in dilute isooctane solution ($\gamma_{C=O(iso)}$) and (2) Taft's polar factors (σ^*)[7] for the substituents X and Y. The $\gamma_{C=O(iso)}$ is generally a complex vibration, in which the frequency depends, even within a given class of compounds and in the absence of H-bonding effects (in dilute isooctane), on inductive effects, resonance effects, and bond angle strain.[4,8-10]

Taft has shown that σ^*-values are quantitative measures of the contribution of substituent groups, directly attached to the reaction center, to the polarity of the molecule.[7] Thus, if σ^*-values for X and for the $-NY_2$ group in X-C(O)-NY_2 were available, then $\Sigma\sigma^*$-values could be used to estimate the total polar contribution of the substituents to the electron density on the oxygen atom.

The relative polarity contributions to the carbonyl group of NY_2, as compared to X, may be empirically estimated, by plotting published σ^*-values for X and Y *vs.* $\gamma_{C=O(iso)}$ for the two lowest members of the series (to minimize steric differences), holding X constant and varying Y, and also holding Y constant and varying X.

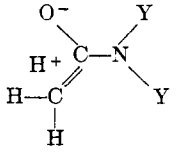
The results are summarized in Table IV. Changes in the N,N-disubstituted acetamide series (X = CH_3, Y = variable) are essentially equivalent to changes in the N,N-dimethylalkanoic acid amide series (Y = CH_3, X = variable).

TABLE IV

EFFECTS OF CHANGES IN THE INDUCTIVE CONTRIBUTIONS OF SUBSTITUENTS ON THE POLARITY OF THE CARBONYL GROUP OF N,N-DISUBSTITUTED AMIDES

X-C(O)-NY_2	Variable	$\Delta\gamma_{C=O(iso)}/\Delta\sigma^*$
Acetamides	Y	43
N,N-Dimethylamides	X	42
Formamides	Y	16

That is, the sum of inductive and resonance contributions for $-NY_2$ fortuitously equals the effect of published σ^*-values for X. This permits the simple summation of published σ^*-values for X and 2Y to obtain the total polar contribution of the substituents. In the formamide series, however, the polar effect of Y is only about 0.4 as great as in the acetamide series (Table IV), which suggests a reduced resonance contribution for NY_2. This qualitatively agrees with the somewhat reduced barrier for the rotation for the formamides as compared to the acetamides.[8] Perhaps the hyperconjugative structures in the acetamides and higher acid amides of the type shown below (structure 2) help stabilize the planar configuration of the molecule, and increase the contribution of the resonance structures to the polarity of the carbonyl group.



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(10) (a) R. E. Kagarise, *J. Am. Chem. Soc.*, **77**, 1377 (1955); (b) E. M. Arnett and C. Y. Wu, *ibid.*, **84**, 1684 (1962).

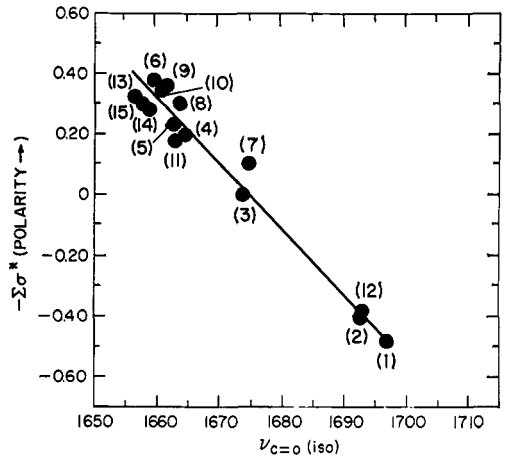


Fig. 1.—$\Sigma\sigma^*$ *vs.* $\nu_{C=O(iso)}$ for N,N-disubstituted amides and related compounds.

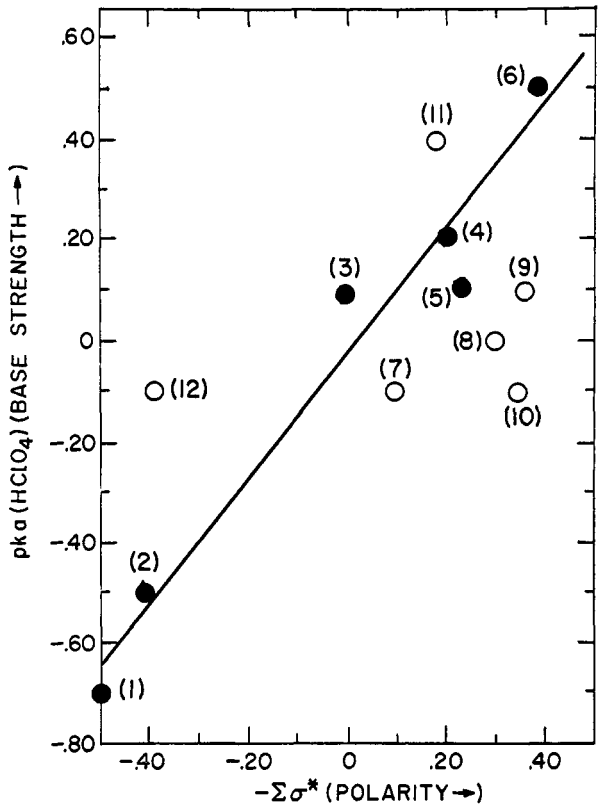


Fig. 2.—$\Sigma\sigma^*$ *vs.* $pK_{a(H_2O)}$ with perchloric acid as acid in nitromethane.

The $\Sigma\sigma^*$-values (with the formamide values corrected) were plotted against $\gamma_{C=O(iso)}$, as shown in Fig. 1. Quite a good linear relationship was obtained for the simple alkanoic acid amides, fitting the equation $+\Sigma\sigma^* = -0.0275\gamma_{C=O(iso)} + 46.1$ with standard deviation for $\gamma_{C=O(iso)}$ of 2.5 cm.$^{-1}$, just slightly higher than experimental error.

The straight line relationship for $\Sigma\sigma^*$ *vs.* $\gamma_{C=O(iso)}$ for the alkanoic acid amides lends confidence to the view that these parameters are accurate measures of carbonyl group polarity through this series. It further indicates that steric effects (B-strain, electron correlation repulsions[10b]) on the polarity of the free bases are negligible. Thus variable steric effects in the associated complexes would be essentially a result of complex formation.

II. Steric Effects in Forming the Associated Species.—The $\Sigma\sigma^*$(or $\gamma_{C=O(iso)}$)-values were plotted against published base strength parameters and against new data obtained in the present study. Deviations from the Taft linear polar energy relationship indicated the onset of variable steric effects in the associated complexes.[11]

Support for use of these parameters and an analysis of the steric factors involved is presented in the Discussion section.

A. Perchloric Acid as Electron Acceptor.—The potentiometric titration technique in nitromethane solvent followed essentially the method of Streuli,[12] and is described in the Experimental section. The collected pK_a data (for the conjugate acids) are given in Table III.

A plot of the base strengths (pK_a) *vs.* polarity of the free bases ($\Sigma\sigma^*$) is given in Fig. 2. A reasonably linear relationship is evidenced for the formamides and acetamides (darkened circles, points (1–6)), with $pK_{a(H_2O)} = -0.0315 - 1.235\Sigma\sigma^*$, and with a standard deviation for $\Sigma\sigma^*$ of 0.07. Deviations from linearity however, were marked for the larger propionamides, with base strengths lower than expected. Deviation was also significant for the cyclically substituted amide, N-formylpyrrolidine, and in the opposite direction. However, ease of hydrolysis make the pK_a data on this compound suspect. With the propionamides, the base strength reached a maximum with N,N-di-*n*-butyl-, and dropped for the N,N-diisobutylpropionamide.

B. With Phenol as Electron Acceptor.—A log K_{assn}–$\Sigma\sigma^*$ plot for nine N,N-disubstituted alkanoic acid amides as bases, with phenol as electron acceptor, was made from literature data. Joesten and Drago[13] determined the association constant in carbon tetrachloride using ultraviolet absorption techniques. Gramstad and Fuglevick[1] used infrared techniques, also in carbon tetrachloride, based on the shift of the hydroxyl stretching frequency of the free and complexed phenol. These were placed on the same temperature basis by the thermodynamic data of Joesten and Drago.[13] The results of both research groups for dimethylformamide agreed closely.

The plot of $\Sigma\sigma^*$ *vs.* log $K_{assn(phenol)}$ is shown in Fig. 3. For the simple alkanoic acid amides, it is evident that deviation from a linear relationship (and the onset of steric effects) occurs at least with N,N-diethylacetamide (entry 4 in Fig. 3). With the larger homologs, or with the cyclic derivatives, the log K_{assn} values are insensitive to increases in polarity of the substituents. Thus steric effects set in more quickly with phenol (in carbon tetrachloride) than with perchloric acid in nitromethane.

C. With Chloroform as Electron Acceptor.—To observe the effects of change of base strength with change in structure using chloroform as electron acceptor, a spectral parameter was used. This parameter was the relative frequency shift of the carbonyl stretching vibration frequency in dilute solution in isooctane and in chloroform $[(\gamma_{C=O(iso)} - \gamma_{C=O(HCCl_3)})/\gamma_{C=O(iso)}]$.

(11) Ref. 7, pp. 620–623.
(12) C. A. Streuli, *Anal. Chem.*, **31**, 1652 (1959); **32**, 985 (1960).
(13) R. L. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 2696 (1962).

Bellamy and Williams showed that plots of $\Delta\gamma_{C=O}/\gamma_{C=O}$ for several N-cyclically disubstituted amides in a set of solvents *vs.* $\Delta\gamma_{C=O}/\gamma_{C=O}$ for a reference solute (acetophenone) in the same solvents are linear.[14] Further, their data show that for the amides of the same range of base strength as those in our study, the slopes of such plots are linearly related to the polarity contribution of the substituents to the carbonyl group.[15]

In this work, instead of using a set of solvents, relative slopes were obtained by frequency measurements for the base in only two solvents: isooctane (in which the base is essentially nonassociated) and chloroform, the acid under investigation. The error in making this approximation for the relative slope is small; for dimethylacetamide, the approximate slope (relative to acetophenone as reference base) is 0.36 rather than 0.38 from the literature.[15]

The spectroscopic data are tabulated in Table II, and the relative slopes (relative frequency shifts $\Delta\gamma_{C=O}/\gamma_{C=O}$ divided into the relative frequency shift of the lowest member of the series, dimethylformamide) are plotted against $\Sigma\sigma^*$ in Fig. 4.

A straight line is indeed obtained for dimethylformamide, diethylformamide, and formylpyrrolidine, but curvature is exhibited at least as early as dimethylacetamide (point 3, Fig. 4), and with almost immediate development at this level of substitution of insensitivity of the base strength to the polarity of the substituents. Thus steric effects set in even more quickly with chloroform than with phenol as reference acid.

D. With Iodine as Electron Acceptor.—A few data for the N,N-disubstituted amides with iodine as electron acceptor are available from the literature,[16] which suggest that the steric interference for iodine complexes is somewhat greater than for phenol complexes. Thus, the deviation of σ^*, taken from the published log K_{assn}–$\Sigma\sigma^*$ plot for dimethylpropionamide,[16] is 0.4 for iodine, and 0.25 for phenol as acid.

To sum up, the order of increasing steric requirements of the acids in the associated species with N,N-disubstituted amides is perchloric acid < phenol < iodine, chloroform. This order should be independent of changes in solvent, as will be indicated in the Discussion, part III.

Discussion

I. Determination of pK_a.—It is recognized that measuring pK_a by titration of weak bases in nonaqueous solvents is a semiempirical technique, yet good estimates of basicity are often obtained, in which the e.m.f. at half neutralization is linearly related to the pK_a values determined in water.[17,18] Particularly good correlations have been obtained for amides titrated with perchloric or sulfuric acids in glacial acetic acid solution.[19]

It has also been shown that thermodynamic pK_a values for amides cannot at present be determined in concentrated aqueous acids using the Hammett acidity function H_0 and the log (protonated amide)/(amide). This is, presumably, a result of decreased hydration of the protonated species with increasing acidity.[20]

This difficulty would not be encountered in the nonaqueous titration method using nitromethane as the solvent, for the latter has practically no associative tendencies with cationic species.[21,22]

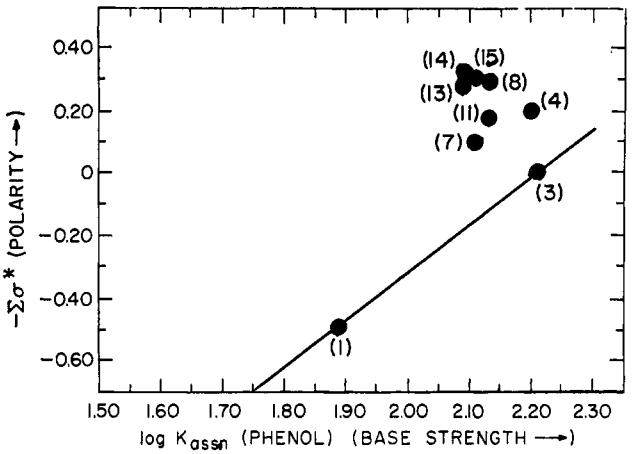


Fig. 3.—$\Sigma\sigma^*$ *vs.* log $K_{assn(phenol)}$ in carbon tetrachloride.

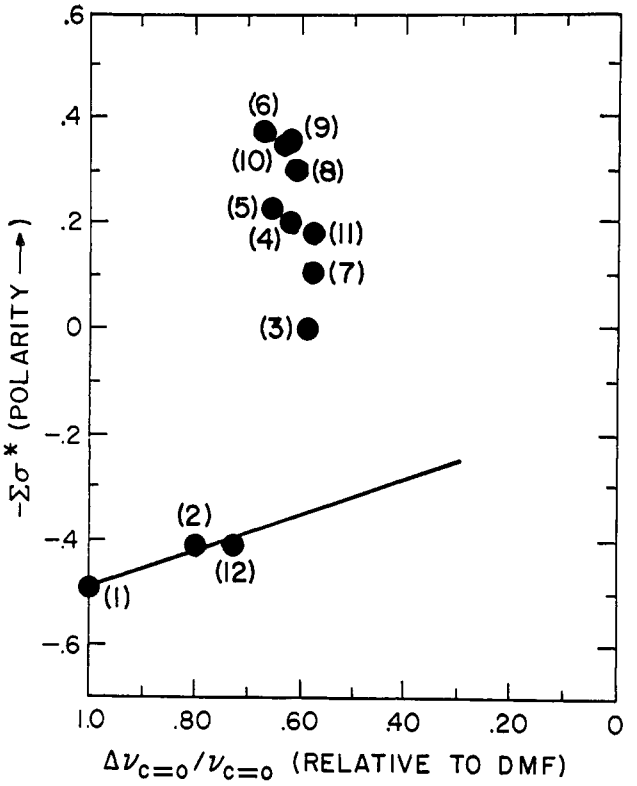


Fig. 4.—$\Sigma\sigma^*$ *vs.* relative frequency shift ($\gamma_{C=O(iso)} - \gamma_{C=O\cdot(HCCl_3)}$)/$\gamma_{C=O(iso)}$. Expressed as $\Sigma\sigma^*$ *vs.* ratio of $\Delta\gamma/\gamma_{(dimethylformamide)}$:$\Delta\gamma/\gamma_{(amide)}$.

(14) L. J. Bellamy and R. L. Williams, *Proc. Roy. Soc.* (London), **255**, 22 (1960), and earlier references.

(15) Specifically note Fig. 16 in ref. 14, the first six points of the plot. These include diethylacetamide, N-acetylpyrrolidine, N-acetylindole, N-acetylpyrrole, N-acetyliminazole, N-acetyl-1,2,4-triazole. The polarity of the carbonyl group was taken to be inversely proportional to the resonance energy of the heterocyclic ring.

(16) R. S. Drago, D. A. Wenz, and R. L. Carlson, *J. Am. Chem. Soc.*, **84**, 1106 (1962).

(17) H. K. Hall, Jr., *J. Phys. Chem.*, **60**, 62 (1956).

(18) E. M. Arnett, "Progress in Physical Organic Chemistry," Vol. I, S. G. Cohen, *et al.*, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp. 248–250, 270–274, and reference cited.

(19) N. F. Hall, *J. Am. Chem. Soc.*, **52**, 5115 (1930).

(20) R. B. Homer and R. B. Moodie, *J. Chem. Soc.*, 4377 (1963), and references cited.

(21) L. C. Smith and L. P. Hammett, *J. Am. Chem. Soc.*, **67**, 23 (1945).

(22) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 34 (1957).

In addition, Van Looy and Hammett have shown that strong acids in nitromethane solvent at concentrations less than 0.1 M probably undergo acid–base equilibria of the following type.[23]

$$\text{Base} + \text{HA} \rightleftharpoons \text{BH}^+\cdot\text{A}^- \quad (1)$$

$$\text{Base} + 3\text{HA} \rightleftharpoons [\text{BH}^+]\cdot[\text{A}(\text{HA})_2^-] \quad (2)$$

At the concentration of our titrations (<0.005 M acid), equilibrium 1 could be highly favored. This gives us an opportunity to compare the steric requirements of three acids, differing widely in the degree of proton transfer in forming the complex, yet uncomplicated by variations in solvation. (See also Discussion, part IV.)

It was recognized that nitromethane is very difficult to purify,[23] and so nitromethane practical grade was used, as it was by Streuli.[12] The linear $pK_{a(H_2O)}$–e.m.f.$_{(1/2)}$ relationship for amides and amines was corroborated. Hall has also shown that linear polar energy relationships exist for tertiary amine–perchloric acid complexes in a variety of solvents, including nitromethane, and that the relative orders of base strengths were equivalent in these solvents.[17,24]

II. Order of Steric Requirements.—The observation that the variable steric effects with amides as bases are smaller with perchloric acid nonsolvated ion pairs than with phenol associates is in line with previous studies using tertiary aliphatic amines as bases. Thus, negligible variable steric effects were observed for tertiary amines with perchloric acid,[24] but were indeed found with phenol as electron acceptor.[25]

Gramstad has shown that N,N-disubstituted amides may be considered to have lower steric requirements (with phenol as acid) than the tertiary amines or aliphatic ethers (the former gave linear log K–$\Delta\gamma_{OH}$ plots, while the amines or ethers did not).[25]

The low steric requirements for the perchloric acid–amide complexes may be due to loose association of the perchlorate anion with the oxonium cations, characteristic of perchlorate ion pairs with large planar cations.[26]

III. Base Strength–Potential Energy Relationships for the Various Electron Acceptors.—With phenol as acid, and for N,N-disubstituted amides at least up to N,N-diethylbutyramide as bases, Gramstad has shown that the enthalpy change on association, $\Delta\Delta H_{assn}°$, is proportional to the entropy change, $\Delta\Delta S_{assn}°$.[27] Thus the standard free energy change, $\Delta\Delta F_{assn}°$, is also proportional to $\Delta\Delta S_{assn}°$. Therefore, $\Delta\Delta F_{assn}°$ or log K_{assn}, the base strength parameters,[28] as well as $\Delta\Delta H_{assn}°$ are proportional to the potential energy change, $\Delta\Delta E_p°$—the quantity related to structural factors such as dipole fields, resonance energies, bond energies, and electronic displacements.[30]

With perchloric acid as electron acceptor, log K ($\Delta\Delta F°$) values were determined. Since variable steric effects were found to be smaller with perchloric acid than with phenol, $\Delta\Delta F°$ is apparently proportional to $\Delta\Delta H°$ (and $\Delta\Delta E_p°$) in this case, also.

With chloroform as electron acceptor, the relative frequency shift was proportional to the polarity, and, therefore, also proportional to $\Delta\Delta E_p°$.[28,31]

Thus, the relative base strengths obtained with the above electron acceptors appear to be directly comparable.

IV. Sources of Deviation in Base Strength–$\Sigma\sigma^*$-Plots.—As mentioned above, variable steric effects involving solvation appear to be minor in these series. For amide–phenol complexes in carbon tetrachloride, linear $\Delta\Delta F°$–$\Delta\Delta H°$–$\Delta\Delta S°$ relationships were exhibited,[27] which indicate negligible variable entropic or enthalpic solvent effects. With perchloric acid in nitromethane, the ion pair was essentially nonsolvated (see Discussion, part I). Variable steric effects occurred most quickly with chloroform as acid, when no added solvent was present.

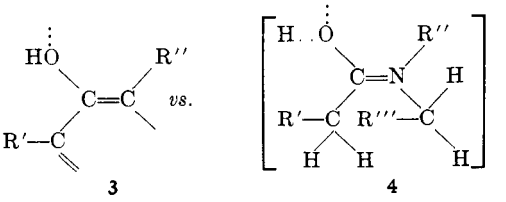
Thus, the primary source of the variable steric effects in the $\Sigma\sigma^*$–base strength plots appears to be internal rather than external. In addition, it involves steric strain rather than interference to internal motion. The latter conclusion is evidenced by the linear $\Delta\Delta F°$–$\Delta\Delta S°$ relationship in the phenol associated complexes.[27]

V. Sources of Variable Steric Strains.—In general, the potential energy term $\Delta\Delta E_p°$ may be considered as the sum of independent inductive, resonance, and steric repulsion (strain) effects.

For the planar N,N-disubstituted amide complexes, the inductive and resonance effects have been accounted for in the estimation of the polar contribution, $\Sigma\sigma^*$, for X and NY_2. However, where steric strains exist, these may result in inhibition of resonance, a reduction in the contribution of the planar structure, and a reduction of the polar contribution of the substituents.

The steric strain might be accommodated, then, by either (a) an opening or twisting of the C–O···H bond, and/or (b) steric inhibition of resonance by twisting the C–N bond.

An estimate of the contribution of (a) and (b) might be made by considering the *ortho*-substituted phenols as limiting models for the planar N,N-disubstituted amide complexes. These structures appear quite similar (structures **3** and **4**). (1) The bond lengths appear to be



3 **4**

essentially equivalent, 1.39 ± 0.02 for the C–C bond in benzene[32] or resorcinol[33] and 1.38 ± 0.05 for the C–N bond in acetamide.[34] (2) The amide structure is essen-

(23) H. Van Looy and L. P. Hammett, *J. Am. Chem. Soc.*, **81**, 3872 (1959); E. M. Arnett and C. F. Douty, *ibid.*, **86**, 409 (1964).
(24) H. K. Hall, Jr., *ibid.*, **79**, 5441 (1957).
(25) T. Gramstad, *Acta Chem. Scand.*, **16**, 807 (1962).
(26) N. N. Lichtin, "Progress in Physical Organic Chemistry," Vol. I, S. G. Cohen, *et al.*, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp 83–84.
(27) T. Gramstad, *Spectrochim. Acta*, **19**, 497 (1963).
(28) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 262.
(29) Ref. 7, pp. 660–663.
(30) Ref. 28, pp. 76–78.
(31) L. J. Bellamy, G. Eglinton, and J. F. Mormon, *J. Chem. Soc.*, 4762 (1961).
(32) V. Schomaker and L. Pauling, *J. Am. Chem. Soc.*, **61**, 1769 (1939).
(33) J. M. Robertson and A. R. Ubbelohde, *Soc. Proc. Roy.* (London), **A167**, 122 (1938).
(34) F. Senti and D. Harker, *J. Am. Chem. Soc.*, **62**, 2008 (1940). The base strength of acetamide is in the same range as the N,N-disubstituted amides [R. Huisgen and H. Brade, *Ber.*, **90**, 1432 (1957)].

tially planar. (3) Rotational interference between $R'CH_2$ and $R'''CH_2$ groups (structure **4**) as shown by models, is minimized by a conformation in which R′ is *trans* to the nitrogen atom.

In the phenols, however, steric inhibition of resonance by twisting of the C=C bond is highly unlikely, and steric strains are accommodated only by the change in the C–O–H bond angle.[31] Published spectral data on these *ortho*-disubstituted phenols also indicate that increased size and branching of R′ and R″ is not reflected in change of the C–O–H bond angle until the substituents get much larger than in our amide complexes. That is, a reasonably linear relationship was observed between the free or the associated hydroxyl stretching vibration frequencies and the polarity ($\Sigma\sigma^*$) of the di-*ortho*-alkyl substituents up to 2,6-di-*t*-butylphenol.[31,35]

Since the free and also the associated C–O–H bonds are so resistant to accommodating steric strains in the *ortho*-disubstituted phenols, it seems likely that the C–O · · · H bond in the amide complexes would be similarly unaffected. We therefore propose that steric strain in amide complexes can be partially relieved by twisting around the C–N bond, to avoid unfavorable *cis* interactions.

This conclusion is reasonable in terms of the low energy barrier restricting internal rotation (6–9 kcal./mole) in the N,N-disubstituted amides.[2,3] Further, the eventual insensitivity of the base strength to $\Sigma\sigma^*$-values with phenol or with chloroform as acids supports the view of the C–N bond twist. Thus, if the molecule remained planar, increasingly large deviations in base strength with increase in size of the substituents would have been expected. This is seen in the enthalpy of dissociation of 2-alkylpyridine–boron trifluoride addition compounds.[36]

With continued increase in size of the substituents, restriction to internal motions (entropy effects) would eventually be superimposed on the steric strain, and the log K_{assn} for the phenol–amide complexes would then deviate significantly from a linear correlation with $\Delta\gamma_{OH}$. This was indeed reported for the phenol–ether[31] or the phenol–tertiary amine complexes.[25]

The lower N,N-disubstituted amides, then, form a group in which variable steric strains are evidenced before variable steric interference to internal motion, due to the low energy barrier to rotation around the C–N bond. This indicates an exception to the "strain–entropy" principle, which postulates that steric strains are always preceeded or accompanied by steric interference to internal motions.[37]

Experimental

I. **Solvents.**—The tetramethylurea was obtained from the Du Pont Industrial and Biochemicals Department and redistilled. The acetylpiperidine was Eastman technical grade. The N-methylpyrrolidone was obtained from the General Aniline and Film Corp. and was distilled under reduced pressure. All of the other N,N-disubstituted amides were Eastman White Label grade. These were shaken with a saturated solution of sodium bicarbonate in water until evolution of carbon dioxide ceased. The crude products were distilled under reduced pressure, treated with anhydrous sodium sulfate, then Drierite, and redistilled under reduced pressure. The 80% center cuts were retained and stored over Drierite. Data on the amides are assembled in Table I. Methanol-free chloroform was obtained by washing the stabilized product six times with equal volumes of water, followed by drying and distillation under nitrogen and storage under nitrogen. The isooctane (Phillips spectroscopic grade 2,2,4-trimethylpentane) was boiled, and a 5% foreshot removed. For spectroscopic studies, 0.1% solutions by volume (approximately 0.01 *M*) of the amides in chloroform and in isooctane were prepared in volumetric flasks which had been scoured with detergent, washed with water, rinsed with acetone, vacuum-dried, flamed under nitrogen, and prerinsed with pure solvent.

II. **Infrared Spectroscopy.**—The spectroscopic data were obtained with a Perkin-Elmer No. 21 double beam spectrometer, with NaCl optics. Temperature was 72°F., and relative humidity 50%. Calibration of frequency values was made against H_2O, CO_2 in the 5–6-μ region and checked against a grating instrument. Values were correct to within 2 cm.$^{-1}$. Infrared data for the carbonyl band on diluted samples of amides in CCl_4 or $HCCl_3$ agreed with Bellamy's data within 2 cm.$^{-1}$. (See Table II.)

III. **Determination of pK_a Values *via* Potentiometric Titrations.**—The potentiometric titration procedure used for the determination of the pK_a of these bases (where $K_a = [B][H^+]/[BH^+]$ for the reaction $BH^+ \leftrightharpoons B + H^+$) was based on the method of Streuli[12] which he applied to a variety of amines, amides, and ureas. It involves the potentiometric titration of these weak bases with perchloric acid in dilute nitromethane solution. In summary, linear p$K_{a(H_2O)}$–e.m.f.$_{(1/2)}$ correlations resulted. Some differences in slope were observed between our data and those of Streuli. However, our data for N,N-disubstituted amides and amines agreed closely with those of Streuli in relative p$K_{a(H_2O)}$ values, which was sufficient for our present purposes.

The relative pK_a values in our series, with their limited structure variation and the precautions taken in their measurement, have the desired level of precision, to about 0.03 pK units.

Titrations were performed point by point with a Beckman Zeromatic pH meter Model 9600 using a Beckman calomel aqueous sleeve electrode 4925-N60 and Beckman glass electrode 1190-80. Equivalent results were obtained with another set of glass calomel electrodes. The nitromethane was Matheson practical grade and used directly. The perchloric acid solution was prepared by diluting 4.2 ml. of 72% acid to 1 l. in nitromethane and was stored in a closed brown bottle. Streuli reported that the perchloric acid solutions were stable for about 1 month, but that the HNP (half-neutralization potential) values could vary by as much as 100 mv. over several days' time. He eliminated this difficulty by determining the ΔHNP; the difference between the HNP for the compound being tested and the HNP for a N,N′-diphenylguanidine sample (HNP $\approx$ 0) run the same day. The HNP was reproducible within 5–6 mv.

We further ensured against variation in the stock solutions by (a) using the same stock solution of CH_3NO_2 for all dilutions, and (b) determining the HNP value at the beginning and again at the end of the series of runs, which was completed within a 15-hr. period. An increase in 50 mv. was observed for the HNP of the diphenylguanidine over this period, and so the ΔHNP values for the amides titrated were appropriately corrected, depending on the time during this period in which the individual titrations were carried out. Approximately 0.0010 mole ($\approx$0.1000 g.) of compound was dissolved in nitromethane and made up to volume in a 100-ml. Kimex volumetric flask. A 25.00-ml. aliquot was diluted with 25.0 ml. of nitromethane (concentrated 0.005 *M*) and, using a magnetic stirrer, was titrated with the 0.05 *N* perchloric acid in nitromethane solution from a microburet well beyond the point of complete neutralization.

Steady e.m.f. values were obtained within 2–3 sec. of mixing in all cases except for the first 5% per cent-of-neutralization values. A typical moderate base–strong acid titration curve was obtained for bases as strong as pyridine (pK_a of the conjugate acid $\approx$ 5). With weaker bases such as the N,N-disubstituted amides (lower pK) the titration curves were reduced to an inflection point at complete neutralization. Streuli carried out his titrations at 0.00125 *M* concentrations rather than 0.005 *M*, and we observed with dimethylacetamide that a sharper inflection point did appear to result at the lower concentration. However, at the higher concentration, the inflection point still occurred at the calculated stoichiometric end point for the titration, and the e.m.f. value at half neutralization was not appreciably changed (within 10 mv.) by the increased dilution of the base (and the decreased

(35) See L. J. Bellamy and R. L. Williams, *Proc. Roy. Soc.* (London), **A254**, 119 (1960), for other supporting data.

(36) H. C. Brown and R. H. Horowitz, *J. Am. Chem. Soc.*, **77**, 1733 (1955); see also ref. 7, p. 674.

(37) Ref. 7, p. 669–670.

amount of water present) during the titration. Therefore, all titrations were carried out at 0.005 *M* concentrations. The pK_a point was always in the desired flat portion of the titration curve. The e.m.f. at half neutralization was taken as one-half the calculated stoichiometric end point. As mentioned above, the latter was always very close to the observed inflection point, and resulted in a maximum error of e.m.f. values of about 5 mv. Runs were carried out in duplicate. Repeat determinations were always within 10 mv. and generally within 5 mv. The collected Δe.m.f. values at half neutralization (ΔHNP values, referred to N,N′-diphenylguanidine) are given in Table III. A plot of these ΔHNP values *vs.* literature $pK_{a(H_2O)}$ values for several of these bases (diphenylguanidine, triethylamine, pyridine, acetamide, and urea) indicated a straight-line relationship, and so the $pK_{a(H_2O)}$ values for the series of N,N-disubstituted amides are interpolated from this line (Tables I and III).

The least-squares calculation of $pK_{a(H_2O)}$ *vs.* ΔHNP was $pK_{a(H_2O)} = 10.10 - 0.0118\Delta HNP$, with a standard deviation of 33 mv. This is appreciably different in slope from the equation calculated from Streuli's reported data for these compounds, of $pK_{a(H_2O)} = 10.10 - 0.0152\Delta HNP$.[12] On the other hand, our equation based on amides, ureas, and amines is quite close to Streuli's equation reported for amines and for N,N-disubstituted amides ($pK_{a(H_2O)} = 10.12 - 0.0129\Delta HNP_{(CH_3NO_2)}$).

Acknowledgment.—We are deeply indebted to Miss N. Schlichter, Du Pont Central Research Department, for the infrared measurements, and to Dr. H. K. Hall, Jr., Du Pont Textile Fibers Department, and Professor G. S. Hammond for stimulating discussion.

Reaction of Cyclic Phosphoramidites with Disulfides. I. A Novel Synthesis of Phosphoramidothioates

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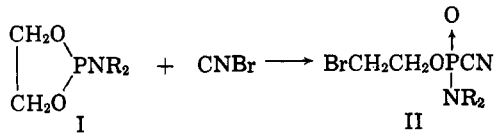
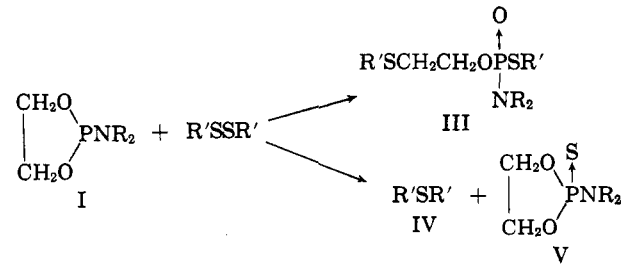
N,N-Disubstituted cyclic esters of phosphoramidous acid react readily with aromatic disulfides, tetraalkylthiuram disulfides, and certain heterocyclic disulfides to give derivatives of phosphoramidothioic acid in which the ring of the phosphoramidite has been opened. Benzhydryl and allyl disulfide are desulfurized by cyclic phosphoramidites without ring opening to give *sym*-tetraphenylethane and allyl sulfide, respectively. Simple aliphatic disulfides are not reactive towards cyclic phosphoramidites at the temperature of refluxing toluene. Alkyl aryl disulfides are cleaved by preferential attachment of the alkylthio moiety to phosphorus. A mechanistic rationalization of these experimental facts is presented.

The chemistry of cyclic esters of phosphoramidous acid (I) has received only scant attention; Arbuzov found that they react abnormally with alkyl halides to form poorly defined products although they add sulfur normally[3] and apparently undergo a typical Arbuzov reaction with cyanogen bromide to give phosphoramidocyanidates (II).[4] Their brief chemistry has recently been reviewed.[5,6]



We were interested in reactions of disulfides with cyclic phosphoramidites; they have not been studied although the reaction of trialkyl and triaryl phosphites with disulfides has been investigated extensively[7-11] and reviewed recently.[5,12] These latter reactions are mainly ionic and supposedly proceed by a Michaelis–Arbuzov mechanism. Since cyclic phosphoramidites are more nucleophilic than trialkyl phosphites, reaction with disulfides seemed a distinct possibility. This has been shown to be the case as discussed in more detail below.

At least two possible courses can be envisioned for the reaction of a cyclic phosphoramidite with a disulfide: Michaelis–Arbuzov rearrangement with cleavage of the phospholane ring to form the phosphoramidothioic ester (III), or desulfurization, with no ring cleavage, to form the corresponding sulfide (IV) and cyclic phosphoramidothionate (V). We have found that both reactions



do occur, the path being determined by the nature of the disulfide reactant. For example, when an N,N-disubstituted cyclic phosphoramidite of general structure I [R = C_2H_5, $-(CH_2)_5-$, $-(CH_2)_2O(CH_2)_2-$] is mixed with an aromatic disulfide, a vigorously exothermic reaction occurs and an acyclic phosphoramidothiolate (III, R′ = aryl) is formed in almost quantitative yield. Tetramethylthiuram disulfide reacts analogously with cyclic phosphoramidites derived from propylene glycol (VI) to give mixed anhydrosulfides

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(5) J. I. G. Cadogan, *Quart. Rev.* (London), **16**, 208 (1962).

(6) R. S. Edmundson, *Chem. Ind.* (London), 1770 (1962).

(7) H. I. Jacobson, R. G. Harvey, and E. V. Jensen, *J. Am. Chem. Soc.*, **77**, 6064 (1955).

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