Furthermore, they help to clear up some of the paradoxes of the excited-state theory discussed in the introduction, and to clarify the relationship between π bonding and the $\pi^* \leftarrow \pi$ excited states.

Turning now to the nature of the acetylene orbital which is used to form the metal–acetylene π bond, we find that at experimental values of the *cis*-bending angle it is an almost equal mixture of π_g and σ_u molecular orbitals. As the σ_u orbital is antibonding between the carbon 2s orbitals, the formation of the metal–acetylene π bond will lead to a reduction in the 2s character of the acetylene carbon–carbon bond, which should be reflected by a corresponding reduction in the carbon–carbon nuclear spin coupling constant.

The above discussion suggests that the theory of metal–acetylene π bonding could be tested experimentally by measuring the change in the acetylene C≡C nuclear spin coupling constant which accompanies the formation of an acetylene complex.

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The Hydrogen-Bonding Interaction of Aromatic Amine Oxides with Phenols

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Abstract: The use of pyridine 1-oxide σ constants (σ_{pyNO}) has been extended to the quinoline 1-oxide system. The hydrogen-bonding interactions of *p*-chlorophenol, phenol, and *p*-methylphenol with 4-substituted pyridine 1-oxides and 4- and 6-substituted quinoline 1-oxides (the substituents being $(CH_3)_2N$, CH_3O, CH_3, H, Cl, Br, CN, CO_2CH_3, and NO_2) have been studied. ΔH values for the reactions have been calculated and are tabulated. Correlations have been obtained with σ_{pyNO} constants for the change in the hydrogen–oxygen stretching frequency $\Delta\nu_{\text{OH}}$. It is found that $\Delta\nu_{\text{OH}}$ frequencies for the interactions with 4-substituted pyridine 1-oxides and 4-substituted quinoline 1-oxides correlate with σ_{pyNO} constants, whereas, the $\Delta\nu_{\text{OH}}$ values for the interactions of 6-substituted quinoline 1-oxides are best correlated with Hammett σ constants.

The availability of several 4-substituted pyridine 1-oxides[3] has prompted many attempts to correlate substituent constants for the various groups with observable properties of either the N-oxides themselves or their complexes. In almost every instance it was necessary to use adjusted Hammett σ constants (σ^+, σ^-, or σ^*) rather than the σ constants themselves in order to obtain these correlations. In fact, some correlations utilized σ^+, σ, and σ^- on the same plot.

Many reasonable correlations between measured physical properties of a system containing substituted pyridine 1-oxides and a hybrid set of substituent parameters have been found.[4–14] Nevertheless, it is indeed unfortunate that one single set of substituent parameters has not been employed. As is now the practice, use of a hybrid set of substituent parameters makes comparison of the various properties of analogous systems very difficult. Anomalies of interaction are not easily recognized.

Therefore, we suggested a return to the fundamental definition of substituent parameters. An internally self-consistent set of values based upon the measured acid dissociation constants, K_{BH^+}, was calculated from the Hammett relationship[15] for the pyridine 1-oxides. All of the presently available data may be satisfactorily correlated with σ_{pyNO} constants. There exists no example to our knowledge where adjusted σ_{pyNO} values are necessary.

Until now, no correlations have been made with any of the properties of the quinoline 1-oxides. An investigation of the hydrogen-bonding properties of a series of 4- and 6-substituted quinoline 1-oxides was undertaken to test the applicability of these new constants and to compare the properties of the quinoline 1-oxides with those of the pyridine 1-oxides. The hydrogen-bonding properties of the 4-substituted pyridine 1-oxides were also investigated[6] for comparison purposes. The hydrogen–oxygen stretching frequency, ν_{OH}, of phenols upon hydrogen-bond formation is sensitive to base strength.[16–19] *p*-Chlorophenol, phenol,

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(1) National Institutes of Health Predoctoral Fellow, 1966–1968.

(2) National Science Foundation Trainee, 1966–1969.

(3) E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).

(4) D. S. Dyer and R. O. Ragsdale, *Inorg. Chem.*, **6**, 8 (1967).

(5) R. G. Garvey and R. O. Ragsdale, *J. Inorg. Nucl. Chem.*, **29**, 745 (1967).

(6) D. W. Herlocker, R. S. Drago, and V. I. Meek, *Inorg. Chem.*, **5**, 2009 (1966).

(7) C. R. Kanekar and H. V. Venkatasetty, *Curr. Sci.*, **34**, 555 (1965).

(8) S. I. Shupack and M. Orchin, *J. Amer. Chem. Soc.*, **85**, 902 (1963).

(9) T. Kubota and H. Miyazaki, *Bull. Chem. Soc. Jap.*, **39**, 2057 (1966).

(10) W. E. Hatfield and J. S. Paschal, *J. Amer. Chem. Soc.*, **86**, 3888 (1964).

(11) H. H. Jaffé and G. O. Doak, *ibid.*, 77, 4441 (1955).

(12) H. H. Jaffé and H. L. Jones, *Advan. Heterocycl. Chem.*, **3**, 209 (1964).

(13) F. E. Dickson, E. W. Gowling, and F. F. Bentley, *Inorg. Chem.*, **6**, 1099 (1967).

(14) P. D. Kaplan and M. Orchin, *ibid.*, **6**, 1096 (1967).

(15) J. H. Nelson, R. G. Garvey, and R. O. Ragsdale, *J. Heterocycl. Chem.*, **4**, 591 (1967).

(16) A. Allerhand and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **85**, 371 (1963).

(17) M. D. Joesten and R. S. Drago, *ibid.*, **84**, 3817 (1962).

(18) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman & Co., San Francisco, Calif., 1960.

and *p*-methylphenol were chosen as reference acids for this study.

Experimental Section

Reagents. Pyridine 1-oxide, quinoline 1-oxide, 4-methylpyridine 1-oxide, 4-methoxypyridine 1-oxide, and 4-nitropyridine 1-oxide were obtained from Aldrich Chemical Co. and were purified by sublimation under reduced pressure. 4-Chloro- and 4-bromopyridine 1-oxide and 4-nitro-, 4-methyl-, 4-chloro-, and 4-methoxyquinoline 1-oxides were prepared by the method of Ochiai.[3] Isoquinoline 2-oxide was prepared by the method of Robison.[20] 4-Cyanoquinoline 1-oxide was prepared from 4-cyanoquinoline.[21] 4-Cyanopyridine 1-oxide was obtained from Reilly Tar and Chemical Co. 4-Methylisonicotinate 1-oxide, 4-N,N-dimethylaminopyridine 1-oxide, and 4-N,N-dimethylaminoquinoline 1-oxide were prepared by the method of Katritzky.[22] The 6-substituted quinoline 1-oxides were prepared from the corresponding amines (Eastman Chemical Co. or Aldrich Chemical Co.) by the method of Colonna and Risaliti.[23] All N-oxides were recrystallized from acetone and sublimed prior to use. Melting points agreed well with published values.

Spectrograde carbon tetrachloride was dried over Linde 3A molecular sieves prior to use. The phenols were sublimed immediately prior to use.[24]

Instruments. Infrared measurements were carried out on a Beckman IR5-A and a Perkin-Elmer Model 521 spectrophotometer using 0.1-mm matched sodium chloride cells. The results appear to be accurate to within ±5 cm^{-1} for the unassociated OH frequencies and to within ±10 cm^{-1} for the broader absorption bands of the hydrogen-bonded OH groups. All measurements were carried out at an average room temperature of 25°. The small variations of room temperature have no observable effect on the positions of the absorption frequencies.[25] All measurements were made at least twice and some as many as five times.

Statistical Treatment of Data. All errors are estimated at the 90% confidence level. For the correlations, the slope variances[26] were calculated by using the equation $Y = \alpha + \beta X$. All terms are defined in the cited reference. The ρ values and the variances are listed in Table I.

Table I. Statistical Parameters for the Correlations of $\Delta\nu_{OH}$ with Substituent Constants

Correlation[a]	Variance,[b] cm^{-1}		Slope (ρ)	
	σ	σ_{pyNO}	σ	σ_{pyNO}
p-ClC_6H_4OH + 4ZQNO	304	219	−412	−244
C_6H_5OH + 4ZQNO	90	40	−234	−122
p-ClC_6H_4OH + 6ZQNO	84	123	−284	−175
C_6H_5OH + 6ZQNO	41	61	−111	−67
p-$CH_3C_6H_4OH$ + 4ZPyNO	350	260	−222	−158
C_6H_5OH + 4ZPyNO	444	101	−530	−188

[a] Abbreviations used: 4ZQNO, 4-substituted quinoline 1-oxides; 6ZQNO, 6-substituted quinoline 1-oxides; 4ZPyNO, 4-substituted pyridine 1-oxides. [b] The variances were calculated by taking the absolute values of $\Sigma\Delta\nu_{OH}$ (calcd) − $\Delta\nu_{OH}$ (exptl). $\Delta\nu_{OH}$ (calcd) was obtained from the least-squares equations for the correlations.

Table II. Aromatic Amine N-Oxide Hydrogen-Bonding Interactions in Carbon Tetrachloride

Acid	Base	Substituent Z	$\Delta\nu_{OH}$, cm^{-1} [a]	$-\Delta H$, kcal mole^{-1} [c]
p-ClC_6H_5OH	4ZQNO	$(CH_3)_2N$	820	11.8
		CH_3O	660	10.0
		CH_3	517	8.5
		H[b]	438	7.6
		Cl	380	7.0
		CN	267	5.7
		NO_2	228	5.3
	6ZQNO	CH_3O	564	9.0
		CH_3	520	8.5
		H	438	7.6
		Br	380	7.0
		Cl	392	7.1
		NO_2	$\leqslant$260[f]	5.7
C_6H_5OH	4ZQNO	$(CH_3)_2N$	610	9.5
		CH_3O	500	8.3
		CH_3	465	7.9
		H[b]	425	7.5
		Cl	400	7.2
		CN	300	6.1
		NO_2	270	5.8
	6ZQNO	CH_3O	482	8.1
		CH_3	472	8.0
		H	450	7.7
		Br	410	7.3
		Cl	415	7.4
		NO_2	370	6.9
	4ZPyNO[e]	CH_3O	~600[g]	9.4
		CH_3	512	8.4
		H	468	7.9
		3,4-$(CH_3)_2$[d]	465	7.9
		Cl	435	7.6
		CH_3CO	400	7.2
		NO_2	220	5.2
p-$CH_3C_6H_4OH$	4ZPyNO	$(CH_3)_2N$	612	9.5
		CH_3O	485	8.1
		CH_3	416	7.4
		H	365	6.8
		Cl	267	5.7
		Br	256	5.6
		$CO(CH_3)$	278	5.9
		CN	228	5.3
		NO_2	222	5.2

[a] The frequencies (cm^{-1}) for the free phenols are: *p*-chlorophenol 3600, phenol 3610, and *p*-methylphenol 3605. [b] Values of −6 kcal mole^{-1} and −7.22 ± 0.4 kcal mole^{-1} have been reported for the interaction of phenol and *p*-chlorophenol, respectively, with quinoline 1-oxide: T. Kubota, *J. Pharm. Soc.* (Japan), **74**, 831 (1954); *ibid.*, **75**, 1540 (1955). These values were determined spectroscopically by the ultraviolet technique. [c] ΔH values were calculated from the equation[19] $-\Delta H = 0.011\Delta\nu_{OH} + 2.79$. This equation was derived for use with phenol only; however, it has recently been shown to be applicable to the interactions with *p*-chlorophenol and *p*-alkylphenol: T. D. Epley and R. S. Drago, private communication. [d] Isoquinoline 2-oxide: this work. [e] $\Delta\nu_{OH}$ values taken from ref 6. [f] The OH stretching frequency could only be assigned as being greater than 3340 cm^{-1} due to intense C–H vibrations appearing in this region. [g] Value adjusted to fit the line in Figure 4, since it was not possible to successfully measure this point.[6]

Results

The frequency shifts of the phenols upon hydrogen-bond formation are listed in Table II. Although both the reference and sample cells contained equal amounts of phenol, the extinction coefficients for the C–H stretching vibrations of the phenol–amine oxide adducts were much greater than those of phenol alone, giving rise to net absorptions in the 3000–3100-cm^{-1} region. This factor, coupled with the large frequency shifts upon hydrogen-bond formation, gave an asymmetric peak with greater absorption on the high-energy side. The reported shifts were found by (1) choosing fre-

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(19) T. D. Epley and R. S. Drago, *J. Amer. Chem. Soc.*, **89**, 5770 (1967).

(20) M. Robison and B. Robison, *J. Org. Chem.*, **21**, 1337 (1956).

(21) A. Kaufmann, *Ber.*, **51**, 116 (1918); H. U. Daeniker and J. Druey, *Helv. Chim. Acta*, 41, 2148 (1958).

(22) A. R. Katritzky, *J. Chem. Soc.*, 2404 (1956).

(23) M. Colonna and A. Risaliti, *Gazz. Chim. Ital.*, **83**, 58 (1953).

(24) M. D. Joesten and R. S. Drago, *J. Amer. Chem. Soc.*, **84**, 2037 (1962).

(25) Small variations of temperature may have a considerable effect on hydrogen-bonded equilibria, but the effect on infrared frequencies is very small; see, *e.g.*, E. D. Becker, *Spectrochim. Acta*, **17**, 436 (1961).

(26) H. A. Laitinen, "Chemical Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 556.

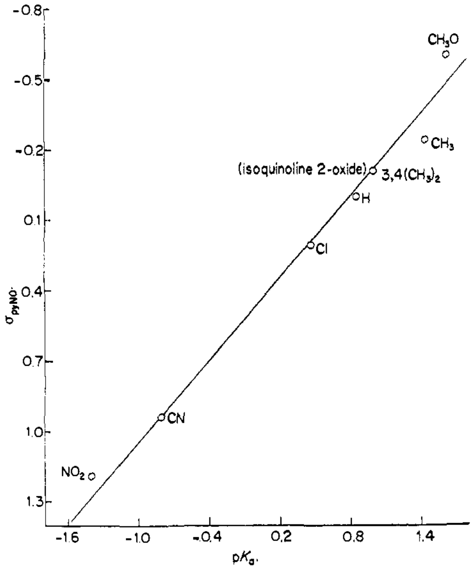

Figure 1. Correlation of pK_a with σ_{pyNO} constants for 4-substituted quinoline 1-oxides.

quencies where the carbon tetrachloride solutions of the phenols gave no absorption and assuming that any absorption at these frequencies upon hydrogen-bond formation was due to the hydrogen-bonded O–H stretching frequency; (2) constructing a symmetrical curve for this absorption; and (3) finding the maximum absorption as previously reported.[17]

Many authors have demonstrated that the infrared frequency shifts of phenols are often either solvent dependent,[27,28] concentration dependent,[29–32] or temperature dependent.[25] The spectra were all run with the same concentration of proton donor (the phenols) and at the same temperature so that the data would be consistent. All spectra were run with carbon tetrachloride as the solvent. To ensure that there was no concentration dependence of the frequency shifts, replicate measurements were made with varying concentration of the proton acceptors (N-oxides), and the frequency shifts were constant within the experimental error. The data obtained are listed in Table II.

Discussion

Since pyridine 1-oxide and quinoline 1-oxide have similar resonance interactions, the electronic effect displayed by various substituents should also be similar. Thus, as can be seen in Figure 1, a linear correlation is obtained between the pK_a's of the 4-substituted quinoline 1-oxides and σ_{pyNO} values (Table III). The two systems show the same systematic trends in basicity with changing substituents. Therefore, one would assume that the correlations which appeared with the pyridine 1-oxides[15] could be found for the quinoline 1-oxides.

The majority of the correlations with pyridine 1-oxides involved a measurement of the nitrogen–oxygen stretching frequency, ν_{N-O}, of the free bases and the various complexes formed by them. A similar correlation was obtained in this work for ν_{N-O} of the hydrogen-bonded complexes of *p*-methylphenol with the 4-substituted pyridine 1-oxides. However, an attempt to correlate ν_{N-O} for the quinoline 1-oxides was unsuccessful.[33] Shindo attributed this to the presence of two or more absorptions in the regions of 1150 and 1350 cm^{-1} due to coupling with the vibrations originating in the quinoline ring. The N–O frequencies, therefore, do not show any correlation to the structure. As a result, correlations can only be obtained with other properties of the quinoline 1-oxides or their complexes.

Table III. Substituent Constants for Aromatic Amine Oxides

Z	pK_a 4ZPyNO[a]	pK_a 4ZQNO[b]	σ	σ_{pyNO}[a]
$(CH_3)_2N$	3.88	...	−0.60	−1.48
CH_3O	2.05	1.62[d]	−0.268	−0.603
CH_3	1.29	1.44	−0.170	−0.240
H	0.79	0.86	0	0
Cl	0.36	0.47	0.227	0.206
Br	...	...	0.227	0.206
CO_2CH_3	−0.41	...	0.31	0.574
CN	−1.17	−0.80[d]	0.63	0.94
NO_2	−1.7	−1.39	0.778	1.19
3,4-$(CH_3)_2$[c]	1.01	...	...	−0.105

[a] Reference 15. [b] R. Whyman, D. B. Copely, and W. E. Hatfield, *J. Amer. Chem. Soc.*, **89**, 3135 (1967). [c] Isoquinoline 2-oxide. [d] Values obtained spectrophotometrically in this laboratory.

Heats of Interaction. In 1937 Badger and Bauer[34] proposed that the shift in the infrared stretching frequency of a group, X–H, upon complexation was linearly related to the enthalpy for hydrogen-bond formation. During recent years there has been considerable research to determine the validity of this statement. Gordon has reviewed the work in this area.[35] Epley and Drago[19] have demonstrated its validity and have experimentally obtained an equation relating enthalpies of hydrogen-bond formation to the phenol frequency shifts. By utilizing this equation ($-\Delta H = 0.011\Delta\nu_{OH}$ (cm^{-1}) $+ 2.79$), the enthalpies of interaction have been calculated. These values are presented in Table II.

The trends in ΔH are as expected. The largest values are found for the interactions of the strongest acids and the strongest bases (*p*-chlorophenol with the 4-substituted quinoline 1-oxides, −11.8 to −5.3 kcal $mole^{-1}$). The smallest values were found for the weakest interactions (*p*-methylphenol and 4-substituted pyridine 1-oxides, −9.5 to −5.2 kcal $mole^{-1}$). In Figures 2–4 are illustrated the correlations of $\Delta\nu_{OH}$ with the substituent parameters. Since ΔH is linearly related to $\Delta\nu_{OH}$ by the above equation, the ΔH values also correlate with the changes in basicity. The enthalpies are all in the range expected for O–H···O hydrogen bonds.[18]

4-Substituted Quinoline 1-Oxides. The $\Delta\nu_{OH}$ range (Table II) for the phenol interactions with 4-substituted quinoline 1-oxides (500 cm^{-1} for 4-CH_3O to 270 cm^{-1} for 4-NO_2) is, as expected, quite diminished compared to that of the pyridine 1-oxides (~600 cm^{-1} for 4-CH_3O to 220 cm^{-1} for 4-NO_2). The added aromatic ring in quinoline functions as an "electron sink" and hence serves

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(27) L. J. Bellamy and R. L. Williams, *Trans. Faraday Soc.*, **55**, 14 (1959).

(28) L. J. Bellamy, C. P. Conduit, R. J. Pace, and R. L. Williams, *ibid.*, **55**, 1677 (1959).

(29) L. J. Bellamy, H. E. Hallam, and R. L. Williams, *ibid.*, **54**, 1120 (1958).

(30) H. Tsubomura, *J. Chem. Phys.*, **23**, 2130 (1955).

(31) E. V. Shuvalova, *Opt. Spectry.* (USSR), **6**, 452 (1959).

(32) S. S. Mitra, *J. Chem. Phys.*, **36**, 3286 (1962).

(33) H. Shindo, *Chem. Pharm. Bull.* (Tokyo), **8**, 845 (1960).

(34) R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937).

(35) J. E. Gordon, *J. Org. Chem.*, **26**, 738 (1961).

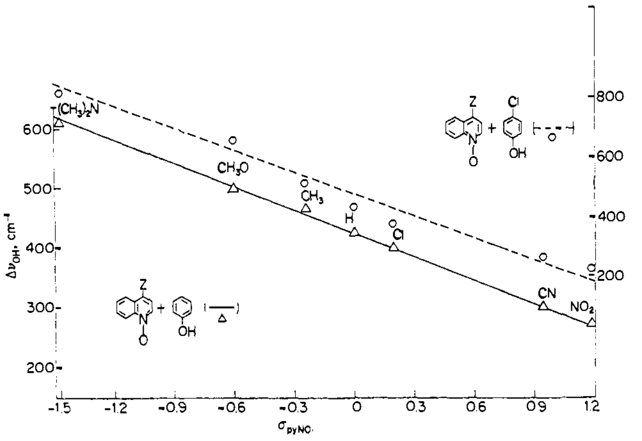

Figure 2. Correlation of $\Delta\nu_{OH}$ frequencies and σ_{pyNO} constants for the interactions of 4-substituted quinoline 1-oxides with phenol and *p*-chlorophenol.

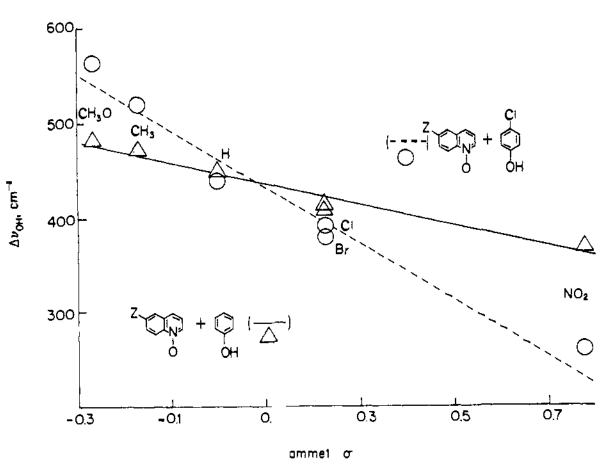

Figure 3. Correlation of $\Delta\nu_{OH}$ frequencies and Hammett σ constants for the interactions of 6-substituted quinoline 1-oxides with phenol and *p*-chlorophenol.

to "buffer" the resonance and inductive effects of the substituents, giving rise to a smaller range. Therefore, in this case $\Delta\nu_{OH}$ could be correlated almost as well with σ as with σ_{pyNO} constants (see the variances in Table I). The correlation with either set of substituent constants is brought about by the diminished range of $\Delta\nu_{OH}$. In view of this, the hydrogen-bonding interaction of *p*-chlorophenol with the 4-substituted quinoline 1-oxides was studied. Being a stronger acid than phenol, *p*-chlorophenol exhibits a greater interaction, thus increasing the range in $\Delta\nu_{OH}$ and distinguishing between the two sets of constants. $\Delta\nu_{OH}$ for the *p*-chlorophenol–quinoline 1-oxide interaction correlates better (Table I) with the σ_{pyNO} constants than it does with σ constants (Figure 2).

6-Substituted Quinoline 1-Oxides. The resonance interaction of the 6-substituted quinoline 1-oxides can only proceed to a position one atom removed from the reaction site. Hence, the resonance interaction here is not as important as in the 4-substituted N-oxides. In fact, the 6-substituted quinoline 1-oxides resemble benzoic acid more than they do pyridine 1-oxide in the nature of resonance interaction. It is, therefore, not unreasonable to assume that a better correlation of $\Delta\nu_{OH}$ values would be obtained with Hammett σ values than with σ_{pyNO} for the 6-substituted quinoline 1-oxides. In the case of phenol, the range of $\Delta\nu_{OH}$ (482–370 cm^{-1}) values is so small that either set of constants, σ or σ_{pyNO}, correlate rather well (Table I). However, with a stronger reference acid, such as *p*-chlorophenol, $\Delta\nu_{OH}$ (564–$\leqslant$260 cm^{-1}) is correlated better with σ_{pyNO} (Table I). The correlations with Hammett σ constants are shown in Figure 3.

4-Substituted Pyridine 1-Oxides. The hydrogen-bonding interaction of a weaker acid (*p*-methylphenol) was studied with the 4-substituted pyridine 1-oxides to test the hypothesis that the diminished range was the factor which gave rise to correlations of σ_{pyNO} in the case of the 6-substituted quinoline 1-oxides with phenol. The data obtained for the interaction of phenol and the 4-substituted pyridine 1-oxides could only be satisfactorily correlated with σ_{pyNO}[15] (Table I). The data obtained for the *p*-methylphenol–pyridine 1-oxide system revealed that the range of $\Delta\nu_{OH}$ (485 cm^{-1} for 4-CH_3O to 222 cm^{-1} for 4-NO_2) values was diminished relative to the phenol–pyridine 1-oxide interaction (~600 cm^{-1} for 4-CH_3O to 220 cm^{-1} for 4-NO_2). Consequently, $\Delta\nu_{OH}$ could be reasonably correlated with either σ or σ_{pyNO}. A slightly better correlation was obtained with σ_{pyNO}. *p*-Methylphenol is not a weak enough acid to decrease the range to the point that either set of constants will correlate with $\Delta\nu_{OH}$ equally as well. It is interesting to note that in this case, a reaction between a weak acid and a weak base, a leveling effect has occurred. The interactions between *p*-methylphenol and 4-chloro-, 4-bromo-, 4-carbomethoxy-, 4-cyano-, and 4-nitropyridine 1-oxide are weak. This infrared technique is not able to distinguish between the strength of these bases. The correlations with σ_{pyNO} are shown in Figure 4.

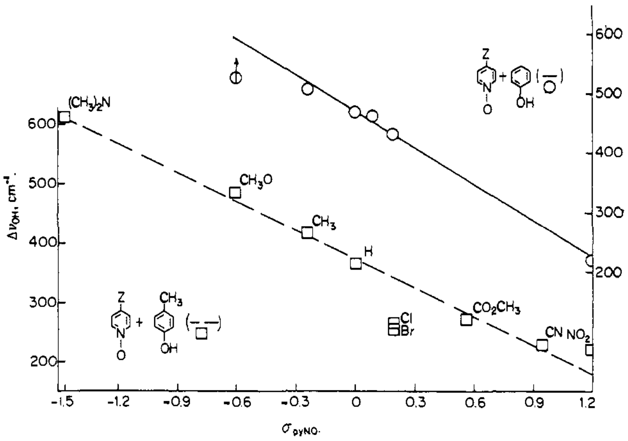

Figure 4. Correlation of $\Delta\nu_{OH}$ frequencies and σ_{pyNO} constants for the interactions of 4-substituted pyridine 1-oxides with phenol and *p*-methylphenol.

We have been successful in obtaining the first correlations of the properties of a system involving the quinoline 1-oxides, and the σ_{pyNO} substituent constants have now gained greater versatility. With this knowledge we can look for several more correlations of other properties of the quinoline 1-oxides or their complexes.

We feel that unless an unusual effect occurs σ_{pyNO} constants should be used for all correlations involving 4-substituted aromatic amine oxides. When a different system is studied, such as the 6-substituted quinoline N-oxides, another set of constants may be necessary.