acid (50 ml) and concentrated hydrochloric acid (30 ml) for 12 hr, a dark violet precipitate of the diamino compound was produced. Oxidation of this compound with ferric chloride in hydrochloric acid, as described in the previous section, yielded linear N-methylindanthrone (**18**), which on crystallization from boiling quinoline was obtained as fine dark green needles, mp >375°; infrared spectrum showed ν_{max} 3320 (NH) and 1662 cm^{-1} (C=O). It dissolves in concentrated sulfuric acid with a greenish brown color. Addition of methanolic potassium hydroxide to a suspension of the substance in pyridine affords a bright red color. It yields a reddish brown vat with alkaline sodium hydrosulfite.

Anal. Calcd for $C_{29}H_{16}N_2O_4$ (456): C, 76.31; H, 3.53; N, 6.14. Found: C, 76.22; H, 3.60; N, 6.21.

The mass spectrum had a molecular ion peak at *m/e* 456, and a strong peak at 441 due to loss of CH_3.

7,16-Dimethyl-7,16-dihydrodinaphtho[2,3-*b*:2′,3′-*i*]**phenazine-5,9,14,18-tetrone** (**19**).—Linear N-methylindanthrone (**18**, 0.5 g) was refluxed with a mixture of methyl *p*-toluenesulfonate (3.5 ml) and potassium carbonate (3.5 g) in *o*-dichlorobenzene (200 ml) for 18 hr. The mixture was cooled and filtered, and the residue was washed with ethanol, water, and finally ethanol. The black residue was crystallized from quinoline (charcoal) affording dark green needles of linear N,N′-dimethylindanthrone (**19**, 150 mg), mg >375°, having no absorption in the NH region of the infrared spectrum, and a C=O absorption at 1656 cm^{-1}. It dissolves in concentrated sulfuric acid with a green color. Its green solution in hot pyridine was unchanged on addition of methanolic potassium hydroxide. It gives a reddish brown vat with alkaline sodium hydrosulfite. This dimethyl compound was also obtained by methylation of the linear indanthrone **2**, using the same experimental conditions as described for the methylation of linear N-methylindanthrone.

Anal. Calcd for $C_{30}H_{18}N_2O_4$ (470): C, 76.58; H, 3.86; N, 5.96. Found: C, 76.32; H, 3.56; N, 5.65.

Its mass spectrum had a molecular ion peak at *m/e* 470, with peaks at 455 and 440 due to loss of one and two methyls, respectively. There was a strong peak at 235, presumably due to symmetrical cleavage of the molecule into two parts.

2,3-Diaminoanthracene.—A mixture of 2,3-diaminoanthraquinone (18 g), zinc dust (12 g), and aqueous 5% sodium hydroxide (250 ml) was refluxed with stirring for 12 hr, during which time the mixture turned from deep red to yellow. The mixture was filtered hot and the residue was washed with water. The dried residue was extracted with boiling nitrobenzene (charcoal) affording 2,3-diaminoanthracene (15.2 g) as pale, greenish yellow plates, mp 270–290° dec. It dissolves in concentrated sulfuric acid with a greenish yellow color.

Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.41; H, 6.11; N, 13.65.

5(?),7,16,18(?)-Tetrahydrodinaphtho[2,3-*b*:2′,3′-*i*]**phenazine** (**20**).—2,3-Diaminoanthracene (3.9 g) was refluxed with stirring in a mixture of *o*-dichlorobenzene (40 ml) and acetic acid (2.5 ml) for 4 hr. During this time the pale green solution deposited a bright yellow solid (1.7 g), which crystallized from N,N-dimethylformamide as fine, yellow needles, mp above 360°; infrared spectrum showed ν_{max} 3400 cm^{-1} (NH); ultraviolet spectrum showed λ_{max} 262 mμ (log ε 4.85), 269 (4.72), 318 (3.83). It dissolves in concentrated sulfuric acid with a deep blue color.

Anal. Calcd for $C_{28}H_{20}N_2$: C, 87.47; H, 5.24; N, 7.29. Calcd for $C_{28}H_{18}N_2$: C, 87.93; H, 4.74; N, 7.33. Found: C, 87.70; H, 5.43, 5.23; N, 7.51.

Treatment with methyl *p*-toluenesulfonate in boiling *o*-dichlorobenzene in the presence of potassium carbonate afforded **7,16-dimethyl-7,16-dihydrodinaphtho**[2,3-*b*:2′,3′-*i*]**phenazine**, mp above 360°; ultraviolet spectrum showed λ_{max} 2.62 mμ (log ε 5.22), 269 (5.17), 330 (5.15). It dissolves in concentrated sulfuric acid with a deep violet-blue color. Its solutions in organic solvents have an intense green fluorescence.

Anal. Calcd for $C_{30}H_{22}N_2$ (410): C, 87.77; H, 5.40; N, 6.82. Found: C, 87.38; H, 5.68; N, 6.35.

Its mass spectrum had a molecular ion peak at *m/e* 410.

Oxidation of Compound 20.—Sodium dichromate (2.0 g) was added in small portions to a suspension of compound **20** (0.78 g) in boiling acetic acid (30 ml) during 10 min. After refluxing for an additional 30 min, the mixture was added to water. The resultant precipitate was dried and crystallized from N,N-dimethylformamide affording the phenazine **21** (0.33 g), identical with material obtained by the nitric acid oxidation of linear indanthrone **2**. Reduction of the product with hydrogen in boiling quinoline as previously described afforded the linear indanthrone.

Substituent Effects in 1,10-Phenanthrolines. I. Equilibria

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Received March 30, 1966

The Hammett equation has been applied to the dissociation of substituted phenanthrolinium ions, equilibrium constants for dissociation of substituted phenanthroline–iron(II) and –copper(II) complexes, and formal oxidation–reduction potentials of substituted phenanthroline–iron(II) and –copper(II) complexes. The dissociation constants of 2-, 3-, and 4-substituted phenanthrolinium ions are shown to be macroconstants related to the microconstants for protonation at N^1 and N^{10}. The 5-substituted phenanthrolines appear to undergo protonation at the oxygen atom of the hydrate. Good to excellent correlations with the extended Hammett equation were obtained in most cases. Electrical effects upon oxidation–reduction potentials of tris(5-substituted 1,10-phenanthroline)–iron(II) complexes are very much different in composition from electrical effects on dissociation of these complexes and apparently of electrical effects on dissociation of the corresponding phenanthrolinium ions. The α values obtained from the correlation of the oxidation–reduction potentials of the iron complexes are linear in the H_0 values of the solutions in which they were determined. The significant correlation of dissociation constants for 2-, 3-, and 4-substituted phenanthrolinium ions with the extended Hammett equation shows that the application of the Hammett equation to tautomeric equilibria as described by Kabachnik and co-workers will not be correct in all cases.

Substituted 1,10-phenanthrolines have long been of considerable interest as analytical reagents. A large body of data has accumulated in the literature on the ionization constants of these substances, equilibrium constants for their complex formation with transition metal ions, and oxidation–reduction potentials of the resulting complexes. We have recently studied the application of the Hammett equation[1] (1) to various heterocyclic systems.[2] It seemed of interest to extend these studies to substituent effects in 1,10-phenanthrolines. Although sporadic attempts have been made previously to apply the Hammett equation to these

$$Q_X = \rho\sigma_X + h \qquad (1)$$

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(1) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons Inc., New York, N. Y., 1956, p 565; V. Palm, *Russ. Chem. Rev.*, **31**, 471 (1961); P. R. Wells, *Chem. Rev.*, **63**, 171 (1963); H. H. Jaffé and H. L. James, *Advan. Heterocyclic Chem.*, **3**, 209 (1964).

(2) M. Charton, *J. Am. Chem. Soc.*, **86**, 2033 (1964).

(3) M. Charton, *J. Chem. Soc.*, 5884 (1964).

(4) M. Charton, *J. Org. Chem.*, **30**, 3341 (1965).

(5) M. Charton, *ibid.*, **30**, 4146 (1965).

TABLE I
DATA USED IN THE CORRELATIONS

1. Ionization Constants of 5-Substituted 1,10-Phenanthrolines in Water at 25°[a]

X	Me	H	Ph	Cl	NO_2
pK_a	5.23	4.96	4.80	4.26	3.57

2. Ionization Constants of 5-Substituted 1,10-Phenanthrolines in 50% (v/v) Dioxane–Water at 25°[b]

X	H	NO_2	Cl	Ph	Me	NH_2
pK_a	4.53	2.80	3.43	4.03	4.65	5.23

3. Ionization Constants of 5,6-Disubstituted 1,10-Phenanthrolines in Water at 25°

X	H	Cl	MeO	$(CH_2)_4$	Me
pK_a	4.86[c]	3.47[c]	4.42[c]	5.30[c,d]	5.60[e]

4. Ionization Constants of 4-Substituted 1,10-Phenanthrolines in Water at 25°[c]

X	Pr	Et	H	Ph	Br
pK_a	5.45	5.44	4.86	4.90	4.03

5. Ionization Constants of 4,7-Disubstituted 1,10-Phenanthrolines in Water at 25°[c]

X	MeO	Et	Ph	H	Cl
pK_a	6.45	5.60	4.84	4.86	3.03

6. Ionization Constants of 4,7-Disubstituted 1,10-Phenanthrolines in 50% (v/v) Dioxane–Water at 25°[b]

X	H	Cl	Ph	Me
pK_a	4.53	2.65	4.30	5.40

7. Ionization Constants of 3-Substituted 1,10-Phenanthrolines in Water at 25°[c]

X	Et	Me	H	Ph	Cl
pK_a	4.98	5.00	4.86	4.82	3.99

8. Ionization Constants of 2-Substituted 1,10-Phenanthrolines in Water at 25°

X	Cl	Me	H	Ph
pK_a	4.20[b]	5.30[b]	4.97[b]	4.90[c]

9. Dissociation Constants of Tris(5-substituted 1,10-phenanthroline)-Iron(II) Complexes in Water at 25°[a]

X	Me	H	Ph	Cl	NO_2
pK_{dis}	22.3	21.3	21.1	19.7	17.8

10. Stability Constants of Tris(5-substituted 1,10-phenanthroline)-Copper(II) Complexes in 50% Dioxane–Water at 25°[b]

X	H	NO_2	Cl	Ph	Me	NH_2
Log K_3	4.50	3.25	3.72	4.05	4.60	5.02

11. Stability Constants of Tris(4,7-disubstituted 1,10-phenanthroline)-Copper(II) Complexes in 50% Dioxane–Water at 25°[b]

X	H	Cl	Ph	Me
Log K_3	4.50	3.25	3.75	4.86

12. Formal Oxidation Potentials of 5-Substituted 1,10-Phenanthroline)-Iron(II) Complexes in 0.50 F H_2SO_4 at 25°[f]

X	Me	H	Ph	Cl	NO_2	Br
$E°$	1.04	1.08	1.10	1.14	1.26	1.13[g]

13. Formal Oxidation Potentials of 5-Substituted 1,10-Phenanthroline–Iron(II) Complexes in 1.0 F H_2SO_4 at 25°[a]

X	Me	H	Cl	NO_2	Ph
$E°$	1.02	1.06	1.12	1.25	1.08

14. Formal Oxidation–Reduction Potentials of 5-Substituted 1,10-Phenanthroline–Iron(II) Complexes in 2.0 F H_2SO_4 at 25°[f]

X	NO_2	Cl	H	Me
$E°$	1.22	1.10	1.03	1.00

15. Formal Oxidation–Reduction Potentials of 5-Substituted 1,10-Phenanthrolines in 4.0 F H_2SO_4 at 25°[f]

X	NO_2	Cl	H	Me
$E°$	1.17	1.04	0.96	0.93

16. Formal Oxidation–Reduction Potentials of 5-Substituted 1,10-Phenanthrolines in 6.0 F H_2SO_4 at 25°[f]

X	NO_2	Cl	H	Me
$E°$	1.12	0.97	0.89	0.86

17. Oxidation–Reduction Potentials of Bis(5-substituted 1,10-phenanthroline)-Copper(II) Complexes in 50% Dioxane–Water at 25°[b]

X	H	NO_2	Cl	Ph	Me	NH_2
E_f	0.296	0.379	0.321	0.291	0.299	0.248

18. Oxidation–Reduction Potentials of Bis(4,7-disubstituted 1,10-phenanthroline)-Copper(II) Complexes in 50% Dioxane–Water at 25°[b]

X	H	Cl	Ph	Me
E_f	0.290	0.387	0.229	0.220

[a] W. W. Brandt and D. K. Gullstrom, *J. Am. Chem. Soc.*, **74**, 3532 (1952). [b] B. R. James and R. J. P. Williams, *J. Chem Soc.*, 2007 (1961). [c] A. A. Schilt and G. F. Smith, *J. Phys. Chem.*, **60**, 1546 (1956). [d] σ_I and σ_R for the cyclohexeno group (CH_2CH_2-CH_2CH_2) were assumed equal to those for the butyl group. [e] D. A. Brisbin and W. A. E. McBryde, *Can. J. Chem.*, **41**, 1135 (1963). [f] G. Dulz and N. Sutin, *Inorg. Chem.*, **2**, 917 (1963). G. F. Smith and F. P. Richter, *Ind. Eng. Chem. Anal. Ed.*, **16**, 580 (1944).

compounds,[6] these attempts have not always been successful and no systematic study of the problem is extant. We have therefore examined the correlation of the data taken from the literature with the extended form of the Hammett equation[7] (2). The data used

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h \qquad (2)$$

are reported in Table I. Unless otherwise noted, the σ_I constants have been taken from our compilation,[8] and the σ_R constants have been taken from eq 3.[9] The

$$\sigma_{R,X} = \sigma_{p,X} - \sigma_{I,X} \qquad (3)$$

σ_p constants required by eq 3 are taken from the compilation of McDaniel and Brown.[10]

As some of the sets studied are symmetrically and identically disubstituted, it will be necessary to briefly consider the general problem of the application of the Hammett equation to multiply substituted sets. We may divide such sets into three classes.

(1) **Sets with a Single Reaction Site.**—Examples of such sets are the 3,5-disubstituted benzoic and the 3,4,6-trisubstituted naphthoic acids.

(2) **Sets with Two or More Equivalent Reaction Sites.**—An example of such a set is that of the 4,5-disubstituted-2,7-naphthadioic acids.

(3) **Sets with Two or More Nonequivalent Reaction Sites.**—Such a set would be that of the 3,5-disubstituted-1,7-naphthadioic acids.

For our present purposes we need consider only classes 1 and 2. Class 1 may be divided into two subclasses, those compounds which are symmetrically and identically substituted and those which are not. It is the former of these two subclasses which concerns us here. Neglecting interaction terms[11] we may write for class 1 (assuming simple additivity of substituent effects) (eq 4). Now for the first subclass, with n

$$Q_X = \alpha\Sigma\sigma_{I,X} + \beta\Sigma\sigma_{R,X} + h \qquad (4)$$

identical substituents

$$\Sigma\sigma_{I,X} = n\sigma_{I,X} \qquad \Sigma\sigma_{R,X} = n\sigma_{R,X} \qquad (5)$$

and

$$Q_X = n\alpha\sigma_{I,X} + n\beta\sigma_{R,X} + h \qquad (6)$$

$$Q_X = \alpha'\sigma_{I,X} + \beta'\sigma_{R,X} + h \qquad (7)$$

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(6) P. Ellis, R. Hogg, and R. G. Wilkens, *J. Chem. Soc.*, 3308 (1959); J. Burgess and R. H. Prince, *ibid.*, 5752 (1963).

(7) R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958).

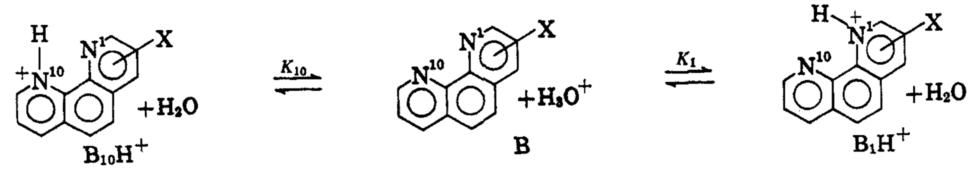
(8) M. Charton, *J. Org. Chem.*, **29**, 1222 (1964).

(9) R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

(10) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

(11) S. I. Miller, *J. Am. Chem. Soc.*, **81**, 161 (1959).

CHART I



Inherent in the definition of class 2 is the fact that its members must be identically and symmetrically substituted. Consider the simplest case of class 2, in which there are two reaction sites, and two substituents located at positions *m* and *n* of the carbon skeleton. Let us again assume that the effect of the substituents is additive, and that interaction terms are negligible. Let us further limit our discussion to equilibria and reaction rates. Then we may write for reaction at reaction site 1

$$\log K^1_{\mathrm{X}} = \alpha^1_m\sigma_{\mathrm{I,X}} + \beta^1_m\sigma_{\mathrm{R,X}} + \alpha^1_n\sigma_{\mathrm{I,X}} + \beta^1_n\sigma_{\mathrm{R,X}} + \log K^1_{\mathrm{H}} \quad (8)$$

$$\log K^1_{\mathrm{X}} = (\alpha^1_m + \alpha^1_n)\sigma_{\mathrm{I,X}} + (\beta^1_m + \beta^1_n)\sigma_{\mathrm{R,X}} + \log K^1_{\mathrm{H}} \quad (9)$$

where α_{1m} refers to the magnitude of the localized electrical effect exerted by the substituent at position *m* upon reaction site 1, the other coefficients have analogous meanings.

As the two reaction sites are equivalent

$$K^1_{\mathrm{X}} = K^2_{\mathrm{X}} \qquad K^1_{\mathrm{H}} = K^2_{\mathrm{H}} \quad (10)$$

and the observed constants K_{X} and K_{H} are given by

$$K_{\mathrm{X}} = K^1_{\mathrm{X}} + K^2_{\mathrm{X}} = 2K^1_{\mathrm{X}} \qquad K_{\mathrm{H}} = K^1_{\mathrm{H}} + K^2_{\mathrm{H}} = 2K^1_{\mathrm{H}} \quad (11)$$

Then

$$\begin{aligned}\log K_{\mathrm{X}} &= \log K^1_{\mathrm{X}} + \log 2 \\ &= (\alpha^1_m + \alpha^1_n)\sigma_{\mathrm{I,X}} + (\beta^1_m + \beta^1_n)\sigma_{\mathrm{R,X}} + \log K_{\mathrm{H}} \quad (12)\end{aligned}$$

$$\log K_{\mathrm{X}} = \alpha''\sigma_{\mathrm{I,X}} + \beta''\sigma_{\mathrm{R,X}} + \log K_{\mathrm{H}} \quad (13)$$

Equations 7 and 13 are equivalent to eq 2. Thus, all correlations have been made with eq 2.

Results

The results of the correlations with eq 2 and 6 are set forth in Table II. Of the 18 sets studied, three are at the 99.5% confidence level (cl), five at the 99% cl, three at the 97.5% cl, and five at the 95% cl. Sets 11 and 14 gave results which were not significant. Over-all, the results are very good. Had six or more data points per set been available, we believe that the results would have been significant for all sets studied and excellent for most. We conclude from these results that eq 2 is generally applicable to substituted 1,10-phenanthrolines.

Ionization Constants.—Protonation at the nitrogen atoms in phenanthroline will result in a tautomeric equilibrium which may be written as shown in Chart I. The observed ionization constant K_{M} will be a macroconstant related to the microconstants K_1 and K_{10} by the equation

$$K_{\mathrm{M}} = \frac{C_{\mathrm{H_3O^+}}C_{\mathrm{B}}}{C_{\mathrm{BH^+}}} \quad (14)$$

where

$$C_{\mathrm{BH^+}} = C_{\mathrm{B_1H^+}} + C_{\mathrm{B_{10}H^+}} \quad (15)$$

and

$$K_1 = \frac{C_{\mathrm{H_3O^+}}C_{\mathrm{B}}}{C_{\mathrm{B_1H^+}}} \quad (16)$$

$$K_{10} = \frac{C_{\mathrm{H_3O^+}}C_{\mathrm{B}}}{C_{\mathrm{B_{10}H^+}}} \quad (17)$$

Then

$$K_{\mathrm{M}} = \frac{K_1K_{10}}{K_1 + K_{10}} \quad (18)$$

Applying the extended Hammett equation to the macroconstant results in

$$\mathrm{p}K^1_{\mathrm{X}} = \alpha_1\sigma_{\mathrm{I,X}} + \beta_1\sigma_{\mathrm{R,X}} + \mathrm{p}K^1_{\mathrm{H}} \quad (19)$$

$$\mathrm{p}K^{10}_{\mathrm{X}} = \alpha_{10}\sigma_{\mathrm{I,X}} + \beta_{10}\sigma_{\mathrm{R,X}} + \mathrm{p}K^{10}_{\mathrm{H}} \quad (20)$$

For $\mathrm{X} = \mathrm{H}$, $K_1 = K_{10}$, and from eq 18

$$K^1_{\mathrm{H}} = 2K_{\mathrm{MH}} \quad (21)$$

If we can estimate values of α_1, α_{10}, β_1, and β_{10}, and if a value of K_{MH} is available, we may then calculate values of $\mathrm{p}K_{\mathrm{MX}}$. Furthermore we may proceed to define

$$K_{\mathrm{T}} = \frac{K_1}{K_{10}} \quad (22)$$

and the quantity

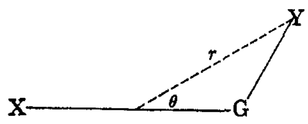
$$f_1 = \frac{C_{\mathrm{B_1H^+}}}{C_{\mathrm{B_1H^+}} + C_{\mathrm{B_{10}H^+}}} = \frac{K_{\mathrm{M}}}{K_1} \quad (23)$$

which represents that fraction of the conjugate and which is protonated at N^1.

We have presented evidence[12] which suggests that α is given by the equation

$$\alpha_{\mathrm{G}} = \frac{(\cos\theta_{\mathrm{G}})r^2_{\mathrm{G^0}}\alpha_{\mathrm{G^0}}}{(\cos\theta_{\mathrm{G^0}})r^2_{\mathrm{G}}} \quad (24)$$

which may be obtained by combining the Hammett and Kirkwood–Westheimer[13] equations. We may write any set of compounds we wish to study in the form $\mathrm{X_iG_jY_k}$ where X is the substituent, Y is the reaction site, and G is the group to which X and Y are attached. Then we may define r and θ as shown. The quantities



bearing the subscript G refer to the group for which α is to be calculated, the quantities bearing the subscript $\mathrm{G^0}$ refer to some reference group. From the above we may conclude that values of α_1 and α_{10} will be approximately equal to the values of α for model systems of geometry similar to that in the 1,10-phenanthroline

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[12] M. Charton, 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April 1960, Abstracts, p 92-O; 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1961, p 57T.

[13] J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506, 513 (1958).

TABLE II

RESULTS OF CORRELATIONS

Set	α	β	h	F[a]	R[b]	r[c]	s_{est}[d]
1	−1.95	−0.843	4.97	201.6	0.998	0.236	0.0655
2	−2.31	−1.30	4.37	39.06	0.981	0.270	0.219
3	−3.95	−0.818	5.06	24.10	0.980	0.587	0.235
4	−3.92	−4.23	4.86	268.0	0.998	0.807	0.0500
5	−6.88	−6.49	4.76	156.8	0.997	0.587	0.142
6	−6.32	−4.57	4.50	258.7	0.99990	0.819	0.0874
7	−1.97	−2.20	4.89	52.06	0.991	0.793	0.0817
8	−2.51	−1.70	4.97	9765.0	0.99997	0.819	0.00573
9	−5.06	−2.77	21.4	99.80	0.995	0.236	0.246
10	−1.64	−0.982	4.36	25.96	0.972	0.270	0.194
11	−3.29	−1.39	4.35	2.706	0.919	0.819	0.497
12	0.225	0.222	1.09	99.00	0.993	0.0694	0.0119
13	0.239	0.223	1.07	95.26	0.995	0.236	0.0127
14	0.245	0.196	1.03	776.0	0.9997	0.207	0.00430
15	0.270	0.207	0.96	441.9	0.9994	0.207	0.00624
16	0.288	0.249	0.90	177.8	0.999	0.207	0.0107
17	0.0947	0.0842	0.301	39.28	0.981	0.270	0.0106
18	0.443	0.473	0.281	2.893	0.923	0.819	0.0513

Set	s_α[d]	s_β[d]	s_h[d]	cl[e]	n[f]	ϵ
1	0.106	0.261	0.0459	99.5	5	0.43
2	0.350	0.336	0.143	99	6	0.56
3	0.637	0.734	0.159	95	5	0.21
4	0.205	0.544	0.0490	99.5	5	1.1
5	0.417	0.436	0.0946	99	5	0.94
6	0.374	0.897	0.0836	95	4	0.72
7	0.306	0.785	0.0780	97.5	5	0.11
8	0.0246	0.0589	0.00548	99	4	0.68
9	0.396	0.978	0.172	99	5	0.55
10	0.310	0.298	0.127	97.5	6	0.60
11	2.13	5.10	0.475	<90	4	0.42
12	0.0179	0.0410	0.00816	99.5	6	0.99
13	0.0205	0.0507	0.00890	97.5	5	0.93
14	0.00709	0.0172	0.00325	95	4	0.80
15	0.0103	0.0250	0.00473	95	4	0.77
16	0.0176	0.0427	0.00808	95	4	0.86
17	0.0170	0.0164	0.00684	99	6	0.89
18	0.220	0.527	0.0491	<90	4	1.1

[a] F test for significance of regression. [b] Multiple correlation coefficient. [c] Partial coefficient of σ_I on σ_R. [d] Standard deviations of estimate, α, β, and h. [e] Confidence level. [f] Number of points in set.

system. Values of α we have estimated in this manner are set forth in Table III with the model systems from which they were derived.

We have further shown[14] that values of β may be calculated from the formal charge q at the atom bearing the reaction site by means of the following equation.

$$\beta = mq + c \qquad (25)$$

Equation 25 has been successfully applied to azaarenes with $m = 33.1$, $c = 0.184$. Values of q were calculated by the method of Dewar.[15] For those cases in which the Dewar method gives $q = 0$, we have made use of the approximation[16]

$$\beta = m^1 \Sigma q_{adj} + c^1 \qquad (26)$$

where Σq_{adj} is the sum of the formal charges on the atoms adjacent to that bearing the reaction site, and $m^1 = 5.77$, $c^1 = 0.384$. Values of β calculated from eq 25 or 26 are given in Table III.

Values of pK_M calculated from eq 18, 19, and 20 for the data of sets 1, 4, 7, and 8 are given in Table IV. Values of pK_T and f_1 for the data of sets 1, 4, 7, and 8 are also given in Table IV.

Comparison of the calculated pK_M values with the observed pK_a values of the 5-substituted 1,10-phenanthrolines (set 1) shows serious deviations for X = Cl and NO_2 (we believe that deviations greater than 0.3

TABLE III

Set	$-\alpha_1$	Model system	$-\alpha_{10}$	Model system
8	10.6[a]	2-Substituted quinolines	1.76[b]	7-Substituted 1-naphthylamines
7	5.32[a]	2-Substituted quinolines	1.38[b]	6-Substituted 1-naphthylamines
4	5.27[a]	4-Substituted quinolines	1.76[b]	5-Substituted 1-naphthylamines
1	3.17[c]	5-Substituted quinolines	2.96[c]	4-Substituted 1-naphthylamines

Set	$-\beta_1$	q	$-\beta_{10}$	q
8	2.85[d]	...	1.45	0.0408[e]
7	1.39	0.174[e]	0.902	0.0217
4	5.71	0.167	0.598	0.0370[e]
1	0.776	0.0179	1.21	0.143[e]

[a] Calculated from data cited in ref 3. [b] Calculated from pK_a values reported by A. Bryson, *J. Am. Chem. Soc.*, **82**, 4862 (1960). [c] Ref 4. [d] Value of β for 2-substituted quinolines. [e] Σq_{adj}.

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(14) M. Charton, 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965, Abstracts, p 13S.

(15) A. Streitweiser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons Inc., New York, N. Y., 1961, p 54.

(16) M. Charton, unpublished results.

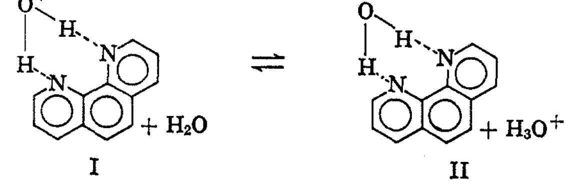
TABLE IV

CALCULATED VALUES OF pK_M, pK_T, AND f_1

Set	X	pK_a	pK_M	Δ	pK_T	f_1
1	5-Me	5.23	5.23	0	−0.0415	0.4760
	5-Ph	4.80	4.77	0.03	−0.0687	0.4605
	5-Cl	4.26	3.77	0.49	−0.2028	0.3853
	5-NO_2	3.57	2.78	0.79	−0.0993	0.4430
4	4-Pr	5.45	5.38	0.07	0.621	0.8069
	4-Et	5.44	5.47	0.03	0.694	0.8318
	4-Ph	4.90	4.87	0.03	0.196	0.6111
	4-Br	4.03	4.08	0.05	−0.522	0.2310
7	3-Et	4.98	5.16	0.18	0.246	0.6378
	3-Me	5.00	5.18	0.18	0.256	0.6430
	3-Ph	4.82	4.68	0.14	−0.340	0.3135
	3-Cl	3.99	4.14	0.15	−1.73	0.0181
8A	2-Cl	4.20	4.19	0.01	−3.82	0.0002
	2-Me	5.30	5.64	0.34	0.610	0.8029
	2-Ph	4.90	4.73	0.17	−0.730	0.1570
8B	2-Cl	4.20	4.19	0.01	−4.14	0.0001
	2-Me	5.30	5.51	0.21	0.448	0.7372
	2-Ph	4.90	4.71	0.19	−0.878	0.1168
8C	2-Cl	4.20	4.19	0.01	−4.32	0.0000
	2-Me	5.30	5.45	0.15	0.358	0.6952
	2-Ph	4.90	4.70	0.20	−0.961	0.0986

pK_a units between calculated and observed values are serious, uncertainties in α_1, α_{10}, β_1, and β_{10} make smaller deviations insignificant). We cannot account for the pK_a values of these compounds in terms of protonation on nitrogen. In support of this observation let us consider the 5,6-disubstituted 1,10-phenanthrolines (set 3). Using the estimated values of α_1, α_{10}, β_1, and β_{10} for the 5-substituted phenanthrolines we may calculate for this set, from eq 12, $\alpha = -6.13$, $\beta = 1.99$. The observed values of α and β for this set, −3.95 and −0.818, are significantly different from the calculated values.

On the basis of the above discussion, it would seem that N protonation does not occur in 5-substituted or 5,6-disubstituted 1,10-phenanthrolines. Our results may be accounted for by the existence of only one basic site in these compounds. Smith and Richter[17] have reported that 1,10-phenanthroline and its derivatives generally form stable monohydrates and that infrared studies show the water molecule to be hydrogen bonded to the nitrogen atoms. Beattie and Webster[18] suggest that 1,10-phenanthroline monohydrate monohydrochloride has the structure I. Then we may represent the ionization of 5-substituted 1,10-phenanthrolines as



I II

in which the basic site is the oxygen atom of the water molecule. As a check on our conclusions we may calculate α for the 5,6-disubstituted 1,10-phenanthrolines from the observed value of α for the 5-substituted phenanthroline by means of eq 6. No calculation of β will be attempted as a "*t* test" shows that the observed value of β for the 5,6-disubstituted phenanthrolines is not highly significant. The calculated value of α is −3.90 and the observed value is −3.95; the agreement is excellent.

In the case of the 4-substituted 1,10-phenanthrolines (set 4) the calculated pK_M and the observed pK_a values are in excellent agreement, the average of the absolute deviation Δ where

$$\Delta = |pK_a - pK_M| \tag{27}$$

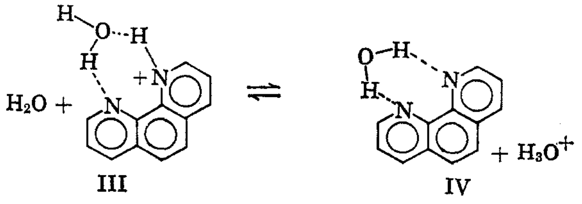
is smaller than the experimental error in the pK_a values. Calculation of α and β for the 4,7-disubstituted 1,10-phenanthrolines (set 5) from the estimated values of α_1, α_{10}, β_1, and β_{10} for the 4-substituted 1,10-phenanthrolines gives values of −7.03 and −6.31, respectively, agreeing excellently with the observed values of −6.88 and −6.49. It is possible therefore to account completely for the observed pK_a values in 4-substituted and 4,6-disubstituted 1,10-phenanthrolines by protonation at the nitrogen atoms.

The calculated values of pK_M for the 3-substituted 1,10-phenanthrolines (set 7) are in very good accord with the observed values of pK_a. The average absolute deviation is 0.16 p*K* units. Thus, in this set as in the 4-substituted 1,10-phenanthrolines, we may account for the observed pK_a values in terms of protonation on the nitrogen atoms.

In calculating values of pK_M for the 2-substituted 1,10-phenanthrolines (set 8) a problem arises in the estimation of β_1. Values of β observed in *ortho*-substituted azaarene sets are not in accord with the values calculated from eq 25. Thus for the ionization of 2-substituted pyridinium, 2-substituted quinolinium, and 1-substituted isoquinolinium ions calculated and observed values of β are pyridinium (20°), calculated −4.92, observed −2.65; pyridinium (25°), calculated −4.92, observed −0.594; quinolinium (25°), calculated −6.80, observed −2.83; isoquinolinium (20°), calculated −7.96, observed −3.90. We have therefore calculated values of pK_M using the observed value of β for quinolinium ions for β_1 as well as values of β_1 of 0.75 and 1.50. With $\beta_1 = 0.75$, the average Δ was 0.12, indicating excellent agreement between calculated pK_M and observed pK_a values. We conclude that protonation occurs at nitrogen in the 2-substituted phenanthrolines.

Our results show that protonation at the nitrogen atoms occurs in 2-, 3-, and 4-substituted 1,10-phenanthrolines, the observed pK_a values being macroconstants related to the microconstants for protonation at N^1 and N^{10}.

As we have noted above our results for 5-substituted 1,10-phenanthrolines are in accord with protonation at the oxygen atom of the hydrate, I. We are unable at the present time to explain why N protonation is predominant in the 2-, 3-, and 4-substituted 1,10-phenanthrolines but it does not seem to occur in the 5-substituted 1,10-phenanthrolines. We wish to propose structure III for the hydrate of a protonated 1,10-phenanthroline. The ionization of a phenanthrolinium ion may therefore be written as shown. Sets 8A, 8B,



III IV

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[17] G. F. Smith and F. P. Richter, "Phenanthroline and Substituted Phenanthroline Indicators," G. F. Smith Chemical Co., Columbus, Ohio, 1944.

[18] I. R. Beattie and M. Webster, *J. Phys. Chem.*, **66**, 115 (1962).

TABLE V

RESULTS OF CORRELATION WITH EQUATION 31

Q	p	d	r^a	$s_{estd}{}^b$	$s_p{}^b$	t^c	n^d	cl
α	−0.0154	0.233	0.973	0.00669	0.00209	7.360	5	99.5
β	−0.00709	0.210	0.567	0.0190	0.00594	1.193	5	90

[a] Correlation coefficient. [b] Standard errors of the estimate and the slope, respectively. [c] Student t test. [d] Number of points in the set.

and 8C were calculated with $\beta_1 = -2.85, -1.50$, and -0.750, respectively. Values of pK_a are from Table I.

Complex Formation.—The formation of complexes differs from the protonation of 1,10-phenanthrolines in that both nitrogen atoms are involved in bonding to the central metal atom and therefore no question of tautomerism can arise. This means that with the possible exception of 5-substituted 1,10-phenanthrolines, comparisons between pK_a values for the ionization of monosubstituted phenanthrolinium ions and log K for complex formation of the corresponding phenanthrolines *are not justified.* The comparison of complex formation with ionization is justified if the identically and equivalently disubstituted phenanthrolines are considered. The quantities of greatest interest to us are the magnitude and composition of the substituent's electrical effect upon complex formation. As a measure of the magnitude of the electrical effect we may use the value of α. On this basis we may compare the value of α obtained for the dissociation constants of tris-(5-substituted 1,10-phenanthroline)–iron(II) complexes (set 9) with the value of α obtained for the ionization of the 5,6-disubstituted phenanthrolinium ions (corrected for disubstitution by a factor of 0.5) the values are 5.06 and 1.93, respectively. Thus complex formation appears to be very much more susceptible to electrical effects in this case. In order to describe the composition of the electrical effect we may write

$$\epsilon = \beta/\alpha \tag{28}$$

Values of ϵ obtained for the sets correlated with eq 2 are reported in Table II. If protonation in 5-substituted phenanthrolines does in fact occur at the oxygen atom in the hydrate we may compare ϵ values for protonation with those for complex formation. The values are 0.43 and 0.55, respectively, indicating about the same composition for the electrical effect. In the case of the stability constants of the tris(5-substituted 1,10-phenanthroline)–copper(II) complexes in 50% dioxane–water (set 10) we may make a comparison with the ionization of the 5-substituted phenanthrolinium ions in the same solvent system (set 2). The α values are -2.31 and -1.64, respectively; thus in the case of the copper complexes, protonation is more susceptible than complex formation to substituent effects. The ϵ values are 0.56 for protonation and 0.60 for complex formation, again indicating the same composition for the electrical effect. The very poor correlation obtained for the stability constants of tris(4,7-disubstituted 1,10-phenanthroline)–copper(II) complexes (set 11) precludes any discussion of this set.

Oxidation–Reduction Potentials.—We have remarked above that if the oxygen atom in the hydrate is the site of protonation in 5-substituted 1,10-phenanthrolines we may make comparisons between this set and other sets. On the basis of such a comparison, the most striking result of the correlation of formal oxidation–reduction potentials for tris(5-substituted 1,10-phenanthroline)–iron(II) complexes (sets 12–16) with eq 2 is the composition of the electrical effect. We find an average value of ϵ for these sets of 0.87. By contrast, the values of ϵ for the dissociation of 5-substituted 1,10-phenanthrolinium ions in water (set 1) and in 50% dioxane–water (set 2) are 0.43 and 0.56, respectively, for complex formation with iron(II) and copper(II) (sets 9 and 10). Values of ϵ are 0.55 and 0.60, respectively. Thus, substituent effects on the oxidation–reduction potentials are of about the same composition as those which may be correlated by the σ_p constants (for which $\epsilon = 1$), whereas in dissociation and complex formation substituent effects are comparable in composition to those which may be correlated by the σ_m constants (for which $\epsilon = 0.33$). The oxidation–reduction potentials [at equal concentration of copper(I) and -(II)] of the bis(5-substituted 1,10-phenanthroline)–copper complexes (set 17) give an ϵ value of 0.89, about the same as the average ϵ value for the iron(II) complexes.

The formal oxidation–reduction potentials of the tris(5-substituted 1,10-phenanthroline)–iron(II) complexes are dependent on the acidity of the medium. To provide further information on the nature of this dependence we have correlated the α and β values obtained for sets 12–16 with the corresponding H_0 values[19] according to the equation

$$Q = pH_0 + d \tag{29}$$

The results of the correlations with eq 31 are reported in Table V.

It would appear that α is linear in H_0. Although no significant correlation between β and H_0 was obtained, the uncertainties in the values of β are so great as not to exclude the possible existence of such a relationship.

Application of the Hammett Equation to the Study of Tautomeric Equilibria.—Kabachnik and co-workers[20] have proposed that, if the same tautomer predominates in all members of a set, a plot of the observed pK_a values against the appropriate σ constants will be linear, whereas, if a changeover from one predominating tautomer to another occurs at some point in the set, *two straight lines intersecting at the changeover point will result.* Our results show that this is not the case for the 2-, 3-, or 4-substituted 1,10-phenanthrolinium ions. We have obtained very good correlation of the pK_a values of these substances with eq 2. Equally good correlations can be obtained with eq 1 by the use of a σ constant having an appropriate value of ϵ. The values

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of f_1 in Table IV show clearly that in these sets we have a changeover from the predominance of one tautomer to that of the other. We conclude therefore that the method of Kabachnik cannot be universally applied.

Acknowledgment.—The author wishes to acknowledge the use of the facilities of the Computer Laboratories of the School of Engineering and Science, Pratt Institute.

Application of the Hammett Equation to Nonaromatic Unsaturated Systems. VI. The Diels–Alder Reaction

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Received July 26, 1966

Rate constants taken from the literature for the reaction of sets of 1-substituted, 2-substituted, and 2,3-disubstituted 1,3-butadienes, and 9-substituted and 9,10-disubstituted anthracenes with various dienophiles and for the reaction of sets of *cis*- and *trans*-1,2-disubstituted and -1,1-disubstituted ethylenes with various dienes have been successfully correlated with the extended form of the Hammett equation $Q_X = \alpha\sigma_I + \beta\sigma_R + h$. Arguments are presented which show that for most of the reactions studied a concerted mechanism is involved. In some sets the available data did not permit any conclusions concerning the mechanism. The magnitude of the values of β obtained for several of the sets studied have been interpreted as evidence for a transition state which is closer to reactants than to adduct. Rates of per cent *endo*/per cent *exo* product formed in the reaction of 4-substituted cinnamoyl chlorides and cinnamic acids and of 4-nitrocinnamoyl and cinnamoyl derivatives with cyclopentadiene were also correlated with the extended Hammett equation; good results were obtained for the latter three sets. Rates of per cent 1,3/per cent 1,4 adduct formed in the reaction of substituted ethylenes with isoprene and of per cent *syn*/per cent *anti* adduct in the reaction of 2-substituted anthracenes with maleic anhydride have also been successfully correlated.

We have been engaged for some time in a study of the application of the Hammett equation[1] to nonaromatic unsaturated systems.[2] In this paper we extend our investigations to structural effects observed in the Diels–Alder and related reactions. In particular, we have studied the effect of substituents upon the reaction rates of dienes and dienophiles. Substituent effects upon the stereochemistry and the orientation in Diels–Alder reactions were also examined. Previous studies of structural effects upon the Diels–Alder reaction by means of the Hammett equation are extant.[3–8] In all of these studies, however, the substituents were bonded to a benzene ring attached to the diene or dienophile. No previous attempt to apply the Hammett equation or any other linear free-energy relationship to directly substituted dienes or dienophiles has been reported. We have therefore correlated by multiple linear regression analysis, sets of data taken from the literature with the extended Hammett equation

$$Q_X = \alpha\sigma_{I,X} + \beta\sigma_{R,X} + h \qquad (1)$$

For the correlation of disubstituted sets we have assumed that interaction terms[9] may be neglected and have used the equation

$$Q_X = \alpha\Sigma\sigma_{I,X} + \beta\Sigma\sigma_{R,X} + h \qquad (2)$$

The data used in the correlations are given in Table I. The σ_I constants were taken from our compilation.[10] The σ_R constants were obtained from the equation

$$\sigma_{R,X} = \sigma_{p,X} - \sigma_{I,X} \qquad (3)$$

The necessary σ_p constants were taken from the collection of Brown and McDaniel[11] when possible; otherwise they were obtained from previous papers in the series.[2]

For purposes of comparison, some of the substituted benzene sets previously correlated with the Hammett equation have been reexamined here by correlation with eq 1.

Results

Results of the correlations with eq 1 are set forth in Table II.

Substituent Effects on Diene Reaction Rates.—We have examined seven sets of substituted or disubstituted dienes (sets 1–7). Good-to-excellent results were obtained for sets 1–6. The elimination of the values for X = Et, *i*-Pr, and *t*-Bu from set 1 appears to give improved results (set 1A). This may be due to a steric effect of bulky groups in the 2 position of butadienes. Such groups may favor the formation of the s-*cis* conformation through which the Diels–Alder reaction proceeds. Because of these results, we included in set 2 only those singly substituted 1,3-butadienes which were members of set 1A. We have also considered that subset of set 2 which excludes all compounds in which one of the substituents is hydrogen (set 2A) to determine whether a second substituent introduces some change in α and β. The results show that no significant difference between values of α and β for sets 2 and 2A is observed. The results for set 6 seem to be improved by including in the set only those substituents which

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