m,m′-Dichlorobicumyl.—The reaction of *m*-chlorocumene and di-*t*-butyl peroxide was carried out as in the preceding section. On cooling of the reaction mixture, crystals formed which were removed by filtration, washed with acetone, and recrystallized from absolute ethanol: mp 134–135°. Characteristic *meta*-substitution bands were observed in the ir region at 11.3 and 12.8 μ. The nmr spectrum (CS_2 solution) possessed signals at δ 1.3 (singlet, CH_3, 12 H) and 7.08 (multiplet ArH, 7.8 H).

Anal. Calcd for $C_{18}H_{20}Cl_2$: C, 70.36; H, 6.56; Cl, 23.08. Found: C, 70.40; H, 6.50; Cl, 23.11.

1,1′-Di-*p*-tolyldicyclohexyl.—A solution of 0.1343 g of 1,1′-di-*p*-tolylazocyclohexane in 13 ml of toluene was heated under nitrogen at 60° for 24 hr. The solid remaining after the solution was evaporated to dryness weighed 0.1188 g (95% yield). Purification was accomplished by dissolving the solid in a minimum amount of carbon disulfide, adding 3 ml of pentane, cooling in Dry Ice, and isolating the crystallized solid. After repeated recrystallization in this manner, followed by drying at 100° (6 mm), the material melted at 207–208°, apparently with decomposition. In the nmr spectrum (CS_2 solution) signals were present at δ 0.95–2.4 (multiplet, CH_2, 2.28 (singlet, CH_3), and 6.8 (doublet, ArH). The ratio of ArH to RH was 4:13.2 (theory, 4:13). In the ir spectrum, absorption occurred at 12.3 μ (*para* substitution) and 12.1, 12.7, and 13.45 μ (assigned to the 1,1-disubstituted cyclohexane ring). A similar three-band pattern (11.9, 12.25, and 12.6 μ) is exhibited by bicyclohexyl-1,1′-diol.[25] In the mass spectrum, no peak appeared in the molecular ion region (*m/e* 346), but a strong one was present at *m/e* 173, conceivably due to thermal dissociation.

Anal. Calcd for $C_{26}H_{34}$: C, 90.11; H, 9.89, mol wt, 346. Found: C, 90.28; H, 9.82; mol wt, 330.

***p*-Cyclohexyltoluene and Di-*t*-butyl Peroxide.**—A mixture of *p*-cyclohexyltoluene (6.44 g) and di-*t*-butyl peroxide (2.68 g) was heated at 125–149° for 26 hr. After an additional 1.4 g of di-*t*-butyl peroxide was added, the mixture was heated at 120–140° for 24 hr longer. Dilution of the cooled mixture with acetone (50 ml) precipitated a yellow solid. Purification was effected several times by dissolving the filtered solid in benzene and reprecipitating with acetone. The material was dried at 100° (6 mm); it softened at 180°, turned to a clear orange gel at 200–220°, then melted at 220–290°. The product showed a broad band at 12.25 μ (*para* substitution) in the ir spectrum, with no other absorption in the 12–13.5-μ region. The nmr spectrum gave a broad complex signal from δ 0.8 to 3.5 (RH) and 6.5–7.5 (ArH), with a ArH/RH ratio of 4:12.7 (theory, 4:13).

Anal. Found: C, 88.66; H, 8.94; mol wt, 4400.

***m*-Chlorocumene.**—*m*-Cumidine hydrochloride was prepared by passing hydrogen chloride through a solution of *m*-cumidine[26] (6 g) in ether (200 ml). Isoamyl nitrite[27] (6.3 g) was added dropwise as rapidly as possible to a suspension of the salt in 200 ml of refluxing carbon tetrachloride. After being washed with water, dilute sodium hydroxide, and water, the mixture was distilled: 2.2 g, bp 70–72 (7.2 mm), $n^{20}{}_D$ 1.5015 [lit.[28] bp 66–68° (8 mm), $n^{20}{}_D$ 1.5136.

***p*-Chloro-α-methylstyrene.**—The synthesis from *p*-chloroacetophenone was accomplished by adaptation of the method of Benkeser and coworkers.[29] Dehydration of the *p*-chlorocumyl alcohol was carried out with iodine.[30]

***p*-Fluoro-α-methylstyrene.**—*p*-Fluoroacetophenone, bp 81–83° (6.5–7.2 mm), lit.[31] bp 79° (10 mm), was produced by Friedel–Crafts acylation[31] of fluorobenzene. Treatment of the ketone with 1 equiv of methyl Grignard reagent afforded crude *p*-fluorocumyl alcohol.[32] Dehydration by heating with iodine[30] furnished *p*-fluoro-α-methylstyrene, bp 50–51° (6.6–7 mm) [lit.[32] bp 93–94° (80 mm)].

***p*-Chlorocumene.**—The preparation from *p*-chloroacetophenone has been described.[5]

Acknowledgment.—We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of a portion of this work, and to Mr. C. K. Liang for helpful discussions.

[25] (25) The Sadtler Standard Spectra, No. 25042.

[26] (26) P. Kovacic, J. A. Levisky, and C. T. Goralski, *J. Amer. Chem. Soc.*, **88**, 100 (1966).

[27] (27) We are grateful to Dr. Lester Friedman and Mr. Paul Caruso for this procedure.

[28] (28) R. A. Benkeser, R. A. Hickner, and D. I. Hoke, *ibid.*, **80**, 2279 (1958).

[29] (29) R. A. Benkeser, J. Hooz, T. V. Liston, and A. E. Trevillyan, *ibid.*, **85**, 3984 (1963).

[30] (30) H. Hibbert, *ibid.*, **37**, 1748 (1915).

[31] (31) M. W. Renoll, *ibid.*, **68**, 1159 (1946).

[32] (32) P. A. J. Janssen, British Patent 881,893 (1961); *Chem. Abstr.*, **57**, 2198 (1962).

Linear Free-Energy Relations (LFER) for Amphoteric 5- (or 6-) Substituted Benzimidazoles

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Aqueous thermodynamic pK_a values at 25° have been obtained spectrophotometrically for a series (Br, CH_3, CF_3, Cl, F, H, NH_2, and NO_2) of 5- (or 6-) substituted benzimidazoles. ΔpK_a (acidity) values are excellently correlated with corresponding ΔpK^+ (basicity) values with $\Delta pK^+ = (1.16 \pm 0.05)\Delta pK_a - 0.02\ (\pm 0.04)$ with standard error in ΔpK^+ of 0.09 and correlation coefficient 0.995. ΔpK^+ and ΔpK_a give good correlations with Taft's σ_I and $\sigma_R{}^0$ and Lupton and Swain's $\mathfrak{F}$ and $\mathfrak{R}$. The relative importance of resonance and nonresonance effects is near the same for ΔpK^+ and ΔpK_a. The composite substituent constant ($\sigma_I + 0.8\ \sigma_R{}^0$) or ($\mathfrak{F} + \mathfrak{R}$) lies midway between σ_m and $\sigma_p{}^0$ in the importance of resonance. Both the ΔpK_a and ΔpK^+ series show a sensitivity to the polar (*i.e.*, nonresonance) effects of substituents that is characteristic of benzene derivatives undergoing a change in formal charge of one on the first atom of a side-chain reaction site. Hammett indicator plots of log [(anion)/(molecule)] *vs.* log C_{OH} give slopes of unity for the title compounds.

In an earlier paper[2] aqueous thermodynamic cation acidity constants (pK^+) as a measure of the basicity of some 5- (or 6-) substituted benzimidazoles were reported. Since there is a paucity of data in the literature[3] in which a series of ampholytes have had both teeir acid and base strengths measured by precise methods and under the same conditions and have had substituent effects on both acidity and basicity correlated, we felt it would be of interest to determine the aqueous thermodynamic molecule acidity constants (pK_a) of the title compounds.

We also wished to establish whether molecule acidity constant changes would lend themselves to quantitative

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[1] (1) Work performed as National Science Foundation Undergraduate Research Participant and in partial fulfillment of the requirements for the B.S. degree in chemistry.

[2] (2) H. Walba, D. H. Stiggall, and S. M. Coutts, *J. Org. Chem.*, **32**, 1954 (1967).

[3] (3) For a brief discussion of relationships between acidity and basicity of amphiprotic compounds, see E. M. Arnett, "Progress in Physical Organic Chemistry," Vol. 1, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Jr., Ed., Interscience Publishers Inc., New York, N. Y., 1963, p 322.

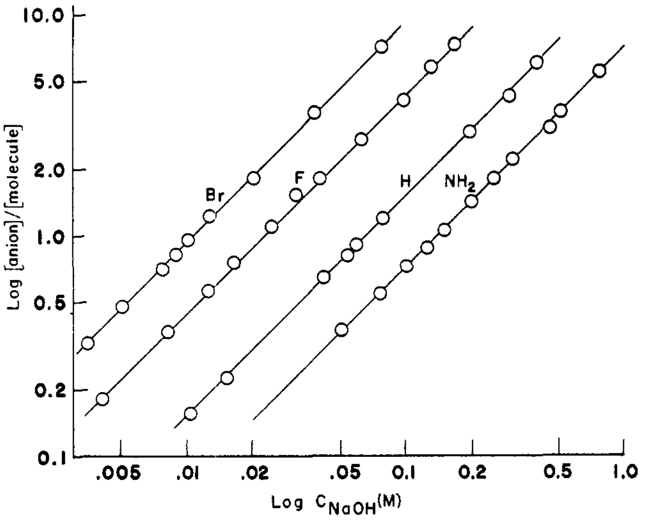


Figure 1.—The logarithm of ionization ratio *vs.* logarithm of sodium hydroxide concentration for some 5- (or 6-) substituted benzimidazoles. The curve for a given compound is indicated by the symbol for its 5 (or 6) substituent.

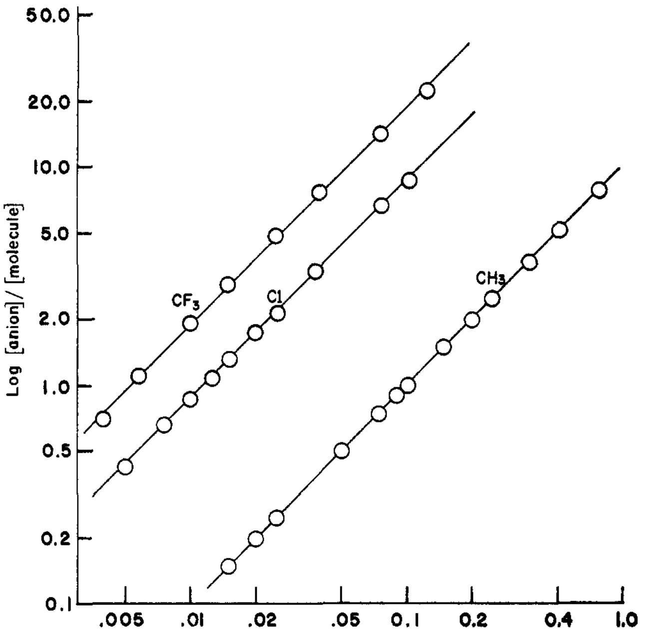
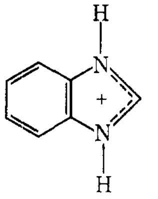


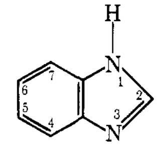
Figure 2.—The logarithm of ionization ratio *vs.* logarithm of sodium hydroxide concentration for some 5- (or 6-) substituted benzimidazoles. The curve for a given compound is indicated by the symbol for its 5 (or 6) substituent.

dissection into polar (*i.e.*, nonresonance) and resonance contributions as was found for cation acidity constants,[2] and, if so, whether the blending of polar and resonance effects is the same or different for the two series.

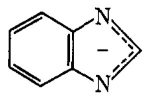
The cation, molecule, and anion involved in the acid–base equilibria are shown in formulas **1** through **3** for the parent compound.



1



2



3

Experimental Section

Preparation of Compounds.—All compounds were prepared according to reported methods and recrystallized to a constant melting point and constant uv spectrum. For the halogen compounds see ref 4a; for the methyl and nitro compounds see ref 4b; for the CF_3 and NH_2 derivatives see ref 4c and 4d, respectively.

Spectral Data and Method.—Spectral measurements were performed on a thermostated Cary Model 16 spectrophotometer. The temperature was controlled to 25.0 ± 0.1°. Isobestic points were used as a check on medium effects and Beer's law. Instead of using a matched pair of cells, as is common practice, we found it more convenient and accurate to employ a single cell with air as a reference when working at the single analytical wavelength used for equilibrium measurements. We found that transferring solutions from volumetric flasks to cells with pipets gave better precision than directly pouring into cells. Possibly more uniform wetting of cell windows results from pipetting.

The analytical wavelengths in millimicrons chosen for the equilibrium measurements are as follows: Br, 291; CH_3, 287; CH_3, 289; Cl, 291; CF_3, 284; F, 287; H, 282; NH_2, 289 and NO_2, 360.

The spectra of neutral molecules were measured in borax and Tris buffered solutions having a pH close to halfway between the cation acidity constant (pK^+) and the molecule acidity constant (pK_a) of the ampholytes studied. The pK^+ and pK_a of the ampholytes were sufficiently separated (~7 p*K* units) such that anion and cation concentrations are negligible at the "halfway" pH. Absorbance readings for equilibrium solutions were measured in CO_2-free NaOH solutions of known concentration. To correct for change in concentration of NaOH accompanying neutralization of ampholyte, eq 1 was used. C_{OH} is the equilibrium hydroxide ion concentrations; M_{OH} and M_{IH} are the stoichiometric concentrations of hydroxide ion and neutral molecule; and A, A^0, and A^- are the absorbances of the equilibrium solution, molecule, and anion, respectively, all measured at the same concentration or adjusted to the same concentration.

$$C_{OH} = {}'M_{OH} - \left[\frac{(A - A^0)M_{IH}}{(A^- - A^0)}\right] \qquad (1)$$

The absorbances of the anions did not lend themselves to direct measurement and were obtained by use of simultaneous equations. The method is described in an earlier work[5] except that in the present study constant ionic strength was not maintained as can be justified from subsequent work[6] as well as by results given in this section. Iterations were performed where they improved accuracy. Equation 2, which leads to the simultaneous equation solution for A^-, was used to calculate the hydrolysis constants of the anions, K_b. Solving for A^- by simultaneous equations requires two hydroxide ion concentrations. To favor accuracy, the lower C_{OH} of the pair was generally chosen so as to be close to half-neutralization or so as to give $A - A^0$ differences >0.25 OD units. The higher C_{OH} used was such as to give close to the highest percentage neutralization possible, and thus favorable $A - A^0$ differences, without inducing significant spectral shifts from medium effects. Reported values are based on hydroxide ion concentrations <0.9 *M*. Plots of reciprocals $1/(A - A^0)$ *vs.* 1/OH give excellent linearity.[7] A^- and K_b were calculated from slope and intercept and gave good agreement with the method of simultaneous equations. Unweighted least-squares treatment of the linearly related reciprocals gave correlation coefficients which in no case were <0.9998. The linearity observed here, as well as the Hammett indicator plots discussed in the next paragraph, indicate that the molar activity coefficient factor

$$K_b = [C_{OH}(A^- - A)]/(A - A^0) \qquad (2)$$

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[4] (a) D. J. Rabiger and M. M. Joullié, *J. Chem. Soc.*, 915 (1964); (b) D. J. Rabiger and M. M. Joullié, *J. Org. Chem.*, **29**, 476 (1964); (c) A. Sykes and J. C. Tatlow, *J. Chem. Soc.*, 4078 (1952); (d) M. Stäube, *Helv. Chim. Acta*, **32**, 135 (1949).

[5] H. Walba and R. W. Isensee, *J. Amer. Chem. Soc.*, **77**, 5488 (1955).

[6] (a) J. T. Edward and J. C. Wang, *Can. J. Chem.*, **40**, 399 (1962); (b) G. Yagil, *J. Phys. Chem.*, **71**, 1034 (1967).

[7] R. S. Stearns and C. W. Wheland, *J. Amer. Chem. Soc.*, **69**, 2025 (1947). Also see C. G. Overberger, T. St. Pierre, and S. Yaroslavsky, *ibid.* **87**, 4310 (1965).

TABLE I

THERMODYNAMIC CONSTANTS OF THE HYDROLYSIS OF THE ANION, pK_b, AND OF THE MOLECULE ACIDITY, pK_a, FOR SOME 5- (OR 6-) SUBSTITUTED BENZIMIDAZOLES IN WATER AT 25 ± 0.1°

Substituent	Registry no.	pK_b[a]	n[b]	S.D.[c] in log units	Uncertainty from imprecision at 0.01 level in log units[d]	pK_a[e]
Br	4887-88-1	1.978	5	0.008	±0.016	12.02
CH_2	614-97-1	1.000	5	0.004	±0.008	13.00
CF_3	326-55-6	2.278	7	0.012	±0.017	11.72
Cl	4887-82-5	1.935	6	0.006	±0.010	12.07
F	1977-72-6	1.668	6	0.015	±0.025	12.33
H	51-17-2	1.196	5	0.007	±0.014	12.80[f,g]
NH_2	93-422-5	0.875	5	0.005	±0.010	13.13[h]
NO_2	94-52-0	3.137	6	0.010	±0.016	10.86[i]

[a] Negative logarithm of the arithmetic mean of n (column four) independent determinations of K_b obtained as indicated in the Experimental Section. [b] Number of independent determinations. [c] Standard deviation in log units. $(\text{S.D.})^2 = \sum_{i=1}^{n} [\text{p}K_{bi} - (-\log \Sigma K_{bi}/n)]^2/(n-1)$. [d] The uncertainty from imprecision is derived from a computed standard error, which error is equal to S.D./$n^{1/2}$. The uncertainty is equal to $t_{0.01} \times (\text{S.D.}/n^{1/2})$ where $t_{0.01}$ is the value of Student's "t" for $n - 1$ degrees of freedom exceeded in absolute value with 0.01 probability. See ref 9. [e] pK_a = 14.00 − pK_b. [f] A value of 12.86 was found by G. Yagil, ref 6b, and 12.78 by H. Walba and R. W. Isensee, *J. Org. Chem.*, 26, 2789 (1961). [g] Values of 11.7 and 12.3 are found in D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworth, London, 1965. [h] A value of 11.2 is found in the reference in footnote *g*. [i] Values of 10.31 and 11.2 are found in the reference in footnote *g*; a value of 10.6 was obtained by T. C. Bruice and G. I. Schmir, *J. Amer. Chem. Soc.*, **80**, 148 (1958).

$(f_{IH}f_{OH^-})/(f_{I^-}f_W)$ is very close to unity for the hydrolysis of the anion (K_b) in the ranges of hydroxide ion concentrations employed. This condition, or at least a constant activity coefficient ratio, is necessary if the simultaneous equations method involving eq 2 is to be valid.

Hammett indicator plots of log (C_{I^-}/C_{IH}) *vs.* log C_{OH} are shown in Figures 1 and 2. The indicator ratio used in these plots is equal to $(A - A^0)/(A^- - A)$ with A^- calculated by method of simultaneous equations. A least-squares treatment gives the following results (the substituent symbol of compound, the slope with plus and minus values in parentheses for the standard error in the slope, and the range of C_{OH} used in the correlation with the indicator ratio are given in order): Br, 1.001 (±0.007), 0.004–0.08 *M;* CH_3, 1.006 (±0.003), 0.02–0.8 *M;* Cl, 1.001 (±0.004), 0.005–0.1 *M;* CF_3, 1.010 (±0.008), 0.004–0.1 *M;* F, 0.995 (±0.004), 0.004–0.2 *M;* H, 0.998 (±0.006) 0.01–0.5 *M;* NH_2, 0.993 (±0.006) 0.05–0.8 *M*. Since all slopes are unity within error, the molar activity coefficient factor that may be applied to eq 2 to give thermodynamic basicity constants is unity. Thermodynamic pK_b values may be obtained directly from the least-squares equations for lines in Figures 1 and 2 by calculating the value of log C_{OH} at half-neutralization, *i.e.*, where pK_b = − log C_{OH}. These values agree within 0.003 pK units or less with the negative logarithm of the average K_b values calculated from eq 2.

A plot of the log of the indicator ratio *vs.* the reported Hammett acidity function[6,8] H_- for the OH ranges indicated above would give very close to unit slopes since for these ranges $H_- = \text{p}K_W + \log C_{OH}$. Thus the anions of the compounds in Figures 1 and 2 are charged Hammett bases.

For stronger Hammett bases than those treated in this study, H_- values are now available for concentrated aqueous KOH[6b] and NaOH solutions[6] (above 1 *M* OH^-, $H_- \neq \text{p}K_W + \log C_{OH}$). Such H_- values could be used directly in various methods (simultaneous equations, etc.) for obtaining A^- and pK_a. However, it should be cautioned that H_- values increase in uncertainty[6b] and spectral shifts from medium effects may be expected[6] as the C_{OH} becomes very high. For H_- functions in nonaqueous media, see ref 8. No Hammett indicator plot was made for the nitro compound, but C_{OH} was low enough that eq 2 could be applied with little fear that the acitvity coefficient factor differed significantly from unity.

Results and Discussion

Equilibrium Constants.—Thermodynamic basicity constants, pK_b, of the anionic conjugate bases, formula 3 and its derivatives, are given in column two of Table I. Also given are measures of imprecision.[9] Thermodynamic molecule acidity constants, pK_a, are given in column six for comparison with literature values.

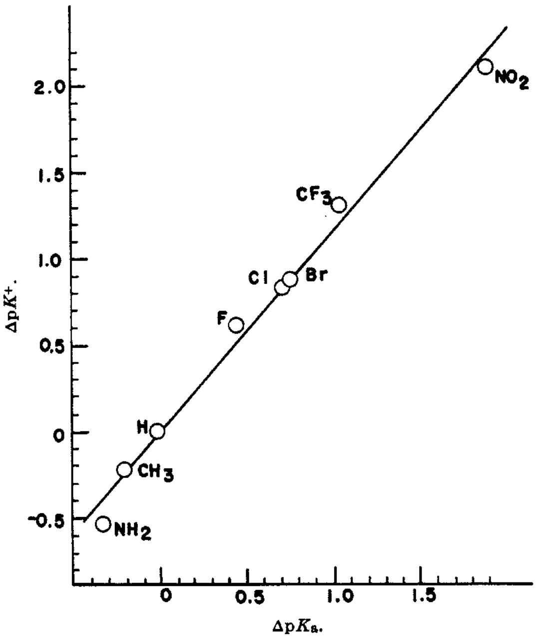

Figure 3.—Variation of basicity (ΔpK^+) with acidity (ΔpK_a) for some 5- (or 6-) substituted benzimidazoles.

Qualitatively, the substituent effects observed in the title compounds are those generally found in *meta*- and *para*-substituted aromatic acids and bases. All substituents are acid strengthening except for the methyl and amino substituents.

Correlations.—In Figure 3 there is a plot of ΔpK^+ (change in cation acidity or molecule basicity) *vs.* the corresponding ΔpK_a (change in molecule acidity). The ΔpK's of the ampholytes are here defined such as to increase with increasing acidity. A standard least-squares treatment for eq 3 where ρ is the slope and i the

$$\Delta\text{p}K^+ = \rho\Delta\text{p}K_a + i \quad (3)$$

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(8) For recent review of H_- function see K. Bowden, *Chem. Rev.*, **66**, 119 (1966).

(9) C. Eisenhart, *Science*, **160**, 1201 (1968).

$$\Delta pK^+ = (1.16 \pm 0.05)\Delta pK_a - 0.02\ (\pm 0.04) \qquad (4)$$

intercept gives eq 4 for all eight points. The plus and minus values are standard errors. The correlation coefficient, C, is 0.995 and the standard deviation from the regression line, $E_{\Delta pK^+}$, is 0.09. The largest deviation (-0.19 ΔpK^+ log units) from the regression line is given by the amino group. This group shows greater electron release in the ΔpK^+ series (-0.54) than in the ΔpK_a series (-0.32). The correlation is improved somewhat by omitting the amino group. Without the amino group, eq 5 obtains with $C = 0.997$ and $E_{\Delta pK^+} = 0.06$.

$$\Delta pK^+ = (1.14 \pm 0.04)\Delta pK_a + 0.03\ (\pm 0.04) \qquad (5)$$

The results show that 5- (or 6-) substituted benzimidazoles have their acid and base strengths well correlated. The group showing the largest deviation, the amino group, is known to show large variability in its acid-weakening power.[10a]

(Reference 10 gives LFER reviews.)

We have found that the Taft equation (6) correlates

$$\Delta pK^+ = f\sigma_I + r\sigma_R{}^0 + i \qquad (6)$$

ΔpK^+ values with excellent precision.[2] The σ_I variable is Taft's polar substituent constant, derived from aliphatic and alicyclic reactivities, and $\sigma_R{}^0$ is Taft's resonance polar substituent constant, obtained from aromatic reactivities where direct resonance interaction with the reaction site is absent. The f and r parameters are relative susceptibilities of a given reaction series to polar (*i.e.*, nonresonance) and resonance effects, respectively.

In view of the excellent correlation found for ΔpK^+ *vs.* σ_I and $\sigma_R{}^0$, and the good correlation for ΔpK^+ *vs.* ΔpK_a, r/f, a measure of the composition of the composite substituent constant ($\sigma_I + r/f\sigma_R{}^0$), approximates a constant ratio for both series or the relative importance of resonance and polar effects is about the same in the two series.

The slopes in eq 4 and 5 differ from unity at the 0.05 significance level.[11] The slope is a little greater than unity showing that basicity (ΔpK^+) is a little more sensitive to substituent effects than acidity (ΔpK_a).

Our results parallel the results of Stewart and Yates[12] for nondeviating *meta*-substituted benzoic acids (Me, H, F, Br, Cl, I, and NO_2). They obtained for nondeviating points a ρ value of 1.09 for pK^+ (basicity) as a function of pK_a (acidity).

Birchall and Jolly[13] recently made a study involving aniline as the ampholyte and compared the effect of substituents upon acidity and basicity. A plot of ΔpK^+ (basicity) *vs.* ΔpK_a (acidity) gave a good correlation with a slope of 0.53. The slope was interpreted as indicating that the molecule dissociation was more sensitive to substituent effects than the cation dissociation. However, they compared aqueous thermodynamic ΔpK^+ values with nonthermodynamic ammoniacal ΔpK_a values. Their low ρ value may, in part if not in the main, be a function of change in solvent rather than the nature of the ionization equilibrium.

As pointed out, ΔpK^+ values lend themselves to dissection into inductive and resonance contributions. The good correlation of ΔpK^+ *vs.* ΔpK_a shows that ΔpK_a values should also be well correlated by σ_I and $\sigma_R{}^0$. Values used in correlations with σ_I and $\sigma_R{}^0$ are given in Table II and the correlations themselves are shown in Table III, sets 1 through 4. Also shown in Table III in sets 5 through 8 are correlations ($\Delta pK = f\mathcal{F} + r\mathcal{R} + i$) with the recently proposed field ($\mathcal{F}$) and resonance ($\mathcal{R}$) substituent constants (values are shown in Table II) of Swain and Lupton.[14] We will first consider ΔpK values in the odd-numbered sets. These sets include all the substituents shown in Table II except for the amino substituent. All odd sets show excellent correlations. The difference between f values in the odd sets using σ_I and $\sigma_R{}^0$ and the corresponding sets using $\mathcal{F}$ and $\mathcal{R}$ are in the main due to σ_I and $\mathcal{F}$ being on different scales. For 42 substituents Swain and Lupton[14] reported a good correlation between σ_I and $\mathcal{F}$. They found $\sigma_I = 0.60\ \mathcal{F}$. The seven substituents of the odd sets in this study give by least squares $\sigma_I = 0.62\ \mathcal{F}$. Multiplying the f values of sets 1 and 3 by 0.6 scales these f values so as to agree quite well with f values of sets 5 and 7. The ratio, $f_{\text{set 1}}/f_{\text{set 3}}$, is 1.14 suggesting that basicity (ΔpK^+) is a little more sensitive to polar effects than acidity (ΔpK_a). The ratio, $f_{\text{set 5}}/f_{\text{set 7}} = 1.13$, is in agreement with sets 1 and 3. That $f_{\Delta pK^+}/f_{\Delta pK_a}$ is close to unity may be rationalized in terms of simple electrostatic theory if one assumes that substituent dipole interactions in the neutral molecule are secondary to substituent dipole interactions in the ions, and that the charged reaction sites approximate what is suggested by the main resonance forms summarized by formulas **1** and **3**. With these assumptions one would conclude that cation dissociation and molecule dissociation are nearly equally sensitive to polar substituent effects since the orientation and distance of the substituent dipoles relative to the charged reaction sites are virtually the same in the cation and the anion.

A more rigorous approach would include consideration of dipole–dipole interactions in the neutral molecule or the electron withdrawing power difference between the reaction and product sites involved in ionization.[15] Such an approach requires additional assumptions and in our hands did not prove fruitful.

The magnitude of $f_{\text{set 1}}$ and $f_{\text{set 3}}$ is within the range predicted empirically by Taft[16] for acid–base equilibria, involving *meta*- and *para*-substituted reactants, that undergo a change in formal charge of one on the atom attached to the benzene ring. Taft gives $\rho_{\sigma_I} = 2.8 \pm 0.5$. In 5- (or 6-) substituted benzimidazoles the two nitrogens of the heterocyclic ring are *ortho* to each other in the homocyclic ring. They appear to behave collectively as would a single atom in interactions with substituents. The substituent in the ions is *meta* to one nitrogen and simultaneously *para* to the other account-

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(10) For recent reviews on linear free-energy relationships see (a) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963); (b) S. Ehrenson, "Progress in Physical Organic Chemistry," Vol. 2, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Jr., Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 195; (c) C. D. Ritchie and W. F. Sager, ref 10b, p 323; and (d) H. H. Jaffé and H. L. Jones, *Advan. Heterocycl. Chem.*, **3**, 209 (1964). (e) Also see monograph P. R. Wells, "Linear Free Energy Relationships," Academic Press Inc., New York, N. Y., 1968.

(11) W. J. Youdon, "Statistical Methods for Chemists," John Wiley & Sons, Inc., New York, N. Y., 1951, p 48.

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(13) T. B. Birchall and W. L. Jolly, *ibid.*, **88**, 5439 (1966).

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TABLE II

VALUES USED IN CORRELATIONS

Substituent	$\Delta pK^{+\,a}$	$\Delta pK_a{}^b$	$\sigma_I{}^c$	$\sigma_R{}^{0\,d}$	$\mathfrak{F}^e$	$\mathcal{R}^e$
Br	0.89	0.782	0.45	−0.19	0.727	−0.176
CH_3	−0.23	−0.196	−0.05	−0.10	−0.052	−0.141
CF_3	1.33	1.082	0.41	0.12	0.631	0.186
Cl	0.85	0.739	0.47	−0.20	0.690	−0.161
F	0.63	0.472	0.52	−0.35	0.708	−0.336
H	0	0	0	0	0	0
NH_2	−0.54	−0.321	0.1	−0.48	0.037	−0.681
NO_2	2.13	1.941	0.63	0.19	1.109	0.155

[a] $\Delta pK^+ = pK_H{}^+ - pK^+{}_{\text{substd}}$. All ΔpK^+ values from ref 2 except for amino. Amino ΔpK^+ from M. T. Davies, P. Mamalis, V. Petrow, and B. Sturgeon, *J. Pharm. Pharmacol.*, **3**, 320 (1951). [b] $\Delta pK_a = pK_{b,H} - pK_{b,\text{substd}}$. This work. [c] R. W. Taft, Jr., E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson and G. T. Davies, *J. Amer. Chem. Soc.*, **85**, 709 (1963). [d] $\sigma_R{}^0 = \sigma_P{}^0 - \sigma_I$; $\sigma_P{}^0$ values from R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960); $\sigma_R{}^0$ for CF_3 from R. T. C. Brownlee, A. R. Katritzky, and R. D. Topsom, *J. Amer. Chem. Soc.*, **88**, 1413 (1966). [e] From ref 14.

TABLE III

CORRELATIONS VS. σ_I AND $\sigma_R{}^0$ (1–4) AND *vs.* $\mathfrak{F}$ AND $\mathcal{R}$ (5–8)[a]

No.	Series	*f*	*r*	*i*	$E_{\Delta pK}$	*C*	% $\mathcal{R}$
1	ΔpK^+	2.61 ± 0.10	2.11 ± 0.13	0.05 ± 0.04	0.06	0.997	37 ± 2
2	ΔpK^+	2.56 ± 0.11	1.96 ± 0.13	0.07 ± 0.05	0.07	0.997	38 ± 2
3	ΔpK_a	2.29 ± 0.16	1.96 ± 0.23	0.04 ± 0.07	0.11	0.989	38 ± 3
4	ΔpK_a	2.18 ± 0.21	1.65 ± 0.24	0.08 ± 0.10	0.14	0.981	38 ± 4
5	ΔpK^+	1.62 ± 0.05	1.66 ± 0.10	0.03 ± 0.03	0.05	0.998	33 ± 2
6	ΔpK^+	1.57 ± 0.13	1.20 ± 0.20	0.05 ± 0.09	0.14	0.988	29 ± 4
7	ΔpK_a	1.43 ± 0.09	1.52 ± 0.20	0.01 ± 0.06	0.09	0.992	34 ± 3
8	ΔpK_a	1.37 ± 0.18	0.92 ± 0.28	0.04 ± 0.13	0.19	0.968	26 ± 6

[a] Odd sets do not include NH_2 derivative. Even sets do. Plus and minus values are standard errors. $E_{\Delta pK}$ is the standard deviation from the regression plane, and *C* is the multiple correlation coefficient. For other terms see text.

ing for the agreement with benzene derivatives having substituents *meta* or *para* to the reaction site.

The *r* values shown in Table III have higher standard errors than *f* values. The *r* values are expected to be more sensitive to error since the major contribution to ΔpK values comes from the polar effect ($f\mathfrak{F}$).

To assess relative importance of polar *vs.* resonance effects in the ΔpK^+ and ΔpK_a series, we follow Swain and Lupton and use per cent resonance defined as

$$\%\,\mathcal{R} = \frac{100\,\psi\,|r|}{\phi\,|f| + \psi\,|r|}$$

where ψ and ϕ are scaling factors. For Taft's constants $\phi = (\Sigma|\sigma_I - \bar{\sigma}_I|)/n$ and $\psi = (\Sigma|\sigma_{R^0} - \overline{\sigma_{R^0}}|)/n$ and for Swain and Lupton constants $\phi = (\Sigma|\mathfrak{F} - \bar{\mathfrak{F}}|)/n$ and $\psi = (\Sigma|\mathcal{R} - \bar{\mathcal{R}}|)/n$. For sets 1 and 3, $\psi = 0.153$ and $\phi = 0.212$, and for the corresponding sets 5 and 7, $\psi = 0.155$ and $\phi = 0.323$. For sets 2 and 4, $\psi = 0.179$ and $\phi = 0.225$, and for corresponding sets 6 and 8, $\psi = 0.194$ and $\phi = 0.365$. The ψ values for odd sets show that Taft's and Swain and Lupton's resonance constants for the seven substituents involved in the odd sets are essentially on the same scale. Taft's constants give higher per cent $\mathcal{R}$ values. More germain, however, is the close agreement in per cent $\mathcal{R}$ for sets 1 (ΔpK^+) and 3 (ΔpK_a) and sets 5 (ΔpK^+) and 7 (ΔpK_a). These results again show that ΔpK^+ and ΔpK_a series are correlated by essentially the same blend of polar and resonance effects. Since the relative weighting of polar (*f*) and resonance (*r*) susceptibilities is about the same for both the ΔpK^+ and the ΔpK_a series, the composite substituent constants ($\sigma_I + r/f\ \sigma_R{}^0$) or ($\mathfrak{F} + r/f\ \mathcal{R}$) may be expected to give good correlations of ΔpK^+ or ΔpK_a data for most substituents in a single regression analysis. For the title compounds $r/f = 0.8$ for correlations with σ_I and $\sigma_R{}^0$ and $r/f = 1$ for correlations with $\mathfrak{F}$ and $\mathcal{R}$.

The 33% $\mathcal{R}$ found for ΔpK^+ and 34% $\mathcal{R}$ found for ΔpK_a (sets 5 and 7) indicate that the composite substituent constants are nearly half-way between σ_m and $\sigma_p{}^0$. For σ_m Swain reports 22% $\mathcal{R}$ and for $\sigma_p{}^0$ 42% $\mathcal{R}$. This nearly half-way position of 34% $\mathcal{R}$ is apparently not fortuitous since, as pointed out earlier, in the ions the substituents are simultaneously "*meta*" to one and "*para*" to the other nitrogen.

The even sets in Table III include the amino substituent. These sets show greater imprecision than the corresponding odd numbered sets. Imprecision is more marked with the $\mathfrak{F}$, $\mathcal{R}$ sets. In all cases for the amino group the mix of the electron-withdrawal potential (σ_I, $\mathfrak{F}$) and electron release potential ($\sigma_p{}^0$, $\mathcal{R}$) is such as to give calculated ΔpK's that are more negative (more acid weakening) than that observed. The $\mathcal{R}$ value for the amino group probably represents an exaggerated resonance capability in correlating ΔpK^+ and ΔpK_a. The $\mathcal{R}$ constant for NH_2 may be shown to be based mainly on the σ_p value of McDaniel and Brown[17] which value is, in turn, based on the effect of the amino group in *p*-aminobenzoic acid. Direct resonance interaction of the amino group with the carbonyl group in *p*-aminobenzoic acid would appear to give a measure of electron release too strong for 5- (or 6-) aminobenzimidazole. Taft's $\sigma_R{}^0$ is less negative than $\mathcal{R}$ but probably still exaggerates the resonance potential of this group. It does so more in the ΔpK^a series than in the ΔpK^+ series.

For examples of LFER involving equilibria whose common amphoteric species is a monoanion, rather

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

than a neutral molecule to which we limited discussion in this paper, see ref 18.

Since in the neutral molecule the five and six positions are not equivalent, tautomerism is possible. However, data to date[2] indicate that the five and six tautomers of 5- (or 6-) substituted benzimidazoles are thermodynamically nearly equivalent. Therefore deviations from linearity in the above correlations, though they may in part be attributed to tautomerism,[2,10d,19] appear in the main to be the result of experimental error and the approximate nature of LFER.

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The Photochromism of 1-Aryl-2-nitroalkenes

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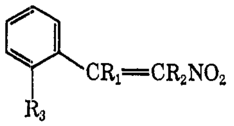
The photochromic properties of eight 1-aryl-2-nitroalkenes are reported. A *cis* relationship of nitro and phenyl groups is required for photochromism. Kinetic data from flash photolysis experiments are given for the dark fading reactions of the colored isomers in ethanol and cyclohexane. Thermodynamic properties of the dark reactions are also reported. The λ_{max} obtained from spectra of the visible transients are listed.

In a previous paper[1] the photochromic behavior of 1-aryl-2-nitroalkenes in ethanol and cyclohexane solutions was reported. On irradiation with ultraviolet light, *trans*-α-methyl-β-nitrostyrene[2] was converted to the *cis* isomer, the isomer which exhibited photochromic properties. A preliminary examination of the kinetics of the color fading reaction of alcoholic solutions of *cis*-α-methyl-β-nitrostyrene and other arylnitroalkenes was reported. This paper presents a comprehensive kinetic study of compounds **1**–**8** listed in Table I.

TABLE I



Compd	R$_1$	R$_2$	R$_3$
1	H	H	H
2	Me	H	H
3	H	H	OCH$_3$
4	H	C$_6$H$_5$	H
5	NO$_2$	C$_6$H$_5$	H
6	C$_6$H$_5$	H	H
7	C$_6$H$_5$	C$_6$H$_5$	H
8	–CH$_2$CH$_2$CH$_2$CH$_2$–		H

Results and Discussion

Preparation and Configuration of the 1-Aryl-2-nitroalkenes.—Only one geometrical configuration about the central double bond is possible in 1,1-diphenyl-2-nitroethylene (**6**), triphenylnitroethylene (**7**), and 1-phenyl-2-nitrocyclohexene (**8**); nitro and phenyl groups bear a *cis* relationship with respect to each other. When flash photolysis measurements of solutions of these compounds are carried out, a photochromic effect is observed on the first exposure to light. In contrast, β-nitrostyrene (**1**) and α-methyl-β-nitrostyrene (**2**) do not show photochromic behavior on the initial flash exposure. However, after either multiple exposures in the flash photolysis apparatus or a preliminary irradiation with ultraviolet light, solutions of these compounds become photochromic. The pure *cis* isomer of **2** shows the photochromic effect without preirradiation. The preliminary exposure to ultraviolet light apparently serves to convert these compounds from the *trans* configuration, obtained from the chemical preparations,[3,4] to the *cis* form.

The *cis* form of **2** was isolated from an ethanol solution following irradiation of the *trans* isomer. In the infrared spectra (neat) of the isomers the stretching absorption band associated with asymmetric NO$_2$ stretching in the conjugated nitroalkene structure, C=CNO$_2$, is at 1520 and 1524 cm^{-1}, respectively, for the *trans* and *cis* isomers. In the nmr spectrum (in CCl$_4$) of the *trans* isomer, the methyl group appears as a closely spaced doublet centered at 2.61 ppm (δ, TMS as an internal standard.) The nmr spectrum of the *cis* isomer shows this doublet shifted upfield to 2.03 ppm (δ). This shift is analogous to that observed for *trans*- and *cis*-α-methyl-β-bromostyrene.[5] The nmr spectra also show more splitting of the phenyl H's in the *cis* isomer.

cis-1,2-Dinitro-1,2-diphenylethylene (**5**) was obtained by passing nitric oxides through an ether solution of diphenylacetylene. Other workers[6–8] found that by using dinitrogen tetroxide a second isomer can also be isolated. By appropriate dipole moment measurements, Bergmann[9] assigned the geometrical configuration of these isomers. In accord with this assignment we found that solutions of **5** are photochromic without requiring preliminary irradiation.

1,2-Diphenyl-1-nitroethylene (**4**) was prepared by alkali treatment of 1,2-diphenyl-1,2-dinitroethane.[10] The *trans* isomer was isolated. Others[6,10,11] have pre-

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(2) The *cis* and *trans* designations in this paper relate to the orientation of the nitro and phenyl groups, with respect to each other.

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