the solution will deposit V, or an intermediate solid with $\bar{n}$ between 2 and 3, or the pure basic bis-(alanine) derivative. Formation of the insoluble olated form of VI must be a reaction of higher order than the simple ring closure necessary to produce V from VII. Hence, as the solution becomes more and more dilute with age, the speed of the olation reaction will decrease more rapidly than that of the chelation reaction. This explains the increase in $\bar{n}$(solid) for successive fractions collected from the same solution. The corresponding decrease in $\bar{n}$(solution) can be explained by postulating a parallel aquation reaction in which chromium–oxygen and chromium–nitrogen bonds are broken in the same way as in dilute solutions.

SINGAPORE

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF SAN DIEGO STATE COLLEGE]

Spectrophotometric Study of the Hydrolysis Constants of the Negative Ions of Some Aryl Imidazoles

BY HAROLD WALBA AND ROBERT W. ISENSEE

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A special spectrophotometric method for determining the hydrolysis constants of some very weak acids in water at 25.0° is given. Medium and salt effects are considered. A linear relationship between the pK_h and the square root of the ionic strength is observed for 2-phenylbenzimidazole. A pK_a of 14.2 is estimated for the acidity constant of imidazole. The effect of resonance on the acid strengths of the aryl imidazoles is discussed.

The amphiprotic nature of imidazole and its derivatives has long been known. Whereas considerable quantitative data on their base strengths may be found in the literature,[1] such data are lacking for the acid strengths. In this study we have obtained quantitative measures of the acid strengths in water of the following compounds: 2-phenylbenzimidazole, 2,4(or 2,5)-diphenylimidazole, benzimidazole, 2-phenylimidazole and 4(or 5)-phenylimidazole. The weakness of these compounds as acids as well as their low water solubility suggested a spectrophotometric study.

$$R^- + HOH = HR + OH^- \qquad (1)$$

The equilibrium studied was the hydrolysis reaction (1) where HR represents the acid and R^- its conjugate base. The classical equilibrium constant for this reaction is the hydrolysis constant, K_h, defined for the case in which water is the solvent by

$$K_h = c_{OH^-}(c_{HR}/c_{R^-}) \qquad (2)$$

where c is the concentration in moles/liter of the species indicated by the subscripts. The classical acidity constant, K_a, is related to K_h by

$$K_a = K_w/K_h \qquad (3)$$

where K_w is the appropriate ionization product of water and is defined by

$$K_w = c_{H^+}\,c_{OH^-} \qquad (4)$$

The hydrolysis equilibrium can be followed spectrophotometrically if the spectrum of the neutral molecule differs from that of the negative ion. The relationship between the spectral data and the concentrations of the neutral acid and its ion has been derived by Stenstrom and Goldsmith[2] and is given by the equation[3]

$$c_{HR}/c_{R^-} = (A^- - A)/(A - A^\circ) \qquad (5)$$

where A^- is the absorbancy of the negative ion, A is the absorbancy of the solution containing un-ionized acid and its negative ion in equilibrium, and A° is the absorbancy of the un-ionized acid. Substituting for c_{RH}/c_{R^-} in (2) one obtains

$$K_h = c_{OH^-}(A^- - A)/(A - A^\circ) \qquad (6)$$

To solve (6) for K_h a knowledge of the absorbancy of the negative ion is needed. In the case of acids having an acidity constant greater than 10^{-10}, the absorbancy of the negative ion may be obtained from solutions with relatively small concentrations of base (about 10^{-2} N). In such cases there is little uncertainty caused by the medium effect, that is, the shifting of the absorption curve with changes in salt concentration. For the aryl imidazoles that are the subject of this paper the medium effect could not be neglected. For instance, even the strongest acid of the series, 2-phenylbenzimidazole, requires a concentration of base greater than 1 N to be converted to the negative ion. At this relatively high concentration of base a medium effect was detectable. Hence the value obtained for the absorbancy could not be used without error in calculations involving lower concentrations of base, which are the ones required for the equilibrium measurements. In addition 2-phenylimidazole and 4(or 5)-phenylimidazole are such weak acids that even in 3.5 N base they are still far from being neutralized.

The equation that is derived below enables the absorbancy of the negative ion to be calculated directly from experimental values even for acids too weak to be neutralized in experimentally attainable concentrations of base. It also helps to eliminate uncertainties caused by optical medium effects.

The relationship between the classical and the thermodynamic hydrolysis constants is given by

$$K_h = K_h^\circ/F_h \qquad (7)$$

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[1] K. Hofmann, "Imidazole and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1953, pp. 15, 251.

[2] W. Stenstrom and N. Goldsmith, *J. Phys. Chem.*, **30**, 1683 (1926).

[3] In the original derivation[2] the molecular extinction coefficient, ϵ, rather than the absorbancy was used. Absorbancy may be substituted for molecular extinction coefficient if all the absorbancies in a series of measurements are obtained at a constant stoichiometric concentration of acid, c, and constant cell length, d. Absorbancy = log (I_0/I) where log $(I_0/I) = \epsilon cd$.

where F_h, the molar activity coefficient function, is defined by

$$F_h = f_{HR}f_{OH^-}/a_{HOH}f_{R^-} \qquad (8)$$

where f is the molar activity coefficient and a denotes activity of the species indicated by the subscripts. In terms of absorbancies

$$K_h^\circ/F_h = c_{OH^-}(A^- - A)/(A - A^\circ) \qquad (9)$$

At a given hydroxyl ion concentration, C_{OH^1}

$$K_h^\circ/(F_h)_1 = C_{OH^1}(A^- - A_1)/(A_1 - A^\circ) \qquad (10)$$

At another hydroxyl ion concentration, C_{OH^2}

$$K_h^\circ/(F_h)_2 = C_{OH^2}(A^- - A_2)/(A_2 - A^\circ) \qquad (11)$$

Under conditions where $(F_h)_1 = (F_h)_2$ equations 10 and 11 may be equated and solved for A^- yielding

$$A^- = [C_{OH^1}(A_2 - A^\circ)A_1 + C_{OH^2}(A^\circ - A_1)A_2/ C_{OH^1}(A_2 - A^\circ) + C_{OH^2}(A^\circ - A_1)] \qquad (12)$$

At constant ionic strength and constant salt mixture, that is, where the concentration and kinds of ions that make up the salts present do not change, the conditions would be met for $(F_h)_1 = (F_h)_2$. Constant ionic strength may be achieved readily by addition of suitable amounts of a neutral salt. Although a constant salt mixture is obviously not attainable at two different hydroxyl ion concentrations, where the reactant ions are equal in number and have the same charge type as the product ions, such as in equilibrium (1), the effect on the activity coefficient function of changing the relative amounts of hydroxyl ion and a given neutral salt may be assumed to be slight. Since in this study very high dilutions of the conjugate acid are used, the effect of the conjugate base salt on the activity coefficient function may be considered negligible. Finally, our experiments show that for the compounds in question varying the relative concentrations of base and neutral salt within the limits of the ionic strength used is without effect on the position of the absorption curves. This "optical constancy"[4] is of course important for the success of equation 12.

Experimental

The Spectral Data.—All spectral measurements were made with a model DU Beckman Spectrophotometer. A matched pair of 1-cm. cells was used. Temperature control was maintained in the cell compartment with Beckman thermospacers. In all cases the solution to be measured was kept at 25 ± 0.1° until immediately before use. The temperature of measurement was probably within ± 0.2° of 25°. Duplicate readings were made on all samples and if agreement was not better than 0.5%, an average of three or more readings was used. The readings were taken against a blank containing the same medium as that used in the cell containing the imidazole derivative. Readings were corrected for any differences in the absorbancies of the two cells when filled with distilled water. As a check on gross errors a suitable isosbestic point for each compound was determined and the absorbancies at five wave lengths that were one mμ apart and passed through the isosbestic point were measured along with the absorbancies at the wave lengths selected for the equilibrium measurements.

To calculate the absorbancy of the negative ion equation 12 was used in all cases. The total ionic strength, defined by

$$I_c = \Sigma c_i z_i^2/2 \qquad (13)$$

where c_i is the concentration of the ion in gram ions/liter and z_i its electrovalence and where the summation is for all the ions in the solution, was 0.5 in all measurements involving the calculation of A^-. Carbon dioxide-free sodium hydroxide standardized against potassium acid phthalate was used as the source of hydroxyl ions, and sodium chloride was used for the neutral salt. To obtain the absorbancy of the neutral molecule the imidazole derivative was measured at 25° in Beckman 0.02 *M* borax buffer of *p*H 9.18 with NaCl added to give a total ionic strength of 0.5. From the known base strengths reported in the literature[1] and the acid strengths determined in this study it may be shown that at *p*H 9.2 no more than 0.15% of either of the ionic species of any of the parent amphiprotic compounds is present.

Preparation of the Compounds.—The preparations of all the imidazole derivatives used in this study have been reported in the literature.[5-10] 2,4(or 2,5)-Diphenylimidazole was prepared according to Kunckell[7] with recrystallizations from ethyl alcohol to give a melting point that agreed with "Compound I" of Haines and Wagner.[8] All compounds were recrystallized until a constant melting point was obtained.

Results and Discussion

The Spectra.—In Fig. 1 are shown the spectra of 2-phenylbenzimidazole's neutral molecule and negative ion, and the positions of the maxima of the two main bands of the positive ion all measured in water. It is to be noted that for the longest

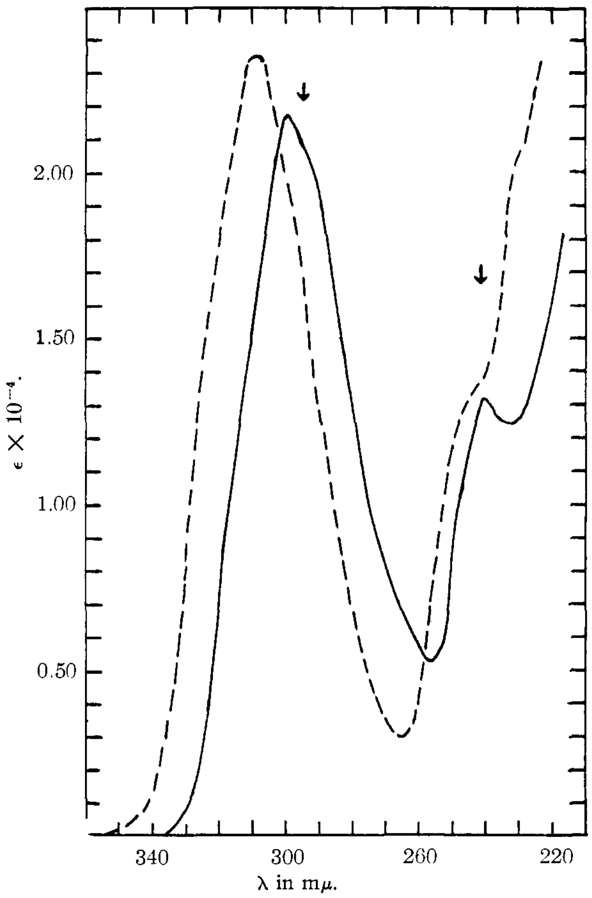

Fig. 1.—Spectra of the neutral molecule (——) and the negative ion (- - -), and the positions of the maxima of the positive ion (↓) of 2-phenylbenzimidazole in water.

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[4] G. Kortum and J. O'M. Bockris, "Electrochemistry," Vol. 1, Elsevier Publishing Co., New York, N. Y., 1951, p. 153.

(5) R. G. Fargher and F. L. Pyman, *J. Chem. Soc.*, **115**, 227 (1919).

(6) A. Pinner, *Ber.*, **35**, 4135 (1902).

(7) F. Kunckell, *ibid.*, **34**, 637 (1901).

(8) P. G. Haines and E. C. Wagner, THIS JOURNAL, **71**, 2793 (1949).

(9) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 65.

(10) R. Weidenhagen, *Ber.*, **69B**, 2263 (1936).

wave length band the loss of a proton is bathochromic and the gain of a proton is hypsochromic. Shifts of the same nature were observed for all the imidazoles that are the subject of this paper. From spectral data obtained from measurements in alcohol, Haines and Wagner[8] have pointed out that the loss of a proton by 2,4(or 2,5)-diphenylimidazole is bathochromic. Steck, *et al.*,[11] have reported the spectra of benzimidazole in 95% ethanol, aqueous 0.01 *N* NaOH and aqueous 0.01 *N* HCl. Their curve in 0.01 *N* HCl agrees with the curve obtained by us in acid solution and is the curve of the positive ion. Although their $\epsilon_{\max}$ for the longest wave length band of the neutral molecule in alcohol is at a longer wave length than their corresponding $\epsilon_{\max}$ in aqueous 0.01 *N* NaOH, this may be attributed to a solvent effect. With water as the sole solvent our study shows that an equilibrium mixture of neutral molecule and negative ion such as exists in 0.01 *N* NaOH gives a curve whose $\epsilon_{\max}$ for the longest wave length band absorbs at a longer wave length than that of the neutral molecule. We plan to report the spectral data for these and related compounds and their ions in a future paper.

Medium Effect on the Spectra.—Table I gives the optical data obtained for 2-phenylbenzimidazole at several wave lengths and at relatively high hydroxyl ion concentrations. As can be seen from Fig. 1 one of the wave lengths, that at 310 mμ, falls at $\lambda_{\max}$ where the absorption curve has near zero slope, and the other wave lengths are on fairly steep sides adjacent to $\lambda_{\max}$. Consideration of the data at λ 310 shows that the neutral molecule is very close to complete neutralization above 1 *N* NaOH. At λ 310 the absorbancies are fairly constant above 1 *N* NaOH; in contrast the absorbancies at the longer wave length side of the $\lambda_{\max}$ increase and those on the shorter wave length side decrease with increasing hydroxyl ion concentration. These variations are what one might expect from a small bathochromic medium effect. The wave lengths most sensitive to such an effect are of course those on the steep sides of the absorption curve.

TABLE I

ABSORBANCIES OF 2-PHENYLBENZIMIDAZOLE AT DIFFERENT OH^- CONCENTRATIONS[a,b]

C_{OH^-}	λ_{330}	λ_{325}	λ_{310}	λ_{292}	λ_{290}
0.552	0.251	0.448	0.742	0.469	0.230
1.094	.263	.458	.748	.466	.226
1.582	.272	.463	.749	.462	.226
2.07	.279	.468	.749	.459	.223
2.52	.284	.470	.750	.454	.220
2.94	.295	.479	.752	.452	.220
3.39	.301	.483	.752	.450	.217

[a] Concn. of 2-phenylbenzimidazole, 3.27×10^{-5} *M*. Absorbancies are given under the designated wave lengths.

TABLE II

DATA[a] FOR CALCULATING A^-; $A^0 = 0.066$[b]

NaCl added to bring total ionic strength to 0.5.

C_{OH^1} $\times 10^2$[c]	C_{OH^2} $\times 10^2$	A_1	A_2	A^-	Dev. $\times 10^3$
1.000	10.00	0.271	0.438	0.475	3
1.000	20.00	.271	.451	.470	2
2.000	10.00	.341	.438	.474	2
2.000	20.00	.341	.451	.469	3
			Mean	.472	

[a] Data shown are for 2-phenylbenzimidazole measured at λ_{332}. Stoichiometric concn. of acid, HR, is 3.31×10^{-5} *M*. [b] A° measured in buffer solution *p*H 9.2, total ionic strength 0.5. [c] The OH^- concentrations were obtained by diluting standard NaOH solutions.

Absorbancy of the Negative Ion.—In Table II are given the data used in the calculation of the absorbancy of the negative ion of 2-phenylbenzimidazole according to equation 12. The absorbancy of the negative ion of this and other compounds was obtained at constant ionic strength of 0.5. In all cases the observed mean deviation in A^- could be accounted for by dilution and spectrophotometer errors. The optical density values used were such that the probable error in A^- in all cases may be estimated at close to 1%. Further the results here and those which follow indicate that for the compounds studied any change in the activity coefficient function and any deviation from optical constancy at constant ionic strength is within experimental error.

The Hydrolysis Constants.—In Table III are given the negative logarithms of the hydrolysis constants calculated from equation 6. The pK_h values are the unweighted means obtained from measurements at three different wave lengths and at least four different concentrations of hydroxyl ion. In the last column is given the mean deviation. All values were obtained at constant ionic strength of 0.5 with respect to NaOH and NaCl. The stoichiometric concentration of any given imidazole was between 10^{-4} and 10^{-5} *M*. In the equilibrium measurements the hydroxyl ion concentration generally varied such that c_{R^-}/c_{HR} varied from $^1/_4$ to $^4/_1$. The variation in hydroxyl ion concentration produced no trend in the observed pK_h values.

TABLE III

HYDROLYSIS CONSTANTS AT 25° AND IONIC STRENGTH OF 0.5

Compound	pK_h	Mean dev.
2-Phenylbenzimidazole	2.022	0.009
2,4(or 2,5)-Diphenylimidazole	1.401	.005
Benzimidazole	1.151	.009
2-Phenylimidazole	0.623	.006
4-Phenylimidazole	0.518	.005

Effect of the Salt Medium at Constant Ionic Strength.—For the stronger acids of the series the salt medium used in the equilibrium measurements was principally aqueous NaCl while in the case of the weaker acids, 2- and 4(or 5)-phenylimidazole, the salt medium was made up of NaOH and NaCl whose concentrations were of the same order of magnitude. Measurements for these weaker acids serve best for determining whether there is any mixed-salt effect. In Table IV are shown the pK_h values observed for 2-phenylimidazole and 4(or 5)-phenylimidazole at different hydroxyl ion concentrations. Here we clearly see from the constancy of the pK_h values that changing the relative amounts of NaOH and NaCl has no ob-

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[11] E. A. Steck, F. C. Nachod, G. W. Ewing and N. H. Gorman, THIS JOURNAL, **70**, 3408 (1948).

servable effect on the activity coefficient function and does not seem to cause any appreciable deviation from optical constancy.

TABLE IV

EFFECT OF MIXED-SALT ON HYDROLYSIS CONSTANTS

NaCl added to bring ionic strength to 0.5.

	2-Phenylimidazole[a]			4(or 5)-Phenylimidazole[b]		
C_{OH^-}[c]	A	pK_h	Dev.	A	pK_h	Dev.
0.1000	0.270	0.615	0.001	0.096	0.520	0.001
.1200	.340	.616	.000	...	...	...
.1400	...	...	...	.121	.516	.003
.2000	.409	.619	.003	.153	.522	.003
.3600	.532	.615	.001	...	...	...
.4000	.553	.614	.002	.217	.518	.001
	Mean	.616		Mean	.519	

[a] Measurements at λ_{310}, $A^\circ = 0.020$, $A^- = 0.877$. Stoichiometric concn. of 2-phenylimidazole, 9.81×10^{-5} M. [b] Measurements at λ_{298}, $A^\circ = 0.002$, $A^- = 0.380$. Stoichiometric concn. of 4-phenylimidazole is 4.35×10^{-5} M. [c] All OH^- concentrations obtained by dilution of standard 0.5 M NaOH solution.

Comparison with the Literature.—The only literature value available for comparison is that of Jordan and Taylor[12] who obtained by electrometric titration a value for the pK_a of 12.3 (in 0.0385 M soln.) for benzimidazole at 25°. Using a pK_w of 13.72 calculated from data of Harned and Mannweiler[13] and our pK_h value of 1.15 we obtain a pK_a of 12.57 for benzimidazole at ionic strength of 0.5 at 25°.

Thermodynamic Hydrolysis Constants.—We have shown that in high concentrations of NaOH there is a small deviation from optical constancy. We have found, however, that at ionic strength 0.1 the absorbancy calculated for the negative ion of 2-phenylbenzimidazole is in agreement with that at 0.5. Thus at ionic strengths less than 0.5 optical constancy may be assumed to hold within experimental error, and it becomes a relatively simple matter to study the effect of ionic strength on the classical hydrolysis constants. The results of this study are given in Table V. In Fig. 2 are given the plots of the negative logarithm of the hydrolysis constant *vs.* the square root of the ionic strength. The method of least squares applied to the data in Table V gives to Fig. 2 the straight line shown whose equation is

TABLE V

THE NEGATIVE LOGARITHMS OF THE HYDROLYSIS CONSTANTS OF 2-PHENYLBENZIMIDAZOLE IN AQUEOUS SALT SOLUTIONS AT 25°

$I_c \times 10^2$	A	pK_h	$I_c \times 10^2$	A	pK_h
0.586	0.228[a]	2.087	11.00	0.311[b]	2.067
0.820	.259[a]	2.080	21.00	.305[b]	2.043
1.000	.316[b]	2.086	21.00	.307[b]	2.051
1.760	.330[a]	2.076	41.00	.302[b]	2.031
5.00	.314[b]	2.078	50.00	....	2.022[c]

[a] Measurement at λ_{325}, $A^\circ = 0.064$, $A^- = 0.457$, here concn. of NaOH in moles/liter is equal to I_c defined by equation 13, stoichiometric concn. of compound is 3.21×10^{-5} M. [b] Measurement at λ_{325}, $A^\circ = 0.072$, $A^- = 0.516$, concn. of NaOH is 10^{-2} M, NaCl added to bring ionic strength to indicated value, stoichiometric concn. of compound is 3.62×10^{-5} M. [c] Average value taken from Table III.

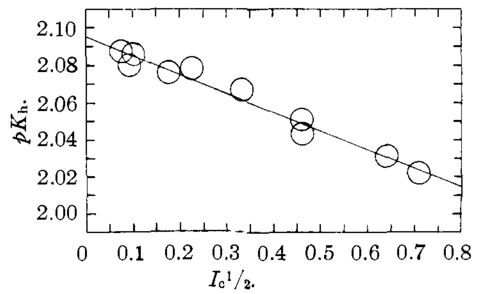

Fig. 2.

$$pK_h = \text{slope } I_c^{1/2} + \text{intercept} \qquad (14)$$

The calculated value for the slope and intercept are −0.10 and 2.095, respectively. The value 2.095 represents the pK_h at infinite dilution or the negative logarithm of the thermodynamic hydrolysis constant, pK_h°. The equation

$$pK_h = -0.10 I_c^{1/2} + pK_h^\circ \qquad (15)$$

will give pK_h values within 0.006 pK unit of the experimentally observed values. An accuracy of between 0.01 and 0.02 pK unit is estimated for pK_h°, the thermodynamic hydrolysis constant.

A similar linear relationship is to be expected for the other imidazoles although the slope might not be the same for all compounds. Since the slope or the effect of the ionic strength is small it is perhaps not unreasonable to assume that equation 15 will give thermodynamic constants that are accurate to better than 0.04 pK unit when the constants are calculated from the values in Table III.

Estimate of the Acid Strength of Imidazole.—The differences in the pK_h values of benzimidazole and 2-phenylbenzimidazole, of 4(or 5)-phenylimidazole and 2,4(or 2,5)-diphenylimidazole are 0.87 and 0.88 pK unit, respectively (see Table III). The value of 0.88 ± 0.02 pK unit is a measure of the effect of a 2-phenyl group on the acid strengths of benzimidazole and 4(or 5)-phenylimidazole. If we assume that the difference between the pK_h values of 2-phenylimidazole and imidazole is also equal to 0.88 pK unit, we then may calculate a pK_h of −0.26 for imidazole at ionic strength 0.5. Using equation 15 and a value of 14.0 for pK_w° we obtain the approximate value of 14.2 for the pK_a of imidazole.

Effect of Phenylation.—The imidazole derivatives listed in Table III may be derived from imidazole by substitution of a phenyl for a vinyl group to yield benzimidazole, or of one or more phenyl groups for C-hydrogens to yield C-phenylimidazoles, or by a combination of phenylations to yield 2-phenylbenzimidazole. In all these phenyl substitutions the phenyl group is conjugated with the acidic group and consequently may be expected by a resonance interaction to affect the ease or difficulty with which the proton is removed from the acidic group. If the resonance interaction is such that both the electron density at the –NH– group, the center of dissociation of a proton in the neutral molecule, and at the $-\bar{N}-CH{=}N-$ group,

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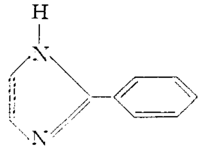
(12) D. O. Jordan and H. F. W. Taylor, *J. Chem. Soc.*, 994 (1946).

(13) H. S. Harned and G. E. Mannweiler, THIS JOURNAL, **57**, 1873 (1935).

the center of association of a proton in the negative ion are decreased, and if, in addition, the resonance interaction is such that the resonance stabilization in the negative ion is greater than that in the undissociated acid, then the resonance effect of the phenyl group will be acid strengthening.

In the undissociated acid and in the negative ion of 2-phenylimidazole the principal resonance forms involving the phenyl group are of the benzenoidal type illustrated by structures (1) and (3) for the acid and ion, respectively, and of the quinoidal type illustrated by structures (2) and (4).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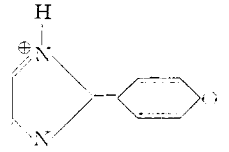
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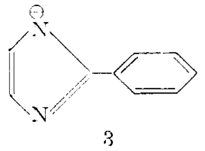
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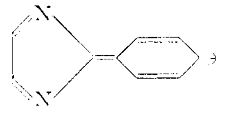
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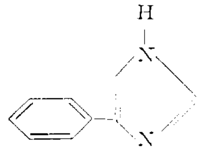
In the ion the energies of the quinoidal forms are nearer to those of the benzenoidal than in the acid, resulting in greater resonance stabilization in the ion than in the acid. Also the resonance results in electrons being drawn into the phenyl group and away from the acidic center in both the acid and the ion. The resonance effect of the 2-phenyl group is therefore acid strengthening.

Structures (5)–(8) show that the above also applies to 4-phenylimidazole. Like resonance forms may be written for the tautomer 5-phenylimidazole. Thus the 4(or 5)-phenyl group is acid strengthening.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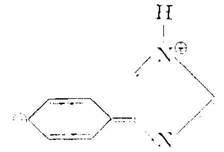
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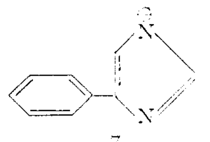
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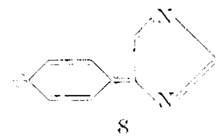
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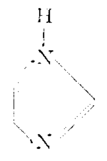
Both the vinyl group in imidazole and the phenyl group in benzimidazole have the same effect as the phenyl groups just discussed; see structures (9)–(16). When a phenyl group replaces the vinyl group in imidazole, the number of resonance forms increases. While for the vinyl group two resonance forms of each of the types shown in structures (10) and (12) may be written, in benzimidazole six forms of each of the corresponding types (14) and (16) may be written. Thus though the acid of benzimidazole is more stabilized by resonance of the phenyl group than the acid of imidazole by resonance of the vinyl group, the negative ion is even more so. As a result the phenyl group here is more acid strengthening than the vinyl group.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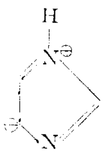
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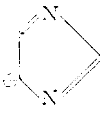
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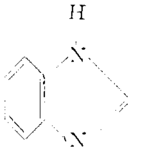
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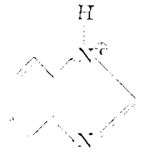
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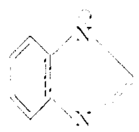
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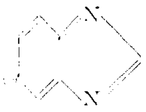
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Since the inductive or polar effect of a phenyl group is also acid strengthening, a consideration of the combined resonance and inductive effects of the phenyl group leads to several qualitative predictions that agree with experiment, namely, that 2-phenylbenzimidazole be a stronger acid than benzimidazole, and that 2,4(or 2,5)-diphenylimidazole be stronger than either 2- or 4(or 5)-phenylimidazole. Experiment shows that 2-phenylimidazole is a little stronger acid than 4(or 5)-phenylimidazole. This is perhaps attributable to the greater symmetry of 2- as compared with 4(or 5)-phenylimidazole. Further predictions are made difficult since we have no quantitative measure of the relative resonance and inductive effects.

A consideration of the principal resonance forms in the negative ion of imidazole and its aryl derivatives leads to an interesting correlation. It can be shown that for the negative ion of imidazole five principal resonance forms may be written, each form with a negative charge on a different atom.[14] For the following compounds the number of principal resonance forms that may be written for the negative ion is as indicated: in 2- and 4(or 5)-phenylimidazole five like those of imidazole plus a paraquinoidal and two orthoquinoidal forms or a total of eight, in benzimidazole a total of nine forms each with a negative charge on a different atom, similarly in 2,4(or 2,5)-diphenylimidazole and in 2-phenylbenzimidazole a total of eleven and twelve, respectively. It is seen that the order of increasing acid strengths is here the same as that of increasing number of resonance forms or increasing resonance stabilization in the ion.

A comparison of the effect of phenylation on the acid strengths with that on the base strengths of these and related amphiprotic compounds would be of interest. This work is now in progress.

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[14] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 267.