

## Spectrophotometric determination of basicities of substituted acetylbiphenyls and biphenyl carboxylic acids

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**Abstract.** The basicities of several 2'-, 3'-, and 4'-substituted 4-acetylbiphenyls and biphenyl-4-carboxylic acids have been determined spectrophotometrically in sulphuric acid media at 30°C. The  $pK_{BH^+}$  of 3'- and 4'-substituted compounds are correlated by the Hammett equation. The 4'-methoxy group deviates considerably in the Hammett plot. This is attributed to its conjugative interaction with the carbonyl or carboxyl group aided by protonation. Good correlation exists between  $pK_{BH^+}$  and  $\sigma^+$ . The basicities of 2'-substituted 4-acetylbiphenyls and biphenyl-4-carboxylic acids reaffirm the existence of  $\pi$ -electron steric effect of 2'-substituents.

**Keywords.** Basicities; acetylbiphenyls; biphenyl carboxylic acids; Hammett equation;  $\pi$ -electron steric effect.

### 1. Introduction

The most important property of sulphuric acid-water mixtures from the point of view of their usefulness as reaction media is their acidity, measured in terms of their acidity function. The investigation of reactions in strongly acid media by Hammett (1932), Stewart and Yates (1958), Bunnett and Olsen (1965, 1966) and Arnett and Anderson (1963) has in recent years generated considerable interest. The importance of the work is brought out by Liler (1971) and Paul (1957). The measurement of the extent of protonation in these media, in conjunction with the acidity functions that the various types of bases obey, results in a large number of pK values whose correlation often leads to new insight into the analysis of the effect of structure on reactivity.

Sulphuric acid media offer an extremely wide and continuous range of acidity, joining on to the dilute aqueous range in which a large number of normally neutral compounds are protonated. The basicity of a large number of 2'-, 3'- and 4'-substituted 4-acetylbiphenyls and biphenyl-4-carboxylic acids was determined by the spectrophotometric technique to test the applicability of Hammett equation to the data on 3'- and 4'-substituted compounds.

### 2. Results and discussion

The results are given in tables 2–5. While determining the  $pK_{BH^+}$  of a base, it is important to choose the right acidity function such that  $pK_{BH^+}$  is thermodynamically

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Table 1. Analytical data

Substituent	m.p. (°)	Formula	Observed(%)		Required(%)	
			C	H	C	H
Substituted 4-acetylbiphenyls						
H	120-121 (121) <sup>a</sup>	C <sub>14</sub> H <sub>12</sub> O	87.8	6.2	87.7	6.1
3'-F	91-92 (90.5) <sup>b</sup>	C <sub>14</sub> H <sub>11</sub> FO	78.3	5.3	78.5	5.1
3'-Cl	58-59 (57.5-58.5) <sup>f</sup>	C <sub>14</sub> H <sub>11</sub> ClO	72.8	4.9	72.7	4.8
3'-Br	45-46 (45-46) <sup>b</sup>	C <sub>14</sub> H <sub>11</sub> BrO	61.4	4.1	61.1	4.0
3'-NO <sub>2</sub>	110-111 (110-111) <sup>b</sup>	C <sub>14</sub> H <sub>11</sub> NO <sub>3</sub>	69.7	4.8	69.7	4.6
3'-CH <sub>3</sub>	78-79	C <sub>15</sub> H <sub>14</sub> O	85.8	6.8	85.7	6.7
3'-OCH <sub>3</sub>	89-90	C <sub>15</sub> H <sub>14</sub> O <sub>2</sub>	79.8	6.3	79.7	6.2
4'-F	105-106 (105-106) <sup>b</sup>	C <sub>14</sub> H <sub>11</sub> FO	78.6	5.3	78.5	5.1
4'-Cl	103-104 (103-104) <sup>b</sup>	C <sub>14</sub> H <sub>11</sub> ClO	72.8	4.7	72.7	4.8
4'-Br	130-131 (131) <sup>d</sup>	C <sub>14</sub> H <sub>11</sub> BrO	61.0	4.1	61.1	4.0
4'-NO <sub>2</sub>	153-154 (152-153) <sup>e</sup>	C <sub>14</sub> H <sub>11</sub> NO <sub>3</sub>	69.9	4.5	69.7	4.6
4'-CH <sub>3</sub>	122-123 (122) <sup>f</sup>	C <sub>15</sub> H <sub>14</sub> O	85.8	6.9	85.7	6.7
4'-OCH <sub>3</sub>	155-156 (153-154) <sup>g</sup>	C <sub>15</sub> H <sub>14</sub> O <sub>2</sub>	79.6	6.3	79.7	6.2
2'-F	85-86 (86-87) <sup>b</sup>	C <sub>14</sub> H <sub>11</sub> FO	78.4	5.3	78.5	5.1
2'-Cl	56-57 (54-56) <sup>b</sup>	C <sub>14</sub> H <sub>11</sub> ClO	72.8	4.9	72.7	4.8
2'-Br	81-82 (81-82) <sup>b</sup>	C <sub>14</sub> H <sub>11</sub> BrO	61.3	4.2	61.1	4.0
2'-NO <sub>2</sub>	110-111 (110) <sup>e</sup>	C <sub>14</sub> H <sub>11</sub> NO <sub>3</sub>	69.9	4.8	69.7	4.6
2'-CH <sub>3</sub>	52-53	C <sub>15</sub> H <sub>14</sub> O	85.6	6.8	85.7	6.7
2'-OCH <sub>3</sub>	63-64	C <sub>15</sub> H <sub>14</sub> O <sub>2</sub>	79.6	6.1	79.7	6.2
Substituted biphenyl-4-carboxylic acids <sup>d</sup>						
H	225-226 (225.8)	C <sub>13</sub> H <sub>10</sub> O <sub>2</sub>	78.9	5.3	78.8	5.1
3'-F	241-242 (240-241.5)	C <sub>13</sub> H <sub>9</sub> FO <sub>2</sub>	75.3	4.4	75.4	4.3
3'-Cl	248-249 (249-250)	C <sub>13</sub> H <sub>9</sub> ClO <sub>2</sub>	67.1	4.0	67.0	3.9
3'-Br	253-254 (252.9-254.4)	C <sub>13</sub> H <sub>9</sub> BrO <sub>2</sub>	56.2	3.5	56.3	3.3
3'-NO <sub>2</sub>	314-315 (313-315)	C <sub>13</sub> H <sub>9</sub> NO <sub>4</sub>	64.3	3.8	64.2	3.7
3'-CH <sub>3</sub>	205-206 (206-207)	C <sub>14</sub> H <sub>12</sub> O <sub>2</sub>	79.4	5.9	79.3	5.7
3'-OCH <sub>3</sub>	197-198 (197-198)	C <sub>14</sub> H <sub>12</sub> O <sub>3</sub>	73.9	5.7	73.7	5.3
4'-F	237-238 (236-238)	C <sub>13</sub> H <sub>9</sub> FO <sub>2</sub>	75.6	4.2	75.4	4.3
4'-Cl	293-294 (290-293)	C <sub>13</sub> H <sub>9</sub> ClO <sub>2</sub>	67.1	4.0	67.0	3.9
4'-Br	304-305 (303-305)	C <sub>13</sub> H <sub>9</sub> BrO <sub>2</sub>	56.1	3.5	56.3	3.3
4'-NO <sub>2</sub>	338-340 (336-338)	C <sub>13</sub> H <sub>9</sub> NO <sub>4</sub>	64.3	3.8	64.2	3.7
4'-CH <sub>3</sub>	242-243 (243-245)	C <sub>14</sub> H <sub>12</sub> O <sub>2</sub>	79.4	5.8	79.3	5.7
4'-OCH <sub>3</sub>	248-249 (247-248)	C <sub>14</sub> H <sub>12</sub> O <sub>3</sub>	73.9	5.4	73.7	5.3
2'-F	231-232 (232-233)	C <sub>13</sub> H <sub>9</sub> FO <sub>2</sub>	75.6	4.2	75.4	4.3
2'-Cl	251-252 (251.5-252.5)	C <sub>13</sub> H <sub>9</sub> ClO <sub>2</sub>	69.2	3.9	69.0	3.9
2'-Br	242-243 (242)	C <sub>13</sub> H <sub>9</sub> BrO <sub>2</sub>	56.5	3.4	56.3	3.3
2'-NO <sub>2</sub>	253-254 (253.5-254.4)	C <sub>13</sub> H <sub>9</sub> NO <sub>4</sub>	64.4	3.6	64.2	3.7
2'-CH <sub>3</sub>	205-206 (206-207)	C <sub>13</sub> H <sub>12</sub> O <sub>2</sub>	79.5	6.0	79.3	5.7
2'-OCH <sub>3</sub>	197-198 (197-198)	C <sub>14</sub> H <sub>12</sub> O <sub>3</sub>	74.0	5.6	73.7	5.3

Values in parentheses are literature values

<sup>a</sup> Long and Henze (1941); <sup>b</sup> Byron *et al* (1966); <sup>c</sup> Inukai (1962) <sup>d</sup> Carpenter and Turner (1934); <sup>e</sup> Grieve and Hey (1932-1934); <sup>f</sup> NgPh *et al* (1951); <sup>g</sup> Ray and Rieveschl (1965)

significant. In order to test this, log *I* is plotted against the H<sub>0</sub> acidity function so that the slope of the straight line is minus unity. The pK<sub>BH+</sub> values show a regular variation with substituents: electron-withdrawing groups decrease and electron-donating groups increase pK<sub>BH+</sub>. With a view to seek Hammett correlation, the pKa values (Byron *et al* 1966) of 3'- and 4'-substituted biphenyl-4-carboxylic acids were converted into  $\sigma_{ij}$

**Table 2.**  $pK_{BH^+}$  of substituted biphenyl-4-carboxylic acids obtained from the plot of  $\log I$  vs  $H_0$ 

Substituent	$r$	$-c$	$-m$	$c/m$	$-pK_{BH^+}$
H	0.999	6.85	0.951	6.90	6.9
3'-F	0.999	6.68	0.952	7.02	7.0
3'-Cl	0.999	6.72	0.949	7.08	7.1
3'-Br	0.995	6.74	0.951	7.09	7.7
3'-NO <sub>2</sub>	0.999	6.85	0.945	7.25	7.2
3'-CH <sub>3</sub>	0.990	6.50	0.949	6.85	6.9
3'-OCH <sub>3</sub>	0.994	6.66	0.949	7.00	7.0
4'-F	0.999	6.59	0.951	6.93	6.9
4'-Cl	0.990	6.66	0.951	7.00	7.0
4'-Br	0.999	6.68	0.952	7.02	7.0
4'-NO <sub>2</sub>	0.998	6.97	0.947	7.36	7.4
4'-CH <sub>3</sub>	0.999	6.46	0.950	6.80	6.8
4'-OCH <sub>3</sub>	0.990	6.15	0.954	6.45	6.4
2'-F	0.999	6.51	0.949	6.86	6.9
2'-Cl	0.999	6.46	0.946	6.82	6.8
2'-Br	0.990	6.43	0.946	6.80	6.8
2'-NO <sub>2</sub>	0.999	6.49	0.952	7.03	7.0
2'-Me	0.998	6.36	0.952	6.68	6.7
2'-OMe	0.990	6.20	0.953	6.51	6.5

$pK_{BH^+}$  values are accurate within  $\pm 0.2$  unit;  $r$  = correlation coefficient;  $m$  = slope in the plot of  $\log I$  vs  $H_0$ ;  $c$  = intercept in the plot of  $\log I$  vs  $H_0$

**Table 3.**  $pK_{BH^+}$  of substituted biphenyl-4-carboxylic acids obtained by Bunnett-Olsen treatment.

Substituent	$r$	[H <sub>2</sub> SO <sub>4</sub> ] at half-protonation		$-pK_{BH^+}$
		$\phi$	% (w/w)	
H	0.999	0.053	79.33	6.9
3'-F	0.995	0.052	80.15	6.8
3'-Cl	0.999	0.075	80.56	6.8
3'-Br	0.988	0.067	80.64	6.8
3'-NO <sub>2</sub>	0.976	0.079	81.78	6.9
3'-CH <sub>3</sub>	0.998	0.045	78.92	6.6
3'-OMe	0.998	0.052	80.07	6.7
4'-F	0.969	0.058	79.74	6.7
4'-Cl	0.997	0.074	80.15	6.7
4'-Br	0.983	0.065	80.15	6.8
4'-NO <sub>2</sub>	0.982	0.079	82.52	7.1
4'-CH <sub>3</sub>	0.993	0.031	78.59	6.5
4'-OMe	0.978	0.041	75.57	6.2
2'-F	0.999	0.053	78.84	6.6
2'-Cl	0.997	0.042	78.27	6.5
2'-Br	0.987	0.028	78.27	6.5
2'-NO <sub>2</sub>	0.998	0.064	80.07	6.7
2'-Me	0.991	0.039	77.70	6.4
2'-OMe	0.992	0.021	76.30	6.3

$pK_{BH^+}$  values are accurate within  $\pm 0.3$  unit

**Table 4.**  $pK_{BH^+}$  of substituted 4-acetylbiphenyl obtained from  $\log I$  vs  $H_0$  plot.

Substituent	$r$	$-c$	$-m$	$c/m$	$-pK_{BH^+}$
H	0.995	5.69	0.909	6.25	6.3
3'-F	0.990	6.08	0.938	6.48	6.5
3'-Cl	0.999	6.12	0.941	6.50	6.5
3'-Br	0.995	6.19	0.953	6.50	6.5
3'-NO <sub>2</sub>	0.999	6.29	0.933	6.74	6.8
3'-Me	0.999	5.85	0.967	6.05	6.0
3'-OMe	0.990	6.10	0.960	6.35	6.4
4'-F	0.999	5.90	0.936	6.30	6.2
4'-Cl	0.998	5.95	0.930	6.39	6.4
4'-Br	0.990	6.01	0.940	6.39	6.4
4'-NO <sub>2</sub>	0.999	6.36	0.926	6.87	6.9
4'-Me	0.990	5.84	0.974	6.00	6.0
4'-OMe	0.995	5.42	0.984	5.51	5.5
2'-F	0.999	5.69	0.931	6.11	6.1
2'-Cl	0.999	5.68	0.937	6.08	6.1
2'-Br	0.999	5.66	0.933	6.07	6.1
2'-NO <sub>2</sub>	0.990	6.20	0.949	6.53	6.5
2'-Me	0.999	5.52	0.936	5.90	5.9
2'-OMe	0.999	5.47	0.974	5.6	5.6

$pK_{BH^+}$  values are accurate within  $\pm 0.2$  unit

**Table 5.**  $pK_{BH^+}$  of substituted 4'-acetylbiphenyls by Bunnett-Olsen treatment.

Substituent	$r$	[H <sub>2</sub> SO <sub>4</sub> ] at half protonation		$-pK_{BH^+}$
		$\phi$	% (w/w)	
H	0.989	0.096	74.0	5.8
3'-F	0.969	0.067	75.7	6.1
3'-Cl	0.993	0.064	76.1	6.1
3'-Br	0.983	0.048	76.1	6.2
3'-NO <sub>2</sub>	0.998	0.073	78.1	6.4
3'-Me	0.960	0.036	72.3	5.7
3'-OMe	0.996	0.043	74.8	6.0
4'-Fe	0.953	0.081	74.3	5.8
4'-Cl	0.997	0.076	75.2	6.0
4'-Br	0.955	0.064	75.2	6.0
4'-NO <sub>2</sub>	0.970	0.083	79.0	6.5
4'-Me	0.992	0.028	71.9	5.6
4'-OMe	0.999	0.017	68.0	5.2
2'-F	0.997	0.073	72.9	5.7
2'-Cl	0.890	0.065	72.5	5.7
2'-Br	0.909	0.060	72.5	5.7
2'-NO <sub>2</sub>	0.965	0.043	76.2	6.3
2'-Me	0.999	0.033	71.1	5.7
2'-OMe	0.951	0.028	68.8	5.4

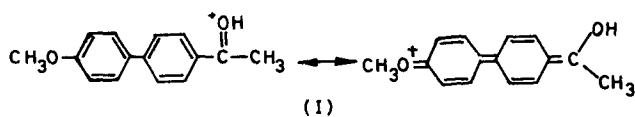
$pK_{BH^+}$  values are accurate within  $\pm 0.3$  unit

**Table 6.** Calculated  $\sigma_{ij}$  values.

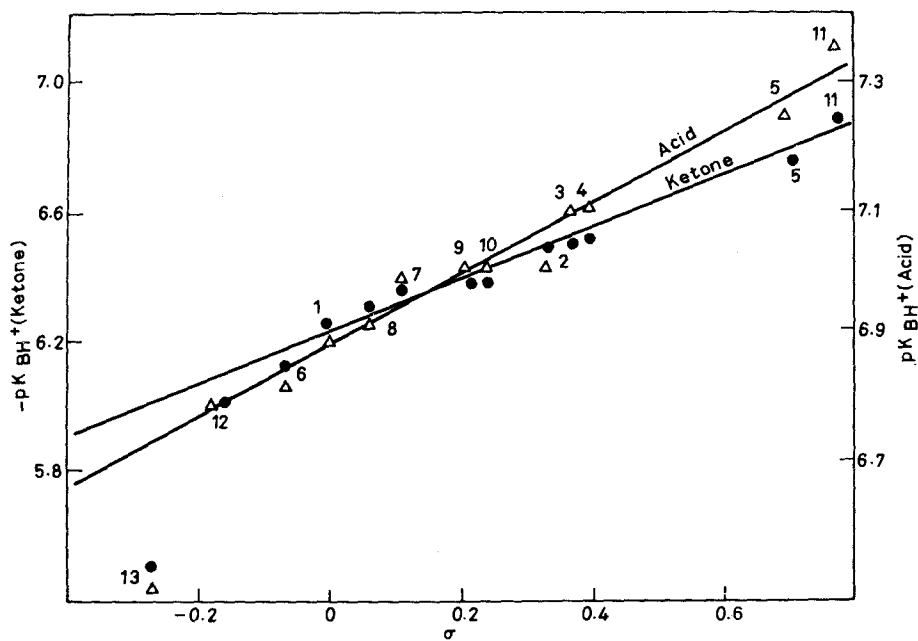
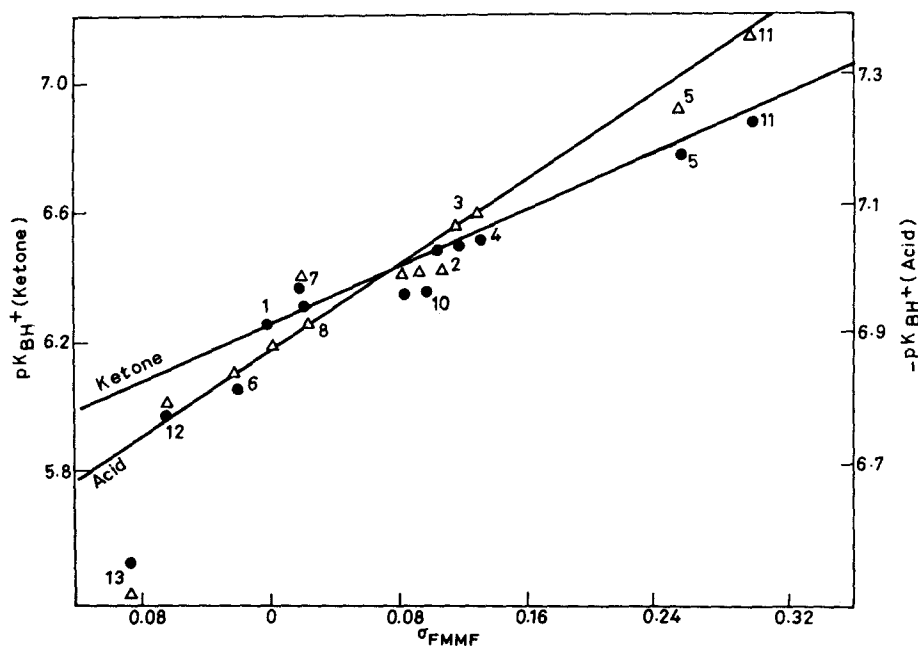
Substituent	By FMMF method	From pKa values
3'-F	0.107	0.146
3'-Cl	0.122	0.146
3'-Br	0.130	0.115
3'-NO <sub>2</sub>	0.255	0.162
3'-CH <sub>3</sub>	-0.030	-0.054
3'-OCH <sub>3</sub>	0.022	-0.031
4'-F	0.044	0.085
4'-Cl	0.093	0.154
4'-Br	0.102	0.154
4'-NO <sub>2</sub>	0.308	0.323
4'-CH <sub>3</sub>	-0.065	-0.039
4'-OCH <sub>3</sub>	-0.084	-0.108

values by dividing the  $\Delta$  pKa values by a  $\rho$  value of 1.32 based on benzoic acid ionization in 50% 2-*n*-butoxyethanol-water. The new  $\sigma$  values thus calculated are given in table 6. The Hammett correlations with these values were very poor, the 4'-OMe group deviating considerably. Neglecting this group the correlation produces  $r = 0.871$  and  $s = 0.127$  in ketones and  $r = 0.812$  and  $s = 0.110$  in acids. The poor correlation possibly lies in the pKa values of Byron *et al* (1966) which generated separate lines for 3'- and 4'-substituted biphenyl-4-carboxylic acids when plotted against ordinary  $\sigma$  values. When the  $\text{pK}_{\text{BH}^+}$  values are plotted (figure 1) against ordinary Hammett  $\sigma_m$  and  $\sigma_p$  values respectively for 3'- and 4'-substituents the correlation seems to be much better without 4'-OMe, with  $r = 0.958$  and  $s = 0.052$  in ketones and  $r = 0.954$  and  $s = 0.041$  in acids. However, the correlation with  $\sigma_{ij}$  values calculated (table 6) based on the Dewar-Golden-Harris treatment (1971) was satisfactory for all the groups except 4'-OMe with  $r = 0.971$  and  $s = 0.062$  for ketones and  $r = 0.968$  and  $s = 0.045$  for the acids. This provides an interesting confirmation that the DGH treatment is fairly successful for biphenyl (figure 2).

Being an electron-donating group, 4'-OMe is involved in extended conjugation with the protonated carbonyl or carboxyl groups as illustrated in (I).



This type of direct resonance may be responsible for the departure of the group from the Hammett plot. When  $\sigma^+$  constants of Brown and Okamoto (1958) are used in place of  $\sigma_m$  and  $\sigma_p$ , the correlation is excellent, the 4'-OMe group also falls on the line (figure 3). The correlation coefficient is 0.977 with  $s = 0.053$  for ketones and 0.965 with  $s = 0.062$  for acids. The plot of  $\text{pK}_{\text{BH}^+}$  vs pKa of the 2'-substituted biphenyl-4-carboxylic acids is linear (figure 4) indicating that protonation and ionization of acids appear to show in comparable degree the  $\pi$ -electron steric effect of 2'-substituents.

Figure 1.  $pK_{BH^+}$  vs Hammett  $\sigma$  plot.Figure 2.  $pK_{BH^+}$  vs  $\sigma_{FMMF}$  plot.

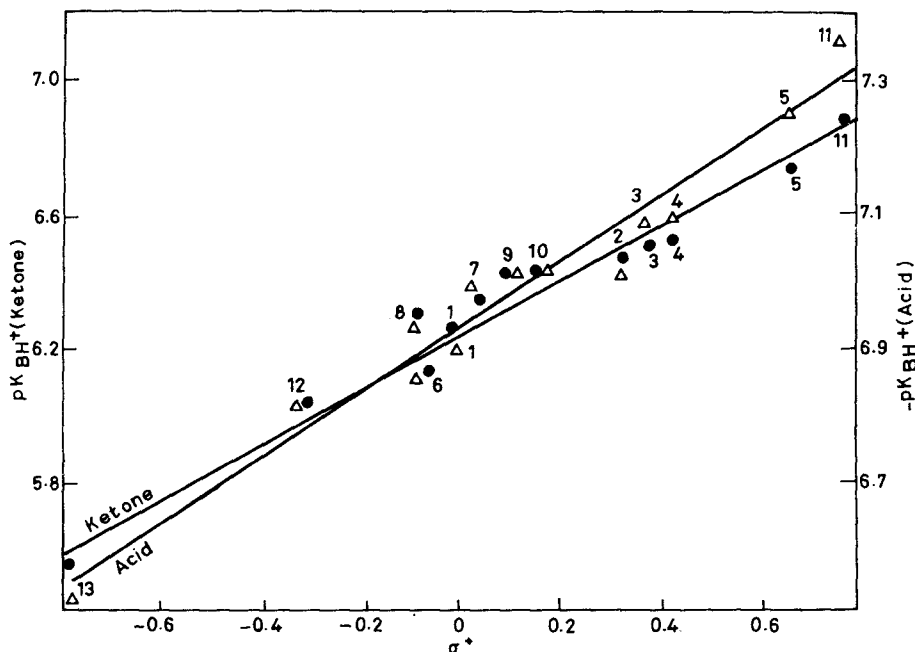


Figure 3.  $pK_{BH^+}$  vs  $\sigma^+$  plot.

### 3. Experimental

#### 3.1 Preparation of compounds

All the ketones were prepared as described by Byron *et al* (1966) and the acids obtained by hypochlorite oxidation. The purity of the compounds tested by TLC gave good carbon and hydrogen analyses (table 1).

#### 3.2 Measurement of $pK_{BH^+}$

Sulphuric acid (E Merck, AR) was diluted with water and 50–98% (w/w) solutions were prepared.  $pK_{BH^+}$  was determined by the procedure adopted by Ananthkrishna Nadar and Varghesetharumaraj (1981). A weighed sample of each compound was dissolved in 85% (w/w) sulphuric acid-water to give a  $4 \times 10^{-4}$  M stock solution, from which 1 ml aliquots was pipetted out into 10 ml volumetric flasks and made up to mark with suitable sulphuric acid-water mixtures so as to give solutions of desired acid concentrations. The  $H_0$  values were taken from the compilation of Paul and Long (1957). Trial experiments indicated that all the ketones and acids were almost unprotonated up to 50% sulphuric acid solution and almost completely protonated in 95% and above sulphuric acid solution. The uv absorption spectra of the compounds were recorded in 50 and 95% sulphuric acid solutions, to obtain the wavelengths of maximal absorption of the unprotonated ( $\lambda_B$ ) and of the protonated ( $\lambda_{BH^+}$ ) forms. The  $\lambda$  values did not change with change in medium. The extinction coefficients in all the other solutions were determined at these two wavelengths.

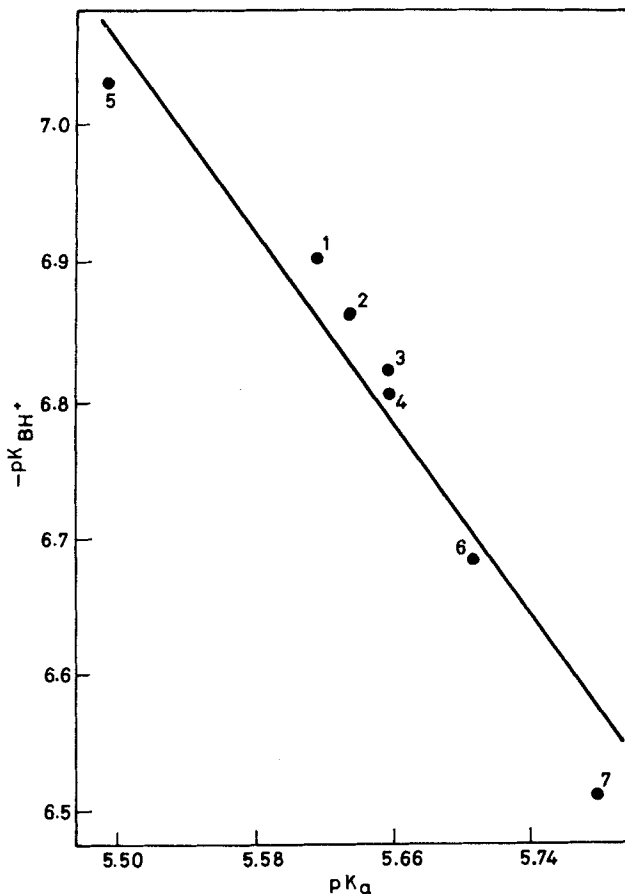


Figure 4.  $pK_{BH^+}$  vs  $pK_a$  plot for 2'-substituents.

The ionization ratio  $I$  in each solution was determined as follows:

$$I = (\varepsilon - \varepsilon_B) / (\varepsilon_{BH^+} - \varepsilon) \quad (1)$$

where  $\varepsilon$  is the molar extinction coefficient in the chosen acid solution,  $\varepsilon_{BH^+}$  and  $\varepsilon_B$  are the corresponding values of the completely protonated and the unprotonated forms respectively. The ionization ratio is related to  $H_0$  through

$$\log I = mH_0 + C. \quad (2)$$

From the plot of  $\log I$  vs  $H_0$ , the  $H_0$  value at half protonation ( $H_0^{1/2}$ ) is taken as  $pK_{BH^+}$ . Following the treatment of Bunnett and Olsen (1965), the  $pK_{BH^+}$  values are also determined graphically employing equation (3)

$$\log [BH^+] / [B] + H_0 = \phi(H_0 + \log CH^+) + pK_{BH^+} \quad (3)$$

The intercept in the plot between  $\log [BH^+] / [B] + H_0$  and  $(H_0 + \log CH^+)$  gives  $pK_{BH^+}$ . The values calculated by the two methods differ by 0.2 to 0.3 units for a given compound. The deviation of the values calculated by (2) is less compared to those



obtained by equation (3) and hence the values obtained from equation (2) are used in the correlation.

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