

Studies on the Effect of Phenyl Substituents  
on Nonadjacent Functional Groups in the Benzene Ring  
I. Phenyl Derivatives of Benzoic Acid

by

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The present paper is an attempt of quantitative determination of the effect of phenyl substituents on the reactivity of functional groups in 5-substituted derivatives of 1,2,3-triphenylbenzene [1], [2].

The value of the  $\sigma$  coefficient [3], [4] from the Hammett equation

$$\lg K/K_0 = \sigma \cdot \rho$$

is a quantitative measure of the effect on the reaction rate and equilibrium of the *m*- or *p*-substituent.

$\sigma$ -Values for the phenyl group, found in the literature range within wide limits, depending on the reactions for which they were determined [5].  $\sigma$ -Values for the phenyl group in the *meta* and *para* positions given by McDaniel and Brown [6] amount to +0.06 and -0.01, respectively. They were calculated from the ionisation data for phenylbenzoic acids in butyl cellosolve [7], [8].

In the present investigations the  $\sigma$ -coefficients were determined from the ionisation data for a number of benzoic acid derivatives in 60 per cent (by volume) aqueous solution of ethanol. The dissociation constants of the acids were measured by potentiometric titration of their  $\text{CO}_2$  free solutions with a  $\text{CO}_2$ -free alcohol solution of KOH. A PHM-type radiometer and a glass-calomel system of electrodes were used.

The results of the measurements are tabulated below.

The  $\rho$ -coefficient evaluated from Hammett's equation [4] for the above series of acids was in experimental conditions 1.66 (correlation coefficient amounting to 0.99).

For calculations the most reliable values of  $\sigma$  reported in the literature were used:

$$\begin{aligned}\sigma_m^{CH_3} &= -0.069 \quad [4], [5], \\ \sigma_p^{CH_3} &= -0.13 \quad [4], [8], \\ \sigma_m^{C_6H_5} &= +0.06 \quad [7].\end{aligned}$$

TABLE  
Dissociation constants of substituted benzoic acids  
in 60% (by volume) ethanol at 23 $\pm$ 1°

Substituent:	$pK'$	$K \cdot 10^6$	Number of tests	Mean error
H	5.73*)	1.87	12	0.01
4-phenyl	5.69*)	2.05	7	0.01
3-phenyl	5.64**)	2.29	15	0.02
3,4-diphenyl	5.64	2.29	14	0.01
3,5-diphenyl	5.60	2.51	9	0.01
3,4,5-triphenyl	5.61	2.46	8	0.01
3-methyl	5.85	1.42	6	0.01
4-methyl	5.94	1.15	10	0.02
3,5-dimethyl	5.97	1.07	11	0.01
3,4,5-trimethyl	6.15	0.708	9	0.02
3,5-dimethyl-4-ethyl	6.11	0.776	9	0.01

\*)  $pK'$  Values found by Berliner and Blommers [7] for benzoic and 4-phenylbenzoic acids in 50% butyl cellosolve are 5.65 and 5.66, respectively.

\*\*\*)  $pK'$  for *m*-phenylbenzoic acid in butyl cellosolve is 5.58 [8].

Hence, the  $\sigma$ -coefficient for the phenyl substituent in *para* position, calculated from the Hammett equation:

$$\sigma = \frac{\lg K/K_0}{\rho} = +0.02 \pm 0.02.$$

The values corresponding to methyl and phenyl substituents are plotted in Fig. 1. The point corresponding to 3,4,5-trimethylbenzoic acid, lies on a straight line, thus indicating the additivity of  $\sigma$ -values for methyl substituents. The deviation from linearity showed by 3,4-diphenyl- and 3,4,5-triphenylbenzoic acids may be explained by their steric structure.

The  $\sigma$ -coefficient for a substituent is a well known measure of resonance and inductive effects [10] exerted by the substituent upon the reaction centre:

$$\sigma = \sigma_I + \sigma_R.$$

Methods of determining the contribution of the inductive effect to the value of  $\sigma$  have been described by Taft and Lewis; the same authors, using own results [11]

as well as those of Roberts and Moreland [12], tabulated values of  $\sigma_j$  [13] and  $\sigma_R$  [14] for various substituents. Their  $\sigma_j$  value of the phenyl substituent is +0.1.

A positive  $\sigma_j$ -value indicates the electron-accepting character of the phenyl substituent, thus the inductive effect of the phenyl substituent enhances the strength of substituted benzoic acid. A conjugation of the carboxyl groups with an aromatic system results in a decrease of acidity [15]. Thus, when the conjugation is inhibited to some extent as in the case of 3,4-diphenyl [16] and 3,4,5-triphenylbenzoic acids, the inductive effect might be expected to appear more distinctly. Hence, 3,4,5-triphenylbenzoic acid should be a stronger acid than 3,5-diphenylbenzoic acid. The experiments showed, however, that the strengths of both acids were identical; the same was found for 3,4-diphenyl and *m*-phenylbenzoic acids.

Since the differences between the strengths of all the acids in question are very small, the interpretation of results is rather difficult.

Nevertheless, the above facts cannot be considered accidental. It seems that the equal strength in the two pairs of acids may be explained as follows.

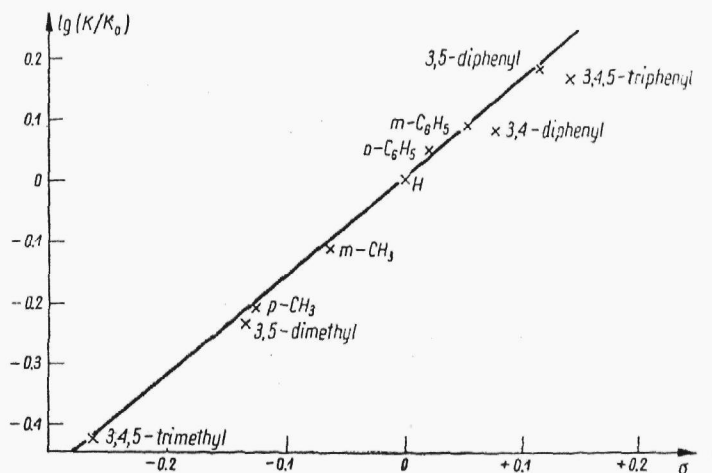


Fig. 1. The  $\sigma - \lg(K/K_0)$  relationship for benzoic acid derivatives from ionization data

In the case of *p*-phenylbenzoic acid the resonance\*) of the *A* and *B* benzene rings with the carboxyl groups is possible. The opposite directions of the resonance and the inductive effects result in an only slight change of acidity as compared with benzoic acid, hence in a  $\sigma$ -value close to zero.

In the case of *m*-phenylbenzoic acid there is a possibility of resonance of the carboxyl group with the ring *A* and simultaneous resonance of ring *C* with ring *A*.

As a result of such cross conjugation the resonance of the carboxyl group with ring *A* is disturbed, thus enhancing the acidity of *m*-phenylbenzoic acid as compared with benzoic acid.

\*) For lack of space the problem of conjugation in the diphenyl system inhibited by steric effects by the hydrogen atoms in *o* and *o'* positions is omitted.

A similar argumentation may be applied to 3,5-diphenylbenzoic acid.

In 3,4-diphenylbenzoic acid as compared with the *p*-phenylbenzoic acid the resonance of ring *B* with ring *A* and the carboxyl group is much more inhibited because of great steric hindrances caused by two neighbouring phenyl groups. This might enhance the acidity of the compound but on the other hand resonance between rings *C* and *A*, which increases the acidity, is also inhibited. Therefore only the inductive effect of the phenyl groups is observed and the strength of 3,4-diphenylbenzoic acid does not differ from that of *m*-phenylbenzoic acid.

Similarly inhibited is the conjugation of the *p*-phenyl substituent with the carboxyl group in 3,4,5-triphenylbenzoic acid, what decreases acidity, but so is the conjugation of phenyl substituents in positions 3 and 5 with the central ring. Therefore the resultant effect of three phenyl substituents in positions 3,4 and 5 is equivalent to the effect of two substituents in positions 3 and 5. Hence, 3,4,5-triphenyl- and 3,5-diphenylbenzoic acids are of equal strength.

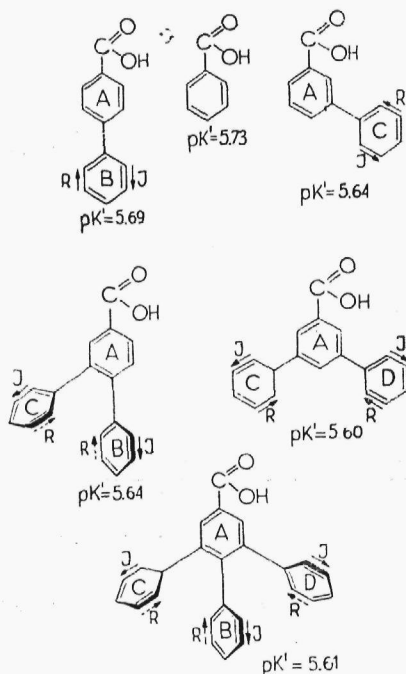


Fig. 2. The influence of substituents in phenyl derivatives of benzoic acid

Thus, the measurements of dissociation constants of phenylbenzoic acids lead to the expected conclusion that in 3,4-diphenyl- and 3,4,5-triphenylbenzoic acids the effect of conjugation is not observed and the effect of the substituents is reduced to a small inductive effect, as measured by  $\Sigma \sigma$ .

Substituting into Hammett's equation

$$\lg K/K_0 = \rho \cdot \Sigma \sigma$$

the values of  $pK'$  for 3,4,5-triphenylbenzoic acid and  $pK'_0$  for benzoic acid and  $\rho = 1.66$ :

$$\Sigma\sigma = +0.09.$$

Assuming the  $\Sigma\sigma$ -value to result only from the inductive effect,  $\sigma_j$  calculated per one phenyl substituent is  $+0.03$  (mean error =  $\pm 0.02$ ).

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