

Studies on the Effect of Phenyl Substituents  
on a Nonadjacent Functional Group in the Benzene Ring  
II. Phenyl Derivatives of Aniline

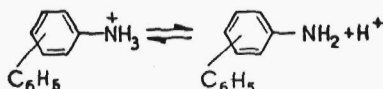
by

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Measurements of dissociation constants showed that the acidity of phenyl derivatives of benzoic acid [1] is only very slightly changed by introducing phenyl substituents. This indicates a weak inductive effect only (as measured by  $\sigma_I^{C_6H_5} = +0.03$ ) calculated from Hammett's equation, and no conjugation of the phenyl groups with the benzene ring in 3,4-diphenyl- and 3,4,5-triphenylbenzoic acids.

To confirm this conclusion another series of reactions was investigated in which the resonance and inductive effects of the phenyl substituent had the same direction. (In the case of dissociation of benzoic acid the inductive and resonance effects of the phenyl substituent are opposed to each other). This occurs in the case of ionisation of an anilinium ion



in which the electron withdrawing inductive effect of the phenyl substituent has the same direction as the effect of conjugation of the amino group with the aromatic system.

Dissociation constants of phenyl derivatives of the anilinium ion were determined by potentiometric titration of  $\text{CO}_2$ -free solutions of hydrochlorides in 75 per cent (by volume) ethanol with a  $\text{CO}_2$ -free alcohol-water solution of KOH.

A PHM3-type radiometer was used for the determinations.

The results of measurements are summarized in the Table.

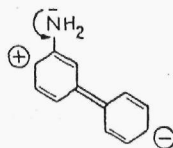
*p*-Toluidine is a stronger base than aniline and *m*-toluidine, since in alkyl substituted aniline derivatives an inductive effect of the methyl group in *meta* position appears along with a distinct effect of hyperconjugation of the methyl group in *para* position.

In the series of phenyl derivatives of aniline nearly the same decrease in basicity can be observed with a phenyl substituent in *meta* and *para* positions. While the decrease brought about by the phenyl substituent in *para* position may easily be explained as a result of the well known effect of conjugation in a 4-aminodiphenyl system, the influence of the phenyl substituent in *meta* position cannot be attri-

TABLE  
Dissociation constants of aniline derivatives in 75 per cent  
(by volume) ethanol at  $22 \pm 1^\circ$

Substituent	$pK'_H$	$K'_B \times 10^{10}$	Number of expts	Mean error
H	4.64	4.38	9	0.03
3-methyl	4.81	6.46	6	0.01
3,5-dimethyl	4.97	9.33	9	0.03
4-methyl	5.19	15.49	11	0.02
3,5-dimethyl-4-ethyl	5.38	23.99	7	0.02
3,4,5-trimethyl	5.45	28.20	9	0.03
3-phenyl	4.45	2.82	11	0.01
4-phenyl	4.48	3.02	11	0.02
3,4-diphenyl	4.37	2.34	8	0.02
3,5-diphenyl	4.34	2.18	7	0.01
3,4,5-triphenyl	4.29	1.95	9	0.02

buted, as Kiefer and Rumpf [2] suggest, to an inductive effect only. Here, a polar resonance effect of a phenyl substituent should also be taken into account [3], [4]. This effect consists in the possibility of migration of the free electron pair of nitrogen towards the benzene ring as a result of conjugation of the substituent in *m*-position with the ring.



In aniline derivatives both the inductive effect and the conjugation of the amino group with the aromatic system cause a decrease of the basicity of the amine. Thus, in systems, where steric hindrances inhibit conjugation, a deviation from additivity of values of the  $\sigma$  coefficient from the Hammett equation might be expected. Indeed, deviation from the  $\sigma$ -values for 3,4-diphenyl and 3,4,5-triphenylanilines may be observed on the diagram presenting the Hammett relationship, for the anilinium ion (Fig. 1)

The coefficient  $\rho$  for ionisation of aniline derivatives hydrochlorides in experimental conditions is +3, the correlation coefficient amounting to 0.98.

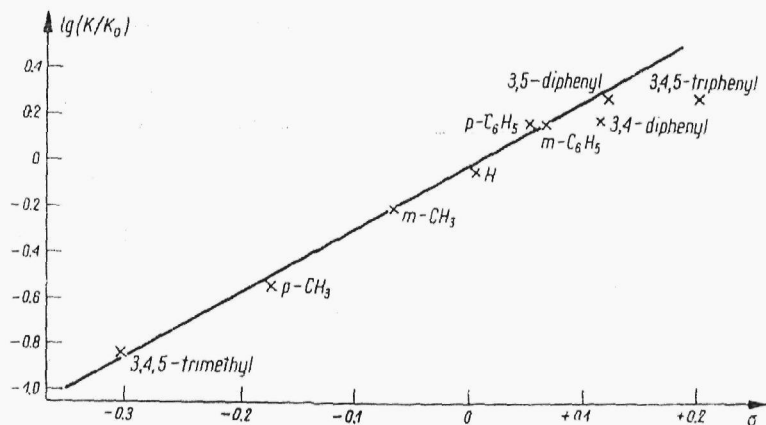


Fig. 1. Plot of  $\lg(K/K_0)$  vs.  $\sigma$  for ionisation of anilinium ions

The decrease of the basicity of the series of phenyl derivatives of aniline given in the Table may be explained, taking into account the effects presented in Fig. 2.

The lower basicity of *p*-phenylaniline as compared with aniline may be attributed to the effect of conjugation of the amino group with diphenyl and to the inductive

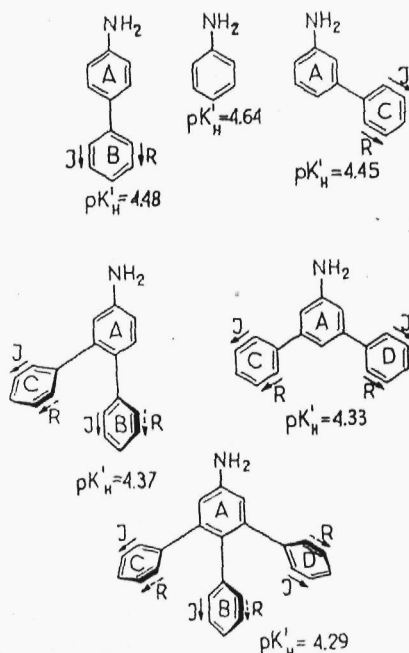


Fig. 2. Effect of substituents in phenyl derivatives of aniline

effect of the phenyl substituent jointly. In *m*-phenyl- and 3,5-diphenylanilines the decrease of basicity is due to both inductive and polar resonance effects.

In 3,4-diphenylaniline, owing to large steric hindrances in the coplanarity of the molecule, the conjugation of the phenyl substituent in position 4 with ring A

and with the amino group is limited, as is the polar resonance effect of the substituent in position 3.

In 3,4,5-triphenylaniline the resonance of the  $\text{NH}_2$  group with the diphenyl system is completely inhibited by a still larger steric hindrance, due to the presence of two phenyl substituents in positions 3 and 5. Similar steric hindrances account for the inhibition of resonance of phenyl substituents in positions 3 and 5 with the central ring; thus the polar resonance effect of these substituents fails to appear.

Substituting in Hammett's equation

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

$pK'_H$  of 3,4,5-triphenylaniline for  $\lg K$  and  $pK'_H$  of aniline for  $\lg K_0$ , the value of  $\Sigma\sigma = +0.12$  is obtained ( $\rho = +3$ ).

If it is assumed, that only the inductive effect accounts for the  $\Sigma\sigma$ -value, as was the case with 3,4,5-triphenylbenzoic acid discussed in a previous paper [1], the  $\sigma$ -value, calculated per one substituent is  $\sigma_f = +0.04 \pm 0.02$ .

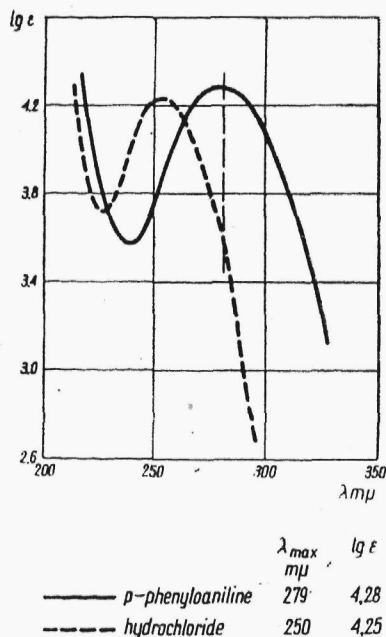


Fig. 3. UV absorption spectra of *p*-phenylaniline and *p*-phenylaniline hydrochloride

Thus, the mean value of  $\sigma_f$  for a phenyl substituent in the 3,4,5-triphenylaniline system is very close to the  $\sigma_f$ -value found from ionization data for the 3,4,5-triphenyl derivative of benzoic acid [1] ( $\sigma_f = +0.03$ ).

The agreement of the results obtained in two different sets of reactions may prove that the obtained  $\sigma$ -value corresponds to the inductive effect  $\sigma_f$  of the phenyl substituent.

The value of  $\sigma_f$  obtained in the described experiments is lower than that given by Taft [4] (+0.1). This could be explained by the fact, that the data used by Taft

for calculations had been obtained from hydrolysis of phenylacetates, where the inductive effect of the phenyl group arises from the difference in electronegativities of the ring carbon atoms ( $sp^2$ ) and the saturated carbon atom ( $sp^3$ ). As there is no difference in the hybridization of the carbon atoms in the whole system under investigation, it seems that the obtained  $\sigma_j$  value characterizes better the electron-attracting properties of the phenyl group than that found by Taft.

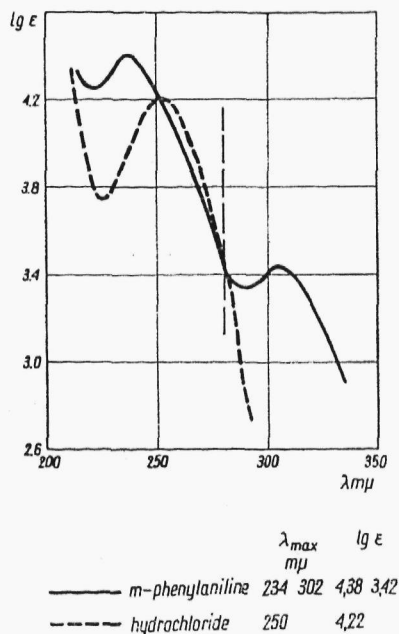


Fig. 4. UV absorption spectra of *m*-phenylaniline and *m*-phenylaniline hydrochloride

To obtain more information concerning the influence of phenyl substituents in position 3,4,5 on a functional group in the benzene ring, UV absorption spectra of phenyl derivatives of aniline and of their hydrochlorides were investigated.

Two distinct bands: *K* at nearly  $250 m\mu$  ( $lg \epsilon$  about 4) and a less intense one, *B* (secondary band) between  $280$  and  $300 m\mu$  ( $lg \epsilon$  about 3.5) are characteristic of the UV absorption spectra of aromatic amines. These spectra may serve as a proof of the existence of conjugation of the amino groups with the aromatic system. Any inhibition of conjugation is made evident by a distinct hypsochromic effect [4].

In the present investigations spectra of amine hydrochlorides served as standards. Since they did not show any conjugation of the amino group with the aromatic system, they were very similar to the hydrocarbon spectra [5], [6]. We expected, that as a result of the inhibited conjugation the differences between the spectra of 3,4-diphenyl- and 3,4,5-triphenylanilines and those of their hydrochlorides would be smaller than in the case of other amines.

The UV absorption spectra of *m*- and *p*-phenylanilines have long been known. The object of measuring them in the present investigations was to compare them

with the spectra of 3,4- 3,5-diphenyl and of 3,4,5-triphenylaniline. (In the absorption diagrams below, the position of the *B* band of the aniline spectrum is represented by a dashed line).

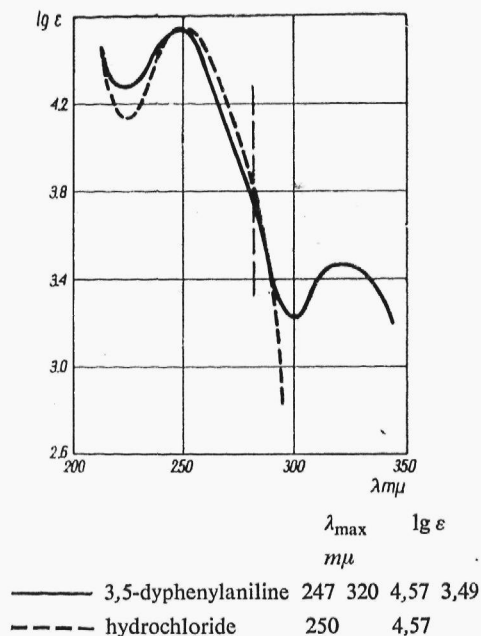


Fig. 5. UV absorption spectra of 3,5-diphenylaniline and 3,5-diphenylaniline hydrochloride

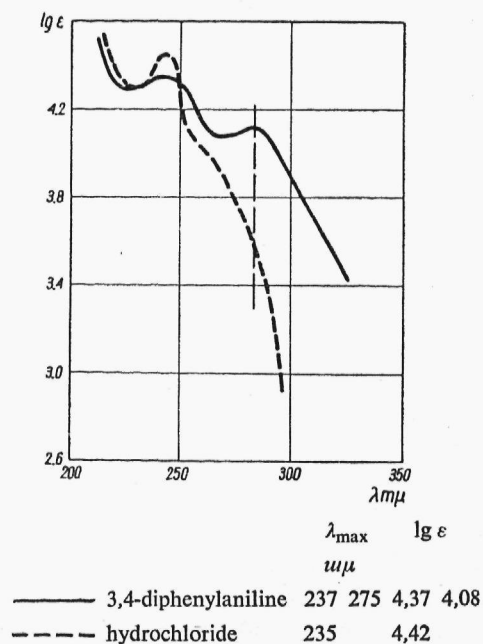


Fig. 6. UV absorption spectra of 3,4-diphenylaniline and 3,4-diphenylaniline hydrochloride

The spectrum of *p*-phenylaniline (Fig. 3) shows only one sharp absorption maximum ( $\lambda_{\max} = 279 \text{ m}\mu$ ,  $\lg \epsilon = 4.28$ ), the secondary *B* band being masked by the *K* band [7], [9].

The spectrum of the corresponding hydrochloride is almost identical with that of diphenyl.

A certain bathochromic displacement ( $22 \text{ m}\mu$ ) of the *B* band ( $\lambda_{\max} = 302 \text{ m}\mu$ ,  $\lg \epsilon = 3.42$ ) of *m*-phenylaniline as compared with the *B* band of aniline can be seen. This is characteristic of *m*-derivatives of diphenyl [9].

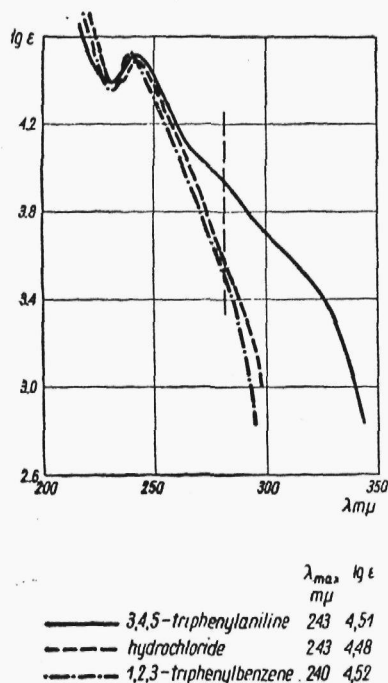


Fig. 7. UV absorption spectra of 3,4,5- triphenylaniline, its hydrochloride and 1,2,3-triphenylbenzene

For 3,5-diphenylaniline a further displacement of the absorption maximum of the *B* band ( $\lambda_{\max} = 320 \text{ m}\mu$ ,  $\lg \epsilon = 3.5$ ) towards longer wavelengths can be observed. The spectrum of 3,4-diphenylaniline shows a less distinct *B* band ( $\lambda_{\max} = 275 \text{ m}\mu$ ,  $\lg \epsilon = 4.08$ ) as compared with 3,5-diphenylaniline. The band is less intense than that characteristic of the conjugation of the amino group with the aromatic system in *p*-phenylaniline. Nevertheless a fairly high  $\lg \epsilon$  value (4.08) may be interpreted as an indication of some, though reduced, resonance of the amino group with the diphenyl system.

The spectrum of 3,4,5-triphenylaniline (Fig. 7) shows no maximum at wavelengths, corresponding to the *B*-band, only a slight change in the slope of the curve, viz. at  $\lambda = 280 \text{ m}\mu$ , can be observed.

It may be seen from the diagram that the absorption curve for 3,4,5-triphenylaniline resembles much more the curve of the hydrocarbon, than those previously described. A slight inflection of the curve may be ascribed to the conjugation of the amino group with the central ring. No band characteristic of the conjugation of the amino group with a diphenyl system was observed.

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