

## Studies on Aminonitrophenols

### I. The Determination of the Protolytic Constants of 4-Amino-2-nitrophenol and 4-Amino-3-nitrophenol

HANS GUSTAF HANSSON

*Department of Inorganic and Physical Chemistry, Chemical Institute, University of Lund, Sweden*

The two substances mentioned above have the formula  $C_6H_3(NH_2)(NO_2)(OH)$ . In acid aqueous solutions they form the ion  $C_6H_3(NH_3^+)(NO_2)(OH)$  and in alkaline aqueous solutions the ion  $C_6H_3(NH_2)(NO_2)O^-$ . The protolytic reactions are accompanied by colour changes of indicator character, which means that the forms  $C_6H_3(NH_3^+)(NO_2)(OH)$ ,  $C_6H_3(NH_2)(NO_2)(OH) \rightleftharpoons C_6H_3(NH_3^+)(NO_2)O^-$  and  $C_6H_3(NH_2)(NO_2)O^-$  have different, well separated light absorption bands in the visible part of the spectrum.

By measuring the light absorption at suitable wave lengths and in proper buffer solutions it has been possible to determine the constants of the protolytic reactions for the two substances investigated. The constants determined are concentration constants referred to the temperature 25°C, the ionic strength 0.50 M (obtained by the addition of NaCl) and a solvent with the composition 99 % water + 1 % ethanol.

The structure of the compounds is discussed and it is shown that the aminonitrophenol molecules have practically no zwitter ion character.

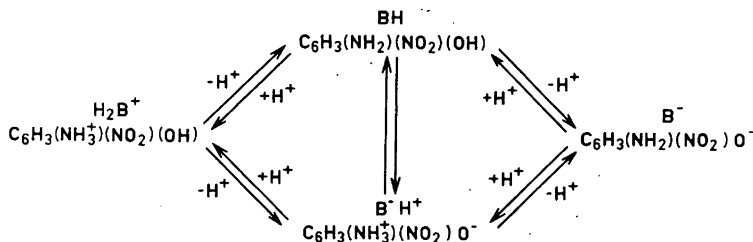
Earlier investigations of the various monoaminomononitrophenols mainly concern the preparation of the substances and their reactions with organic chemicals. But up to now no accurate determination of the protolytic constants of the aminonitrophenols has been performed. Such a determination is of great interest, however, as it may be assumed that the differences between the constants of the various isomers could give important information about the molecular structure of the compounds. In this paper are presented the results of the determination of the protolytic constants of 4-amino-2-nitrophenol and 4-amino-3-nitrophenol. For both substances investigated the ion  $C_6H_3(NH_3^+)(NO_2)(OH)$ , the molecule  $C_6H_3(NH_2)(NO_2)(OH)$  in equilibrium with the zwitter ion  $C_6H_3(NH_3^+)(NO_2)O^-$  and the ion  $C_6H_3(NH_2)(NO_2)O^-$ , representing the

stages in the protolytic reactions, have different, well separated light absorption bands in the visible part of the spectrum.

The determination of the protolytic constants was performed by measuring the light extinction of the aminonitrophenols in a series of solutions with suitable  $[H^+]$ -values. The constants were calculated from coherent values of  $[H^+]$  and the light extinction  $E$ . The way in which the investigation was carried out is thus a modification of the method previously used by the author, among others, in his investigation of some benzaurin derivatives<sup>1-5</sup>. The solutions used for the measurements were prepared by mixing 49 ml of the proper aqueous buffer with 1 ml of a stock solution of the aminonitrophenol in 50 % ethanol (+ a small amount of HCl). The results are thus throughout referred to a solvent with the composition 99 % water + 1 % ethanol. By the addition of NaCl to the buffer solutions, the ionic strength of the measurement solutions was kept constant at 0.50 M. The measurements were performed at the temperature 25°C.

#### THE PROBLEM

The protolytic scheme of an aminonitrophenol can be written as follows\*:



The equilibria above depend on the pH of the solution. This dependence appears as a shift of the colour of the solution. As is well-known the following constants can be defined for an ampholyte.

$$K'_1 = \frac{[H^+] \cdot [BH]}{[H_2B^+]} ; K'_2 = \frac{[H^+] \cdot [B^-]}{[BH]} ; K_a = \frac{[B^-H^+]}{[BH]}$$

$$K''_1 = \frac{[H^+] \cdot [B^-H^+]}{[H_2B^+]} ; K''_2 = \frac{[H^+] \cdot [B^-]}{[B^-H^+]}$$

As expected, equilibrium is reached instantaneously when the pH is changed. This means that separate determinations of  $[BH]$  and  $[B^-H^+]$ , which are always in equilibrium, are impossible. Only the sum  $[BH] + [B^-H^+]$  can be determined. Thus it is convenient to define

$$K_1 = K'_1 + K''_1 ; K_1 = \frac{[H^+] \cdot [HB]}{[H_2B^+]} \quad (1)$$

\*  $H_2B^+$ , BH,  $B^-H^+$  and  $B^-$  are abbreviated formulas, used from now on.

$$\frac{1}{K_2} = \frac{1}{K_2'} + \frac{1}{K_2''}; K_2 = \frac{[\text{H}^+] \cdot [\text{B}^-]}{[\text{HB}]} \quad (2)$$

where  $[\text{HB}] = [\text{BH}] + [\text{B}^-\text{H}^+] = [\text{BH}] \cdot (1 + K_a)$

It follows that

$$K_1 = K_1' \cdot (1 + K_a) \text{ and } K_2 = \frac{K_2'}{1 + K_a}$$

The task is now to determine  $K_1$  and  $K_2$ .

#### FORMULAS

If  $C$  is the total concentration of the aminonitrophenol,

$$C = [\text{H}_2\text{B}^+] + [\text{HB}] + [\text{B}^-] \quad (3)$$

$E$  = the light extinction of the solution at the pathlength  $d$  cm, and  $E_{\text{H}_2\text{B}^+}$  ( $E_{\text{HB}}$ ,  $E_{\text{B}^-}$ ) = the specific light extinction at unaltered pathlength of a solution in which  $[\text{H}_2\text{B}^+]$  ( $[\text{HB}]$ ,  $[\text{B}^-]$ ) =  $C$ , we can write

$$E = E_{\text{H}_2\text{B}^+} \cdot \frac{[\text{H}_2\text{B}^+]}{C} + E_{\text{HB}} \cdot \frac{[\text{HB}]}{C} + E_{\text{B}^-} \cdot \frac{[\text{B}^-]}{C} \quad (4)$$

From eqns. 1–4 we have the following general formula

$$E = \frac{E_{\text{H}_2\text{B}^+} \cdot [\text{H}^+]^2 + E_{\text{HB}} \cdot K_1 \cdot [\text{H}^+] + E_{\text{B}^-} \cdot K_1 \cdot K_2}{[\text{H}^+]^2 + K_1 \cdot [\text{H}^+] + K_1 \cdot K_2} \quad (5)$$

When the two equilibria concerned are well separated, *i.e.* when  $K_1 \gg K_2$ , it is possible to simplify formula (5) when used for the determination of  $K_1$  and  $K_2$ .

A. If  $[\text{H}^+] \gg K_2$  the terms  $E_{\text{B}^-} \cdot K_1 \cdot K_2$  and  $K_1 \cdot K_2$  may be neglected and formula (5) is transformed into

$$E = \frac{E_{\text{H}_2\text{B}^+} \cdot [\text{H}^+] + E_{\text{HB}} \cdot K_1}{[\text{H}^+] + K_1} \quad (6)$$

Eqn. (6) can be transformed into two different expressions, the left members of which are linear functions of  $[\text{H}^+]$ , suitable for a graphic representation of the measured quantities.

$$\frac{1}{E_{\text{H}_2\text{B}^+} - E} = \frac{1}{E_{\text{H}_2\text{B}^+} - E_{\text{HB}}} + \frac{[\text{H}^+]}{K_1 \cdot (E_{\text{H}_2\text{B}^+} - E_{\text{HB}})} \quad (7)$$

$$\frac{[\text{H}^+]}{E - E_{\text{HB}}} = \frac{K_1}{E_{\text{H}_2\text{B}^+} - E_{\text{HB}}} + \frac{[\text{H}^+]}{E_{\text{H}_2\text{B}^+} - E_{\text{HB}}} \quad (8)$$

B. If  $[\text{H}^+] \ll K_1$  the terms  $E_{\text{H}_2\text{B}^+} \cdot [\text{H}^+]^2$  and  $[\text{H}^+]^2$  may be neglected and formula (5) is transformed into

$$E = \frac{E_{\text{HB}} \cdot [\text{H}^+] + E_{\text{B}^-} \cdot K_2}{[\text{H}^+] + K_2} \quad (9)$$

Eqn. (9) can also be transformed into two different expressions, the left members of which are linear functions of  $[\text{H}^+]$ , suitable for a graphic representation of the measured quantities.

$$\frac{1}{E - E_{\text{HB}}} = \frac{1}{E_{\text{B}^-} - E_{\text{HB}}} + \frac{[\text{H}^+]}{K_2 \cdot (E_{\text{B}^-} - E_{\text{HB}})} \quad (10)$$

$$\frac{[\text{H}^+]}{E - E_{\text{B}^-}} = \frac{K_2}{E_{\text{HB}} - E_{\text{B}^-}} + \frac{[\text{H}^+]}{E_{\text{HB}} - E_{\text{B}^-}} \quad (11)$$

### EXPERIMENTAL

The measurements of the light extinctions were performed with a Beckman Quartz Spectrophotometer, Model DU, at 25°C. Before the measurements were made the solutions were kept in a thermostat at this temperature.

The measurements of  $[\text{H}^+]$  were performed with quinhydrone and a platinum-plate electrode or with hydrogen gas and a platinum-plate electrode covered with platinum-black. The reference solution had the composition 0.02 M HCl + 0.48 M NaCl. In some cases  $[\text{H}^+]$  was calculated from the amount of HCl added.

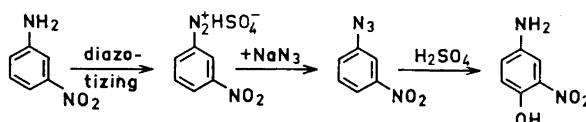
In alkaline solutions there were difficulties in obtaining stable and reproducible values of  $E$ . This is probably due to an oxidation of the aminonitrophenol catalyzed by the small amounts of metal ions present in the solutions. The stability is thus considerably improved by the addition of small amounts of KCN or EDTA to the solutions. Consequently EDTA was added to all alkaline solutions used for the measurements;  $[\text{EDTA}] = 4 \times 10^{-4}$  M. These solutions had reproducible light extinctions that kept stable for at least 1–2 h. The addition of EDTA (or KCN) has no undesired effects (except a slight poisoning of the Pt-electrode by  $\text{CN}^-$ -ions).

The stock solutions of the aminonitrophenols were prepared by dissolving a weighed amount of the substance in 0.01 M HCl in 50 % ethanol. The concentration of the aminonitrophenol in the stock solutions was  $5 \times 10^{-3}$  M. The solutions used for the measurements were prepared by mixing 49.00 ml of a buffer solution with 1.058 ml of a stock solution of the aminonitrophenol. This was added to the buffer from a hypodermic syringe, the volume of which (1.058 ml) had been determined by weighing. Owing to a special stopping equipment of the hypodermic syringe the volume given from this is in fact reproducible within  $\pm 0.1$  %. The concentration of the aminonitrophenol in the solutions used for the measurements was thus of the order  $1 \times 10^{-4}$  M and reproducible within the limits mentioned above. The validity of Beer's law was verified in separate measurements not accounted for.

A short description of the syntheses of the substances investigated is given below. Other chemicals used were of the best qualities obtainable from Baker, Merck etc.

### 4 - Amino - 2 - nitrophenol

The substance was prepared from *m*-nitroaniline according to the following reactions <sup>6,7,10</sup>.



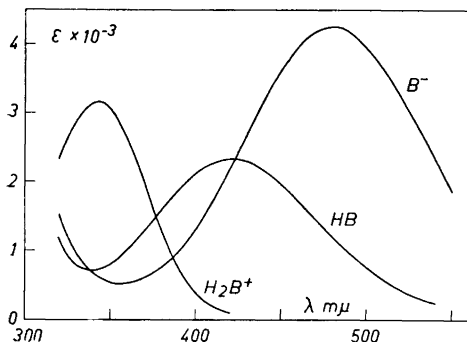
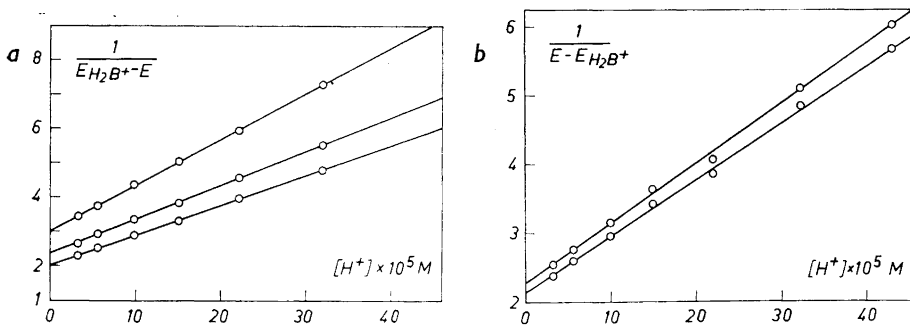


Fig. 1. 4-Amino-2-nitrophenol. Light extinction curves. The molecular extinction coefficient,  $\epsilon$ , as a function of the wave length,  $\lambda$ , in  $m\mu$ .

Before performing the last step the azide  $C_6H_4(NO_2)N_3$  was recrystallised from diluted ethanol. After distillation with water vapour it formed white needles with the melting point  $53-54^\circ C$ . The final product of the aminonitrophenol was recrystallised from ethanol to a constant light absorption. The substance so obtained had m.p.  $128-129^\circ C$ . (Found: C 47.35; H 4.14; N 17.74. Calc. for  $C_6H_6O_3N_2$ : C 46.76; H 3.92; N 18.18).

*Light extinction curves.* In Fig. 1 are shown the curves for the different forms of the substance, i.e. for the red ion  $B^-$ , the yellow "molecule" HB and the pale yellow ion  $H_2B^+$ .

The diagram shows the molecular extinction coefficient,  $\epsilon$ , as a function of the wave length,  $\lambda$ , in  $m\mu$ .  $\epsilon$  was calculated from the equation  $E = \epsilon \cdot C \cdot d$ , and  $E$ , the light extinction, was measured at  $d = 2$  cm for solutions with  $C = 1.067 \times 10^{-4}$  M. The curve of  $H_2B^+$  was taken up in an HCl-solution with  $[H^+] = 0.500$  M (where  $E \approx E_{H_2B^+}$ ), the curve of HB in a  $NaH_2PO_4-Na_2HPO_4$ -buffer with  $[H^+] = 1.51 \times 10^{-6}$  M\* and the curve of  $B^-$  in a NaOH-NaCl-solution with  $[OH^-] = 0.00979$  M (where  $E \approx E_{B^-}$ ). It was found that



Figs. 2 a and b. 4-Amino-2-nitrophenol.  $\pm 1/(E_{H_2B^+} - E)$ , respectively, as a function of  $[H^+]$  for the determination of  $K_1$ . The wave lengths are from above in 2 a:  $360 m\mu$ ,  $330 m\mu$ , and  $345 m\mu$  and in 2 b:  $410 m\mu$  and  $420 m\mu$ . (The line for  $430 m\mu$ , not drawn, almost coincides with that for  $420 m\mu$ .)

\* At this value of  $[H^+]$  the contribution to  $E$  from the forms  $H_2B^+$  and  $B^-$  cannot be neglected at all wave lengths. Therefore, when calculating  $\epsilon$ ,  $E_{HB}$ , obtained from formula (5), is substituted for  $E$ , the measured extinction.

$$\begin{aligned}
 (\varepsilon_{\text{H}_2\text{B}^+})_{\text{max}} &= 3.1(5) \times 10^3 & \text{at} & \lambda \approx 343 \text{ m}\mu \\
 (\varepsilon_{\text{HB}})_{\text{max}} &= 2.3(3) \times 10^3 & \text{at} & \lambda \approx 422 \text{ m}\mu \\
 (\varepsilon_{\text{B}^-})_{\text{max}} &= 4.2(6) \times 10^3 & \text{at} & \lambda \approx 481 \text{ m}\mu
 \end{aligned}$$

*Determination of  $K_1$ .* From the curves in Fig. 1 it is obvious that the measurements should be performed at  $\lambda \approx 345 \text{ m}\mu$  and  $\lambda \approx 420 \text{ m}\mu$  where the difference in  $E$  ( $\varepsilon$ ) between  $\text{H}_2\text{B}^+$  and  $\text{HB}$  is greatest. Two series of measurements were performed, one at the wave lengths 330, 345, and 360  $\text{m}\mu$  and the other at 410, 420, and 430  $\text{m}\mu$ . The solutions used for the measurements were made up from acetate buffers and a stock solution of the aminonitrophenol in the way described above.  $[\text{H}^+]$  was determined (see above) and  $E$  was measured at  $C = 1.067 \times 10^{-4}$  and with  $d = 2 \text{ cm}$ . The measured quantities  $E$  and  $[\text{H}^+]$  are represented graphically according to formula (7) where  $E_{\text{H}_2\text{B}^+}$  is known from direct measurements. A straight line is obtained from which  $K_1$  and  $E_{\text{HB}}$  are calculated; cf. Figs. 2 a and 2 b. The calculated value of  $E_{\text{HB}}$  is compared with the value found by measurement.

Results:		(calc.)	(found)
$\lambda = 330 \text{ m}\mu$	$K_1 = 2.40 \times 10^{-4}$	$E_{\text{HB}} = 0.19$	0.17
$\lambda = 345 \text{ m}\mu$	$K_1 = 2.34 \times 10^{-4}$	$E_{\text{HB}} = 0.18$	0.16
$\lambda = 360 \text{ m}\mu$	$K_1 = 2.27 \times 10^{-4}$	$E_{\text{HB}} = 0.228$	0.220
$\lambda = 410 \text{ m}\mu$	$K_1 = 2.62 \times 10^{-4}$	$E_{\text{HB}} = 0.472$	0.484
$\lambda = 420 \text{ m}\mu$	$K_1 = 2.60 \times 10^{-4}$	$E_{\text{HB}} = 0.484$	0.495
$\lambda = 430 \text{ m}\mu$	$K_1 = 2.52 \times 10^{-4}$	$E_{\text{HB}} = 0.477$	0.488

$$\text{Average value } K_1 = (2.46 \pm 0.15) \times 10^{-4}$$

The agreement between calculated and found values of  $E_{\text{HB}}$  is satisfying. In the first series ( $\lambda = 330\text{--}360 \text{ m}\mu$ )  $E_{\text{HB}}$  (calc.) is obtained as the difference

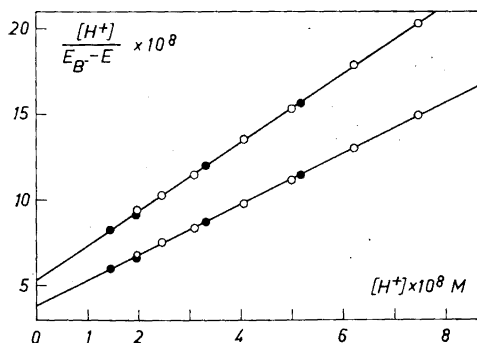


Fig. 3. 4-Amino-2-nitrophenol.  $[\text{H}^+]/(E_{\text{B}^-} - E)$  as a function of  $[\text{H}^+]$  for the determination of  $K_2$ . The wave lengths are from above 460  $\text{m}\mu$  and 480  $\text{m}\mu$ . (The line for 500  $\text{m}\mu$ , not drawn, almost coincides with that for 480  $\text{m}\mu$ .) The points  $\text{O}$  are for  $\text{NaH}_2\text{PO}_4\text{--Na}_2\text{HPO}_4$  buffers and the points  $\bullet$  for  $\text{H}_3\text{BO}_3\text{--NaOH}$  buffers.

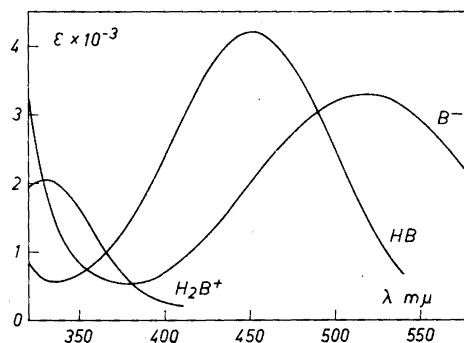


Fig. 4. 4-Amino-3-nitrophenol. Light extinction curves. The molecular extinction coefficient,  $\varepsilon$ , as a function of the wave length,  $\lambda$ , in  $\text{m}\mu$ .

between two larger quantities (0.4–0.6), which explains the deviations between calculated and found values.

*Determination of  $K_2$ .* From Fig. 1 it is evident that a wave length suitable for the measurements is  $\lambda \approx 480 \text{ m}\mu$ . A series of measurements was performed at the wave lengths 460, 480, and 500  $\text{m}\mu$ . The solutions used for the measurements were made up from a stock solution of the aminonitrophenol and buffers containing the same small amount of EDTA (see above). The buffers used were  $\text{NaH}_2\text{PO}_4$ – $\text{Na}_2\text{HPO}_4$ -buffers at  $7.1 \leq \text{pH} \leq 7.7$  and  $\text{H}_3\text{BO}_3$ – $\text{NaOH}$ -buffers ( $\text{H}_3\text{BO}_3$ – $\text{NaH}_2\text{BO}_3$ ) at  $7.3 \leq \text{pH} \leq 7.8$ .  $[\text{H}^+]$  was determined and  $E$  was measured at  $C = 1.067 \times 10^{-4} \text{ M}$  and with  $d = 2 \text{ cm}$ . The values of  $E$  and  $[\text{H}^+]$  are represented graphically according to formula (11) where  $E_{\text{B}^-}$  is known from direct measurements. A straight line is obtained from which  $K_2$  and  $E_{\text{HB}}$  are calculated; cf. Fig. 3. The calculated value of  $E_{\text{HB}}$  is compared with the value found by measurement.

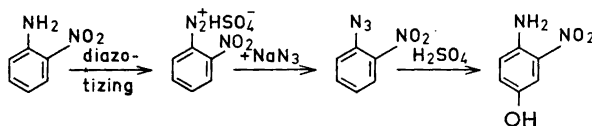
Results:		(calc.)	(found)
$\lambda = 460 \text{ m}\mu$	$K_2 = 2.66 \times 10^{-8}$	$E_{\text{HB}} = 0.35$	0.36
$\lambda = 480 \text{ m}\mu$	$K_2 = 2.56 \times 10^{-8}$	$E_{\text{HB}} = 0.24$	0.26
$\lambda = 500 \text{ m}\mu$	$K_2 = 2.59 \times 10^{-8}$	$E_{\text{HB}} = 0.14$	0.16

$$\text{Average value } K_2 = (2.6 \pm 0.1) \times 10^{-8}$$

Here too,  $E_{\text{HB}}(\text{calc.})$  is obtained as the difference between two larger quantities, which explains the deviations between calculated and found values of  $E_{\text{HB}}$ .

#### 4 - Amino - 3 - nitrophenol

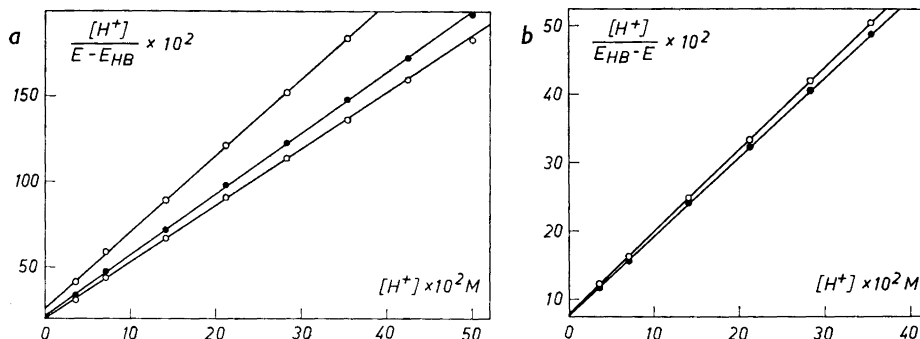
The substance was prepared from *o*-nitroaniline in an analogous manner<sup>6-9</sup>.



The final product of the aminonitrophenol, recrystallised from benzene to a constant light absorption, had the melting point 149–150°C. (Found: C 47.42; H 4.29; N 18.07. Calc. for  $\text{C}_6\text{H}_6\text{O}_3\text{N}_2$ : C 46.76; H 3.92; N 18.18).

*Light extinction curves.* Fig. 4 shows the curves (the molecular extinction coefficient  $\epsilon$  as a function of the wave length  $\lambda$  in  $\text{m}\mu$ ) for the red-violet ion  $\text{B}^-$ , the yellow "molecule" HB and the almost colourless ion  $\text{H}_2\text{B}^+$ . As before,  $\epsilon$  was calculated from the equation  $E = \epsilon \cdot C \cdot d$ .  $E$  was measured at  $d = 2 \text{ cm}$  for solutions with  $C = 1.061 \times 10^{-4} \text{ M}$ .

The curve of  $\text{B}^-$  was taken up in a  $\text{NaOH}$ – $\text{NaCl}$ -solution with  $[\text{OH}^-] = 0.0979 \text{ M}$  (where  $E \approx E_{\text{B}^-}$ ) and the curve of HB in an acetate buffer with  $[\text{H}^+] = 3.30 \times 10^{-5} \text{ M}$  (where  $E \approx E_{\text{HB}}$ ). The curve of  $\text{H}_2\text{B}^+$  can be taken up but indirectly because of the relatively great value of  $K_1$  ( $6 \times 10^{-2}$ ). From the measured  $E$ -values in an  $\text{HCl}$ -solution with  $[\text{H}^+] = 0.500 \text{ M}$  the corresponding  $E_{\text{H}_2\text{B}^+}$ -values were calculated from formula (6) and from these  $E_{\text{H}_2\text{B}^+}$ -values  $\epsilon$  was calculated.



Figs. 5 a and b. 4-Amino-3-nitrophenol.  $\pm [H^+]/(E - E_{HB})$ , respectively, as a function of  $[H^+]$  for the determination of  $K_1$ . The wave lengths are from above in 5 a: 320  $m\mu$  (O-points), 340  $m\mu$  (●-points) and 330  $m\mu$  (O-points) and in 5 b: 440  $m\mu$  (O-points) and 450  $m\mu$  (●-points). (The line for 460  $m\mu$ , not drawn, falls between the two in the figure).

It was found that

$$\begin{array}{lll} (\epsilon_{H_2B^+})_{\max} & = 2.0(5) \times 10^3 & \text{at } \lambda \approx 330 \mu\mu \\ (\epsilon_{HB})_{\max} & = 4.2(1) \times 10^3 & \text{at } \lambda \approx 452 \mu\mu \\ (\epsilon_{B^-})_{\max} & = 3.3(0) \times 10^3 & \text{at } \lambda \approx 420 \mu\mu \end{array}$$

*Determination of  $K_1$ .* From Fig. 4 it is obvious that the measurements should be performed at  $\lambda \approx 330 \mu\mu$  and  $\lambda \approx 450 \mu\mu$ , where the curves of  $H_2B^+$  and HB differ considerably. The solutions used for the measurements were made up from a stock solution of the aminonitrophenol and a series of seven HCl—NaCl-solutions with proper accurately known  $[H^+]$ -values. ( $[H^+]$  is known from the amount of HCl added).  $E$  was measured at  $d = 2$  cm and with  $C = 1.061 \times 10^{-4}$  M. The values of  $E$  and  $[H^+]$  are represented graphically according to formula (8), where  $E_{HB}$  is known from direct measurement. A straight line is obtained from which  $K_1$  (and  $E_{H_2B^+}$ )\* can be calculated. See Figs. 5a and 5b.

Results:

$$\begin{array}{ll} \lambda = 320 \mu\mu & K_1 = 5.84 \times 10^{-2} \\ \lambda = 330 \mu\mu & K_1 = 6.03 \times 10^{-2} \\ \lambda = 340 \mu\mu & K_1 = 6.05 \times 10^{-2} \\ \\ \lambda = 440 \mu\mu & K_1 = 6.64 \times 10^{-2} \\ \lambda = 450 \mu\mu & K_1 = 6.54 \times 10^{-2} \\ \lambda = 460 \mu\mu & K_1 = 6.63 \times 10^{-2} \end{array}$$

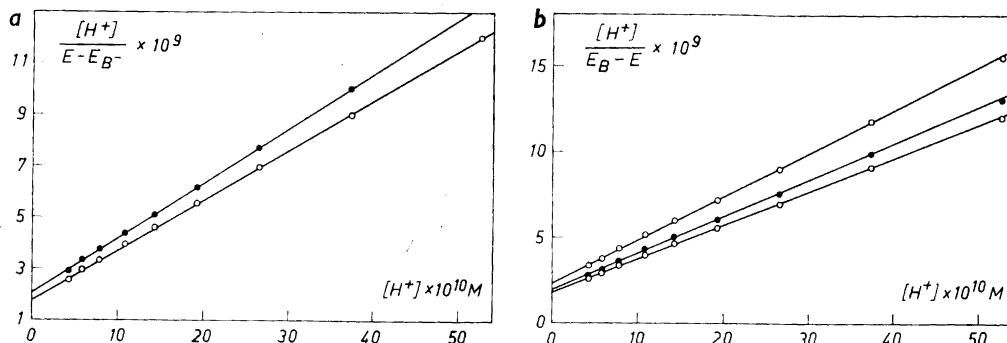
$$\text{Average value } K_1 = (6.3 \pm 0.3) \times 10^{-2}$$

*Determination of  $K_2$ .* To judge from Fig. 4 it seems appropriate to perform the measurements at  $\lambda \approx 450 \mu\mu$  and  $\lambda \approx 520 \mu\mu$  where the difference between the curves of  $B^-$  and HB is relatively great\*\*. The solutions used for the meas-

\* The values of  $E_{H_2B^+}$ , calculated here, agree with those obtained above. But as these, too, were obtained indirectly, the agreement means no real check.

\*\* An attempt was made to perform measurements at  $\lambda \approx 320 \mu\mu$  too. The reproducibility of the  $E$ -values obtained was not good, however. This is probably due to the great slope of the  $B^-$ -curve at this wave length. Nevertheless, the value of  $K_2$  obtained ( $8.1 \times 10^{-10}$ ) is in relatively good agreement with the values obtained from the other measurements.





Figs. 6 a and b. 4-Amino-3-nitrophenol.  $\pm [H^+]/(E - E_{B^-})$ , respectively, as a function of  $[H^+]$  for the determination of  $K_2$ . The wave lengths are from above in 6 a: 450 m $\mu$  (●-points) and 430 m $\mu$  (○-points) and in 6 b: 520 m $\mu$  (○-points), 530 m $\mu$  (●-points) and 540 m $\mu$  (○-points). (The line for 440 m $\mu$ , not drawn, falls between the two lines in 6 a).

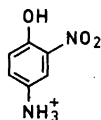
Measurements were made up from a stock solution of the aminonitrophenol and a series of nine  $H_3BO_3$ -NaOH-buffers ( $H_3BO_3$ - $NaH_2BO_3$ ) containing the same small amount of EDTA (see above).  $[H^+]$  was determined and  $E$  was measured at  $C = 1.061 \times 10^{-4} M$  and with  $d = 2$  cm. The values of  $E$  and  $[H^+]$  were represented graphically according to formula (11);  $E_{B^-}$  is known from direct measurement. A straight line is obtained, from which  $K_2$  and  $E_{HB}$  are calculated; cf. Figs. 6a and 6b. The  $E_{HB}$ -values calculated are compared with those obtained from direct measurements (see above). The agreement is strikingly good.

Results:		$E_{HB}$	
$\lambda$ m $\mu$	$K_2 \times 10^{10}$	calc.	found
430	9.30	0.809	0.808
440	9.20	0.861	0.868
450	9.56	0.893	0.894
520	8.99	0.308	0.303
530	9.01	0.220	0.214
540	9.15	0.149	0.143

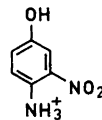
$$\text{Average value } K_2 = (9.2 \pm 0.2) \times 10^{-10}$$

### Summary

4-amino-2-nitrophenol  
(the positive ion of)



4-amino-3-nitrophenol  
(the positive ion of)



Protolytic constants:

$$K_1 = 2.5 \times 10^{-4}$$

$$K_2 = 2.6 \times 10^{-8}$$

$$K_1 = 6.3 \times 10^{-2}$$

$$K_2 = 9.2 \times 10^{-10}$$

## DISCUSSION

It is well known that the presence of the electronattracting  $\text{NO}_2$ -group in the benzene nucleus increases the acidity of protolytic substituents in the nucleus, and that this increasing effect is far more pronounced in the *ortho* (and *para*) than in the *meta* position.

Further it can be assumed that the mutual effects between the OH- and  $\text{NH}_2$ -groups do not essentially disturb the effect of the  $\text{NO}_2$ -group. Thus the constants determined could be compared with those of the corresponding nitroanilines and nitrophenols. As will be seen below such a comparison offers a possibility of determining the molecular structure of the aminonitrophenols.

The basicity constants of aniline, *o*-nitroaniline and *m*-nitroaniline are  $3.8 \times 10^{-10}$ ,  $1 \times 10^{-14}$ , and  $4 \times 10^{-12}$ , respectively\*. The acidity constants of the corresponding positive ions are thus  $2.6 \times 10^{-5}$ , 1, and  $2.5 \times 10^{-3}$ . The strong acidity-increasing effect of the  $\text{NO}_2$ -group is due to the fact that the inductive effect and the resonance effect operate in the same direction (see the formulas). Both effects are far more pronounced in the *ortho* than in the *meta* position. The same is true about the phenols. The acidity constants are  $1.3 \times 10^{-10}$ ,  $6.8 \times 10^{-8}$  and  $5.3 \times 10^{-9}$  for phenol, *o*-nitrophenol, and *m*-nitrophenol, respectively\*.

Thus by removing the  $\text{NO}_2$ -group from the *ortho* to the *meta* position in relation to the  $\text{NH}_3^+$ -group the acidity constant of the nitroanilinium ion is decreased by the factor  $4 \times 10^2$  and in agreement with this  $K_1$  is decreased from  $6.3 \times 10^{-2}$  to  $2.5 \times 10^{-4}$  *i.e.* by a factor of the same magnitude,  $2.5 \times 10^2$ .

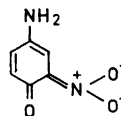
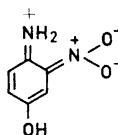
Correspondingly, when the  $\text{NO}_2$ -group is removed from the *ortho* to the *meta* position in relation to the OH-group, the acidity constant of the nitrophenol is decreased by the factor 13 and  $K_2$  by the factor 28 (from  $2.6 \times 10^{-8}$  to  $9.2 \times 10^{-10}$ ).

It is obvious that the values of the constants determined, together with their relationship to other corresponding constants make it probable that the first proton given off from the positive ion of the aminonitrophenol is that of the  $\text{NH}_3^+$ -group and the second that of the OH-group. This means that the aminonitrophenol molecule has practically no zwitter ion character contrary to the aliphatic amino carboxylic acids. The structure is principally that of BH and the constant  $K_a$  is very small. This conclusion is in accordance with the view earlier developed by N. Bjerrum<sup>11</sup>,\*\* The plain light extinction curves of the HB-forms (Figs. 1 and 4) also indicate that *one* of the forms BH or  $\text{B}^-\text{H}^+$  is quite predominating (> 95 %). If not, the curves would presumably have a more complicated course.

\* The values are from C. Noller, *Chemistry of Organic Compounds*. Second Edition, 1957. W. B. Saunders Company, Philadelphia.

\*\* Bjerrum's paper mainly concerns aliphatic amino carboxylic acids and the interpretation of their protolysis as acids and bases, respectively. But in addition he briefly noted the structures to be expected for some aromatic ampholytes.

A closer examination and discussion of the constants must be postponed until further results are available, which will presumably permit more and wider conclusions.



### Resonance structures

#### *4-amino-3-nitrophenol.*

Resonance mainly between the  $\text{NO}_2^-$ - and  $\text{NH}_2$ -groups. The inductive effect of the  $\text{NO}_2^-$ -group is electron attracting.

#### *4-amino-2-nitrophenol.* (negative ion $\text{B}^-$ )

Resonance mainly between the  $\text{NO}_2^-$ - and  $\text{O}^-$ -groups. The inductive effect of the  $\text{NO}_2^-$ -group is electron attracting.

The author's thanks are due to Dr. Stig Sunner, Head of the Thermochemistry Laboratory, University of Lund, for his kind interest in this work. Some of the syntheses were performed by Mrs. Brita Linderot, Lund. The author is indebted to Dr. Börje Holmberg, Malmö, for a careful revision of the English.

### REFERENCES

1. Hansson, H. G. *Svensk Kem. Tidskr.* **73** (1961) 131.
2. Hansson, H. G. *Acta Chem. Scand.* **13** (1959) 1309.
3. Hansson, H. G. *Acta Chem. Scand.* **14** (1960) 407.
4. Hansson, H. G. *Acta Chem. Scand.* **14** (1960) 2021.
5. Hansson, H. G. *Acta Chem. Scand.* **15** (1961) 69.
6. Noeltig, E., Grandmougin, E. and Michel, O. *Ber.* **25** (1892) 3328, p. 3338.
7. Frieländer, P. and Zeitlin, M. *Ber.* **27** (1894) 192.
8. Kehrmann, F. and Gauhe, E. *Ber.* **30** (1897) 2130.
9. Kehrmann, F. and Gauhe, E. *Ber.* **31** (1898) 2403.
10. Kehrmann, F. and Idskowska, M. *Ber.* **32** (1899) 1065.
11. Bjerrum, N. *Z. physik. Chem.* **104** (1923) 147.

Received March 20, 1962.