REACTIVITY OF ORGANIC AZO-COMPOUNDS. XIII.*

APPARENT DISSOCIATION CONSTANTS
OF 4-PHENYLAZO-1-NAPHTHOL DERIVATIVES
IN 50% (BY VOL.) ETHANOL

J.SCHREIBER, J.KULIČ, J.PANCHARTEK and M.VEČEŘA

   Department of Organic Chemistry,
   The Institute of Chemical Technology, Pardubice

Formerly we studied the influence of substituents on acid-base properties of some arylazo compounds, *viz.* o-phenylazophenol[1] and 1-phenylazo-2-naphthol[2,3] derivatives, *i.e.* compounds all of which have an intramolecular hydrogen bond. The substituent influence on the position of tautomeric equilibrium of such substances in aqueous-ethanolic solutions was negligible[4], and a good correlation between experimental pK_a values and σ constants could be found[5-7].

It seemed, therefore, interesting to study the substituent influence on acid–base properties of such substances where the intramolecular hydrogen bond could not be supposed, *e.g.* 4-phenylazo-1-naphthol derivatives: we have chosen a series of sixteen compounds of this type. It was found previously[4] that (especially *para-*) substituents on the benzene nucleus affect the position of tautomeric equilibrium considerably irrespective of solvent polarity.

In contrast to the previous series[1-3], the synthesis of 4-phenylazo-1-naphthol derivatives is complicated by a possibility of simultaneous formation of the respective 2-isomer eventually 2,4-bisazo dyestuff, too. The reaction course can be controlled by adjusting the pH of the reaction mixture[8-11]: 4-phenylazo-1-naphthols are formed predominantly at a pH 6—8.

Taking into account the physical and chemical properties of 4-phenylazo-1-naphthols and the possibility of comparison with the previous series results[1-3], we have chosen the spectrophotometric method of apparent dissociation constant determination[12] for evaluating the substituent influence on acid-base properties. The compounds of this series incline to molecular association which can be eliminated by lowering the concentration and by addition of ethanol to the solutions, eventually by increasing the temperature[13]. The estimation of the substituent influence on the position of tautomeric equilibrium has been based on literature data[14-17].

EXPERIMENTAL

Reagents

The amines used for preparation of the hydroxyazo compounds were either usual commercial samples or prepared by known methods[16-21]. As far as the respective nitro compounds were available, they were reduced with iron in ethanolic medium (except for p-nitroacetophenone which is only slightly soluble in ethanol and was reduced in methanol). The course of the reduction was followed chromatographically (Whatman paper No 3 impregnated with formamide; benzene as eluent). The amines dissolved in hydrochloric acid of appropriate concentration (according to the amine basicity) were diazotized by an addition of 1·05 equivalents of sodium nitrite at 0—5°C. The excess nitrous acid was removed by addition of amidosulfonic acid, and the diazo-

---

*   Part XII: This Journal **35**, 3551 (1970).

TABLE I
Physical Properties, Elemental Analyses and pK_a Values of the 4-(Arylazo)-1-naphthols Prepared

Substituent	M.p., °C		Molecular formula (mol. weight)	Calculated/Found			pK_a	$\sigma_0{}^d$	Analytical wavelength nm
	found	liter.[a]		% C	% H	% N			
H	206–208	205–206	$C_{16}H_{12}N_2O$ (248·2)	—	—	11·28 11·40	9·18 ± 0·02	0·00	490
m-CH₃	197–198	198–199 (decomp.)	$C_{17}H_{14}N_2O$ (262·3)	—	—	10·68 10·42	9·20 ± 0·03	−0·07	490
p-CH₃	214–215	207–208	$C_{17}H_{14}N_2O$ (262·3)	—	—	10·68 10·84	9·14 ± 0·02	−0·15	490
m-OCH₃	196–197	187–189	$C_{17}H_{14}N_2O_2$ (278·3)	—	—	10·06 10·21	9·09 ± 0·02	0·13	510
p-OCH₃	183	167–168 (decomp.)	$C_{17}H_{14}N_2O_2$ (278·3)	—	—	10·06 10·17	9·15 ± 0·02	−0·12	500
m-Cl	235–236	220–221 (decomp.)	$C_{16}H_{11}ClN_2O$ (282·7)	—	—	9·91 10·20	8·86 ± 0·03	0·37	510
p-Cl	249	230–231 (decomp.)	$C_{16}H_{11}ClN_2O$ (282·7)	—	—	9·91 10·20	8·89 ± 0·03	0·27	510
m-Br	227–228	211[b]	$C_{16}H_{11}BrN_2O$ (327·2)	58·73 58·61	3·39 3·48	8·56 8·42	8·83 ± 0·02	0·38	510
p-Br	248–250	227–229	$C_{16}H_{11}BrN_2O$ (327·2)	58·73 58·60	3·39 3·62	8·56 8·29	8·99 ± 0·02	0·26	510
p-I	241–243	—	$C_{16}H_{11}IN_2O$ (374·2)	51·35 51·57	2·96 3·21	7·47 7·22	8·91 ± 0·02	0·27	520
p-COCH₃	256–257	248–249[c]	$C_{18}H_{14}N_2O_2$ (290·3)	74·46 74·59	4·86 4·88	9·65 9·36	9·05 ± 0·02	0·46	540

	M.p.	M.p.	Formula (M.W.)	%C	%H	%N			λ
m-SO₂CH₃	222—224	—	$C_{17}H_{14}N_2O_3S$ (326·4)	62·56 / 62·22	4·32 / 4·48	8·58 / 8·42	8·60 ± 0·02	0·66[e]	520
p-SO₂CH₃	276—279	—	$C_{17}H_{14}N_2O_3S$ (326·4)	62·56 / 62·66	4·32 / 4·49	8·58 / 8·66	8·98 ± 0·02	0·69[e]	540
p-CN	254—256	—	$C_{17}H_{11}N_3O$ (273·3)	74·91 / 74·96	4·06 / 4·25	15·38 / 14·80	8·93 ± 0·02	0·69	540
m-NO₂	238	242—243	$C_{16}H_{11}N_3O_3$ (293·3)	65·97 / 66·04	3·80 / 3·92	14·43 / 14·28	8·55 ± 0·02	0·70	520
p-NO₂	279—280	282—283	$C_{16}H_{11}N_3O_3$ (293·3)	65·97 / 66·12	3·80 / 3·74	14·43 / 14·62	8·91 ± 0·02	0·82	600

[a] Ref.[17] if not otherwise stated; [b] ref.[23]; [c] ref.[24], [d] ref.[6] if not otherwise stated; [e] ref.[26].

nium salt solution was added to the 1-naphthol dissolved in 40% ethanol[8-10] kept at pH 6—8 by means of a phosphate buffer.

The raw dyestuffs were recrystallized from a benzene–ethanol mixture (1 : 1) and further purified chromatographically using an alumina column (activity 4 according to Brockmann) and a benzene–ethyl acetate mixture (3 : 2) as eluent. The 4-phenyl-azo-naphthols obtained were again twice recrystallized from a benzene–ethanol mixture (8 : 2) and dried in vacuum; the respective element·¹ analyses are given in Table I.

Determination of pK_a

Absorption electronic spectra of the compounds were measured by means of a spectrophotometer Unicam SP 800. The spectra of the molecular forms (in 0·05N aqueous ethanolic solution of hydrochloric acid), those of about 50 : 50 mixtures of ions and molecules (in the respective buffer solutions) and those of ions (0·05N-NaOH) form good isosbestic points.

After the determination of analytical wavelengths[12], the precise pK_a measurement was carr-
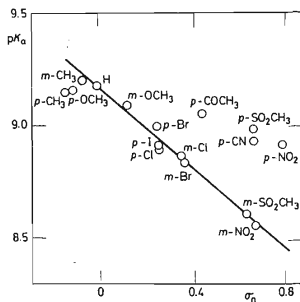

FIG. 1

Dependence of pK_a Values of 4-Phenylazo-1-naphthol Derivatives on σ_0 Substituent Constants

ied out by means of a Zeiss spectrophotometer VSU-1. Quartz cells 1—3 cm were used depending on solubilities of the compounds and their absorption intensities. The extinctions measured were used for the pK_a calculation directly because the analytic concentrations of solutions in hydrochloric acid, sodium hydroxide, and buffers were the same. Spectrum of the molecular form was used for estimation of the tautomeric mixture composition[4].

The pH values of solutions necessary for pK_a calculation were determined by means of a Precision pH-meter OP 205 using a G 200 c indication electrode and a saturated calomel reference electrode with agar bridge. The ionic strength 0·05 of the necessary buffer solutions[22] was adjusted by addition of ethanolic lithium chloride. Standard buffer solution in 50% ethanol was used for adjusting the pH-meter. The measurements were carried out at $25 \pm 0.2°C$.

Freshly prepared solutions of the dyestuff concentration 10^{-5} to 10^{-6} mol/l fulfil the Lambert-Beer law well. Extinctions of the molecular and wholly dissociated form did not change even after two hours, whereas the extinctions of the 50 : 50 mixtures of ions and molecules changed; the extinction of the least stable p-OCH$_3$ derivative dropped as early as 50 minutes after the preparation of the solution. Therefore, the experimental conditions were standardized in such a way that the measurements were carried out within 20 minutes after the preparation of the solution.

The reproducibility of the experimental pK_a values was verified in two ways: by a calculation at a wavelength near to the analytic one and by a parallel experiment. The experimental pK_a values are given in Table I together with further data.

The pK_a values found were compared with σ_0 constants (Fig. 1) which enables an appreciation of substituent influence on acid-base equilibria.

RESULTS AND DISCUSSION

From Fig. 1 it can be seen that a good correlation between pK_a values and substituent constants exists in the case of *meta*-derivatives only. For these substances a regression analysis gave the Eq. (1). p-Halogeno, p-methyl, and p-methoxy derivatives do not significantly deviate from this relationship, whereas the derivatives carrying p-CN, p-COCH$_3$, p-SO$_2$CH$_3$ or p-NO$_2$ group in the benzene nucleus behave anomalously.

$$pK_a = (9.18 \pm 0.02) - (0.87 \pm 0.03)\,\sigma_0\,, \tag{1}$$

$$n = 7\,; \quad s_{xy} = \pm\,0.05\,; \quad r_{xy} = -\,0.997\,.$$

Especially interesting is that these substances appear to be less acidic than they should be according to the Eq. (1) found for m-derivatives, and that they resemble in their acidity to the derivatives carrying p-substituents with negative σ constants in the benzene nucleus.

When studying the tautomeric equilibria of the compounds of this series[4], we found that they behaved differently from the compounds forming intramolecular hydrogen bonds.

The pronounced acidity decrease in the case of derivatives carrying such strongly acidifying substituents cannot be explained by a mere influence of polar substituent effects on acid-base properties of these compounds.

Therefrom it could be supposed that the abovementioned anomaly is caused by spectral properties of the compound studied, especially by the phenomena connected with a possible association. However, the validity of the Lambert–Beer law restricts the possibility of this disturbing influence considerably.

It is, therefore, more probable that this anomaly is rather connected with the changes of the tautomeric mixture composition, particularly with the increased amount of the quinonehydrazone form of the substances carrying the resonating substituents. We called attention to this problem previously[4].

With respect to the fact that the accuracy of determination of the content of tautomeric forms cannot be proved[4], and, especially, that the molar extinction coefficients of the both respective tautomers cannot be ascertained, we can support our explanation of the anomalies found in the 4-phenylazo-1-naphthol series by indirect evidence only. One piece of evidence is represented by the fact itself that this anomaly in comparing the abovementioned series with the ones previously studied[1-3] exists. As the solution of this problem is rather difficult, we intend to bring further indirect evidence in one of our next reports[25].

REFERENCES

1. Socha J., Horská J., Večeřa M.: This Journal *34*, 3178 (1969).
2. Schreiber J., Večeřa M.: This Journal *34*, 2145 (1969).
3. Haase J., Schreiber J., Štěrba V., Večeřa M.: This Journal *34*, 57 (1969).
4. Schreiber J., Socha J., Rothschein K.: This Journal *35*, 857 (1970).
5. Jaffé H. H.: Chem. Rev. *53*, 191 (1953).
6. Taft R. W. jr: J. Phys. Chem. *64*, 1805 (1960).
7. Van Bekkum H., Verkade P. E., Wepster B. M.: Rec. Trav. Chim. *78*, 815 (1959).
8. Ogoleva L. N., Stepanov B. T.: Ž. Org. Chim. *1*, 2083 (1965).
9. Ogoleva L. N., Stepanov B. T.: Ž. Obšč. Chim. *34* (6), 2171 (1964).
10. Banshio Y., Saito J., Yagi T.: J. Chem. Soc. Japan, Ind. Chem. Sect. *63*, 1597 (1960).
11. Zollinger H.: *Chemie der Azofarbstoffe*, Chapter 12. Birkhäuser, Basel, Stuttgart 1958.
12. Albert A., Serjeant E. O.: *Ionization Constants of Acids and Bases*. Wiley, London 1962.
13. Bubser W., Eichmans H.: Palette *20*, 20 (1965).
14. Kuhn R., Bär F.: Ann. *516*, 143 (1935).
15. Ospenson J. N.: Acta Chem. Scand. *4*, 1931 (1950).
16. Ospenson J. N.: Acta Chem. Scand. *5*, 491 (1951).
17. Shingu H.: Sci. Papers Inst. Phys. Chem. Res. (Tokyo) *35*, 78 (1938—9).
18. Becker H.: *Organikum*, p. 497. Deutscher Verlag der Wissenschaften, Berlin 1964.
19. Brewster R. Q.: *Organic Syntheses*, Coll. Vol. 2, p. 347. Wiley, New York 1943.
20. Hodgson H. H., Walker J.: J. Chem. Soc. *1933*, 1620.
21. Doran C. A.: J. Am. Chem. Soc. *51*, 2448 (1929).
22. Berčík J., Tölgyessy J.: *Potenciometria* 2. Ed., p. 94. Published by Slovenské vydavatelstvo technickej literatúry, Bratislava 1964.
23. Hewit J. T., Auld S. Y. M.: J. Chem. Soc. *81*, 176 (1902).
24. Hewit J. T., Mauri G. R., Pope F. G.: J. Chem. Soc. *105*, 2199 (1919).
25. Schreiber J., Kulič J., Kalfus K., Večeřa M.: This Journal, in press.
26. Cohen S. G., Streitwieser A. jr, Taft R. W.: *Progress in Organic Chemistry*, Vol. 2, p. 333. Interscience, Wiley, New York 1964.

Translated by J. Panchartek.