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THE ACIDITIES OF ARYLAZOFORMALDOXIMES. ELECTRONIC TRANSMISSION OF SUBSTITUENT EFFECTS THROUGH THE AZO GROUP

AHMAD S. SHAWALI* and BAHEEGA M. ALTAHOU
Department of Chemistry, Faculty of Science, University of Kuwait, State of Kuwait

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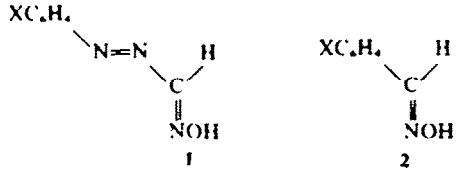
Abstract—A series of *para*- and *meta*-substituted phenylazoformaldoximes have been prepared and their acidities determined spectrophotometrically at 25.0 ± 0.1°C and μ of 0.10 in ethanol–water mixtures containing 1, 50 and 80 vol. % ethanol. The pK_a data obtained were linearly correlated with the Hammett substituent constant, σ_x. The variation with solvent of the reaction constant, ρ, was linear function of the solvent activity function, Y. The ρ value for the series studied in 99 vol. % water has been compared with that reported for the ionization of α-benzaldoximes. The results show that the azo bond transmits electronic effects approximately 1.5 times better than the ethylenic bond.

INTRODUCTION

Despite the many uses of the compounds containing the azo functional group as azo dyes and sources of free radicals,[1] the electronic nature of such a group has received little attention. Recently the Hammett substituent constants, σ, σ^- and σ^+, for the *p*-phenylazo group were reported.[1] In an attempt to clarify the azo bond's capability as a transmitter of electronic effects, we have prepared a series of twelve ring substituted phenylazoformaldoximes (**1a–1l**) and measured their acid dissociation constants, pK_a's, in ethanol–water mixtures at 25.0 ± 0.1°C and at ionic strength of 0.10. The results were compared with those of α-benzaldoximes **2**.[2]



1

2

a: X = 4-MeO **b**: X = 4-EtO **c**: X = 4-Me **d**: X = 3-Me **e**: X = H **f**: X = 4-Cl **g**: X = 4-Br **h**: X = 3-Cl **i**: X = 3-Br **j**: X = 4-EtOOC **k**: X = 4-CH_3CO **l**: X = 3-NO_2

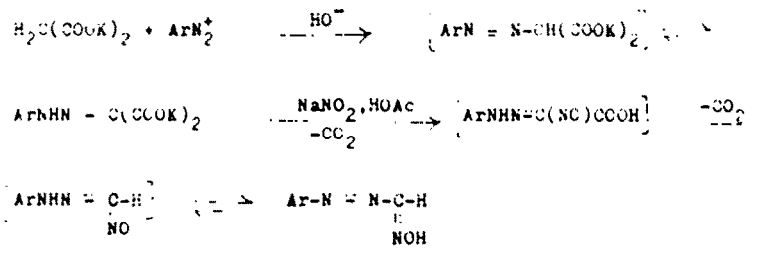
RESULTS AND DISCUSSION

The arylazoformaldoximes **1a–l** have not yet been reported except the unsubstituted compound **1e**. All compounds were prepared in a rigorously similar manner, by coupling diazotized anilines to potassium malonate in presence of sodium nitrite. It is assumed that the reaction follows the sequence presented in Scheme 1. The properties of the compounds thus prepared are listed in Table 1.

Inspection of the spectra (UV, PMR and IR) of these compounds revealed that such compounds have the azooxime structure (AO); no evidence for the tautomeric nitrosohydrazone form (NH) could be obtained. For example, the electronic absorption pattern of **1a–l** in ethanol was characterized, in each case, by two bands: a weak $n - \pi^*$ maximum near 430 nm ($\log \varepsilon < 3$) and an intensive $\pi - \pi^*$ band near 300 nm ($\log \varepsilon > 4$) (Table 2). Such a pattern is similar to that of *trans*-azobenzene: λ_{max}^{EtOH} nm (log e) 445 (2.48); 3.19 (4.29).[4,5] In addition, the absorption pattern of **1** in the UV region was nearly independent of the nature of the solvent, indicating that only one tautomer is present in the solution phase.

The PMR spectra of **1a–l** in chloroform-*d* were also compatible with the azooxime structure (AO). Thus each compound exhibits two singlets in the regions 8.5–8.8 and 9.0–11.0 ppm assignable to the methine CH and oxime NOH protons respectively, Table 2. The NOH PMR signal disappeared upon shaking the solution with D_2O.

The azooxime structure for **1a–l** is further supported by their vibrational spectra. For example, in the solid state and in solution each compound exhibited an intense and somewhat broad band (width at half height ~30 cm^{-1}), similar to that of $\bar{\nu}_{N-O}$ for simple oximes,[6] in the region 1000–1050 cm^{-1}. The high frequency position



NH-form AO-form

Scheme 1

Table 1. Arylazoformaldoximes[a]

Compound No.	Mp. (°C)	Molecular formula	C,% Found	C,% Calcd.	H,% Found	H,% Calcd.	N,% Found	N,% Calcd.
1a	138–9	$C_8H_9N_3O_2$	53.80	53.62	5.09	5.06	23.28	23.45
b	120	$C_9H_{11}N_3O_2$	55.85	55.95	5.77	5.74	21.94	21.75
c	135–6	$C_8H_8N_4O$	55.84	58.88	5.72	5.56	26.28	25.75
d	88–9	$C_8H_8N_4O$	58.72	55.88	5.65	5.56	25.62	25.75
e	94[b]	$C_7H_7N_3O$						
f	140–41	$C_7H_6ClN_3O$	45.77	45.79	3.42	3.29	22.98	22.88
g	148	$C_7H_6BrN_3O$	36.84	36.86	2.99	2.65	18.16	18.42
h	130	$C_7H_6ClN_3O$	45.66	45.79	3.39	3.29	22.95	22.88
i	124	$C_7H_6BrN_3O$	36.92	36.86	2.70	2.65	18.53	18.42
j	115	$C_{10}H_{11}N_3O_3$	54.18	54.29	4.99	5.01	19.00	18.99
k	160	$C_9H_9N_3O_2$	56.54	56.54	4.79	4.74	22.09	21.98
l	160–61	$C_7H_6N_4O_3$	43.29	43.22	3.14	3.11	28.74	28.94

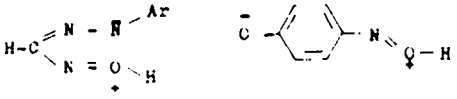
[a]All compounds were crystallized from dilute methanol except **1b** from benzene–ligroin and **1f** from cyclohexane.
[b]Ref. 3 m.p. 94°C.

Table 2. Spectral characteristics of arylazoformaldoximes

Compound	λ_{max}^{EtOH} nm (log ε)	δ* ($CDCl_3$) (ppm)	ν (KBr) (cm^{-1})
1a	430(2.00), 340(4.41)	9.70(s); 8.67(s); 4.0(s); 8.0(d); 7.0(d)	3300–3100, 3060, 1030
b	430(2.03), 348(4.37)	9.67(s), 8.53(s), 4.0(q) 1.4(t), 7.0(d), 8.0(d)	3400–3050, 1020
c	422(2.68), 322(4.41)	9.53(s), 9.0(s), 2.46(s), 7.53(d), 8.1(d)	3400–3100, 1015
d	422(1.51), 312(4.30)	9.6(s), 8.4(s), 7.0–8.0 (m)	3200, 3060, 1030
e	426(2.53), 310(4.38)	9.67(s), 8.8(s), 7.0–8.0 (m)	3400–3000, 1010
f	420(2.59), 318(4.34)	9.8(s), 8.83(s), 7.53 (d), 8.06(d)	3400–3200, 1005
g	420(2.77), 322(4.49)	9.9(s), 8.53(s), 7.5(d) 8.0(d)	3400–3300, 1010
h	430(2.66), 307(4.33)	9.8(s), 8.6(s), 7.0–8.0 (m)	3400–3100, 3080, 1020
i	430(2.73), 307(4.48)	9.85(s), 8.53(s), 7.0–8.0(m)	3100–3400, 1020
j	440(2.76), 315(4.39)	9.6(s), 8.33(s), 7.0–8.0(m), 1.33(t), 4.27(q)	3400–3100, 1020, 1700
k	450(2.69), 320(4.43)	9.67(s), 8.33(s), 2.6(s), 7.0(d), 7.7(d)	3100–3200, 1680, 1040
l	430(2.62), 302(4.35)	11.53(s), 8.33(s), 7.0–8.0(m)	3500–3300, 1020

*(multiplicity): s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

of $\bar{\nu}_{N-O}$ of **1a–l** as compared with that of hydroxylamine ($\bar{\nu}_{NO}$ 912 cm^{-1}) and its *N*-alkyl derivatives ($\bar{\nu}_{N-O}$ 950 cm^{-1}) might be considered to result from the contribution of the resonance structure type **3** by analogy to the case of quinone monoxime **4**.[7]



3 **4**

Furthermore, the IR spectra of **1a–l** in the solid state showed the presence of broad band due to the bonded OH group in the region 3200–3500 cm^{-1}. The solution phase of **1** revealed an additional band near 3580 cm^{-1} assignable to a free OH stretch. Clearly this pattern is parallel to that shown by aldoximes and quinone monoximes.[6,8] The foregoing spectral evidences taken collectively leave no doubt that the predominant form of the compounds studied is the azo oxime structure (AO).

The acid dissociation constants for **1a–l** were determined by a spectrophotometric titration method at 25.0 ± 0.1°C in 1, 50 and 80 vol % ethanol–water mixtures. In all determinations the ionic strength was kept constant at 0.10. At pH < 7 in a given solvent, each compound exhibited an intensive $\pi - \pi^*$ band near 310 nm. In alkaline medium the ambident anion of **1**, NC(NO⁻)N:NAr ↔ HC(N:O):NN⁻Ar, showed an intensive $\pi - \pi^*$ band in the region 325–400 nm. Spectra recorded at different pH values showed an isosbestic point near 325 nm (Fig. 1). The absorbance values of freshly prepared solutions measured at λ_{max} of the anion plotted against pH showed a dependence in the shape of a dissociation curve of a monobasic acid. From the pH-absorbance data, the pK_a values for **1a–l** were cal-

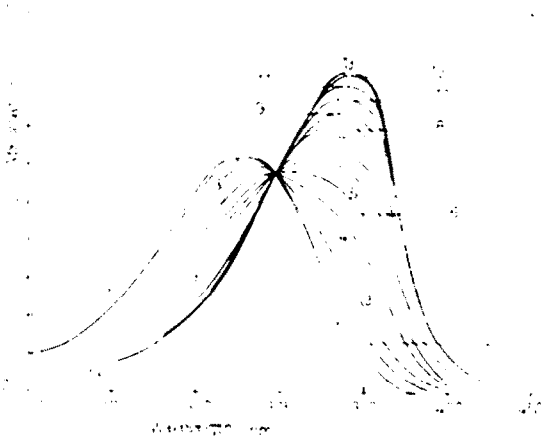


Fig. 1. Absorption spectra of phenylazoformaldoxime **1e** at different pH values. [**1e**] 3.09×10^{-5}M in 1 vol% ethanol-water at 25°C and μ 0.10. (Run no.) pH: (1) 6.20; (2) 7.52; (3) 8.24; (4); (4) 8.49; (5) 8.69; (6) 8.82; (7) 9.04; (8) 9.20; (5) 9.42; (10) 9.71; (11) 10.03; (12) 10.72; (13) 11.27.

culated. At least two independent runs were conducted for each compound. The pK_a values were reproducible to ± 0.02 pK units in different titrations, and the average values thus obtained are listed in Table 3.

Figure 2 demonstrates that the acidities of arylazoformaldoximes could be correlated with the Hammett substituent constant, σ_x. The results of statistical analysis by the least squares method are given in Table 4. As is shown in the latter Table, the ρ values for such correlations were negative indicating that electron withdrawing substituents increase the acidity of **1** or decrease the basicity of the azooxime anion.

The variation of pK_a with solvent is usually expressed $\Delta = pK_a$ (mixed solvent)—pK_a (water).[9] In the present study, the pK_a values determined for **1** in 1 vol % ethanol-water mixture were considered to be approximately equivalent to their pK_a values in water. Variations in the differences, Δ, in each individual solvent composition are relatively small (Table 3), indicating that ionization of different substituted phenylazoformaldoximes is almost equally influenced by the change in solvent composition. However, the ratio of Δ in 80 vol. % ethanol to that in 50 vol. % ethanol is almost 2.5. This suggests that the stabilization of the anion of **1** decreases with increasing the ethanol content.

Table 3. pK_a Values for arylazoformaldoximes in ethanol-water mixtures at 25.0 ± 0.1°C and μ of 0.10

Compound	σ_x	1% EtOH	50% EtOH		80% EtOH	
		pK_a	pK_a	Δ	pK_a	Δ
1a	−0.27	8.70	9.23	0.53	9.95	1.25
b	0.24	8.67	9.21	0.54	9.88	1.21
c	−0.17	8.60	9.14	0.54	9.85	1.25
d	0.07	8.56	9.08	0.52	9.73	1.17
e	0.00	8.48	9.01	0.53	9.69	1.20
f	0.23	8.44	8.82	0.38	9.50	1.06
g	0.23	8.41	8.83	0.42	9.49	1.08
h	0.37	8.27	8.70	0.43	9.39	1.12
i	0.39	8.33	8.68	0.35	9.33	1.03
j	0.45	8.22	8.67	0.45	9.25	1.02
k	0.50	8.21	8.60	0.39	9.24	1.03
l	0.71	8.10	8.45	0.35	9.06	0.95

Table 4. Results of statistical treatment using σ_x constants

% EtOH	Y [a]	ρ [b]	sρ [c]	pK_a^H	s_a [d]	n [e]	r [f]
1	0.00	0.596	0.029	8.52	0.031	12	0.988
50	0.686	0.806	0.012	9.01	0.013	12	0.998
80	0.941	0.895	0.016	9.69	0.018	12	0.998

[a]Solvent activity function defined by $(1 - x^2)$ where x is the mole fraction of water;[12] [b]reaction constant; [c]standard deviation in ρ; [d]standard deviation in pK_a^H; [e]number of points; [f]correlation coefficient.

Fig. 2. Correlation of pK_a of arylazoformaldoximes with substituent constant, σ_x, in different ethanol-water mixtures at 25°C and μ 0.10. ○, 80 vol.% EtOH; ◑ 50 vol.% EtOH; △, 1 vol.% EtOH.

The effect of solvent on pK_a of **1** can be discussed in terms of effects on the susceptibility to substituent effects. The value of the reaction constant, ρ, appears to depend on the ethanol concentration (Table 4). The structural dependence for various water–ethanol mixtures is thus represented by a set of nonparallel lines (Fig. 2). Provided that the influence of the ethanol-water composition on the reaction involving the ionization of =NOH group of **1** can be characterized by any parameter, Y_i, application of the relation: $\rho_i - \rho_o = C(Y_i - Y_o)$ would indicate that the value of C (0.638 for benzoic acid[9] and 0.573 for aniline[10]) is close to 0.30 for arylazoformaldoximes.

The acidities of α-benzaldoximes in water at 25°C were reported[2] to be correlated by the equations, $pK_a = 10.69 - 0.857\sigma_x$. The higher acidity of **1** in aqueous solution containing 1% by volume ethanol as compared with that of **2** can be raionalized in terms of the –I–M electronic character of the arylazo group[1] and the enhanced resonance stabilization of the anion of **1**. If the transmission factor, π', of substituent effects for the azo group is calculated according to the relation $\pi' = \rho_1/\rho_2$ where ρ_1 and ρ_2 are the reaction constants for the ionization of phenyalzoformaldoximes and benzaldoximes respectively, a value of 0.689 is obtained. Comparing this value with that reported for the ethylenic bond ($\pi'_{C=C} = 0.466$)[2] we observe that substituent effects are transmitted by the azo link approximately 1.5 times better than are by the C=C bond. This difference between

the azo and ethylenic links may be due to the enhanced electronegativity of the nitrogen containing group.

If we use in the equation $\pi'(1,4\text{-}C_6H_4N{=}N\text{-}) = \pi'(1,4\text{-}C_6H_4\text{-}) + \pi'(N{=}N)$ the value of $\pi'(N{=}N)$ determined in this work and the value of 0.126 of $\pi'(C{=}N)$ determined in this work and the value of 0.126 $\pi'(1,4\text{-}C_6H_4N{=}N\text{-})$ reported earlier[2], a value of 0.183 is obtained for $\pi'(1,4\text{-}C_6H_4)$. This value compares favourably with the value 0.177 calculated for the 1,4-phenylene bridge.[2]

EXPERIMENTAL

M.ps are uncorrected. IR spectra were recorded on a Pye-Unicam SP1000 spectrophotmeter. Electronic absorption spectra were measured on a Pye-Unicam SP8000 spectrophotometer. Elemental analyses were performed by Alred Bernhardt, Mikroanalytische chemie Laboratorium, West Germany. Potentiometric measurements were carried out on a Radiometer pH meter type 63 fitted with a combined glass electrode type GK2301C. The instrument was accurate to ±0.01 pH unit. It was calibrated using two standard Beckman buffers of pH 4.01 and 7.00 ± 0.01. The pH meter readings (B) recorded in ethanol-water solutions were converted to hydrogen ion concentration [H^+] by means of the widely used relation.[11] $-\log[H^+] = B + \log U_H$, where $\log U_H$ is the correction factor for the solvent composition and ionic strength for which B is read. For this purpose, readings were made on a series of solutions containing known amounts of HCl and NaCl such that μ was 0.10. The values of $\log U_H$ in 50 and 80 vol. % ethanol–water mixtures at 25.0 ± 0.1°C were found to be −0.25 and −0.40 respectively. The value of $\log U_H$ in 1 vol. % ethanol–water was within the accuracy limits of the pH meter, and thus neglected.

Preparation of arylazoformaldoximes

A *meta*- or *para*-substituted aniline (0.1 mol) was diazotized in the usual way and the diazonium salt solution was added to a cold solution of acetic acid (12 g) and sodium acetate (8 g) in water (50 ml). The resulting solutin was added dropwise during 1 hr, while stirring, to a cold (0–5°C) solution of potassium malonate (prepared by dissolving malonic acid (0.1 mol) and potassium hydroxide (15 g) in 250 ml water) containing sodium nitrite (7.5 g). After the addition was complete, stirring was continued for 3 hr at 0°C and the reaction mixture was left overnight in an ice box. The crude solid that precipitated was collected and dissolved in sodium carbonate solution, filtered and the filtrate was extracted with ether. On acidification of the aqueous layer with dil. H_2SO_4, the arylazoformaldoxime precipitated. It was collected, dried and finally crystallized from dil. MeOH. The compounds prepared, their m.ps and analytical data are listed in Table 1.

pK_a Determination

A 50 ml solution of the appropriate arylazoformaldoxime was prepared such that it was $\sim 5.0 \times 10^{-5}$ M with respect to the azooxime, 0.1 M HCl and contained 1, 50 or 80 vol % ethanol. The test solution was transferred to an water-jacketed thermostated cell. The pH of the solution was then measured and the spectrum was recorded using either the ionic medium or the corresponding aq. EtOH as a blank. In both cases identical absorbance values in the wavelength range employed were obtained. The pH of the test solution was then increased by addition of small volume of concentrated carbonate free sodium hydroxide solution made up from the same solvent. Since the total change in volume did not exceed 1%, no correction was made for dilution. After each spectral measurement, the pH was checked and in all cases, the two values before and after the spectral measurements were found to be the same within the limits of the accuracy of the pH meter. Figure 1 shows the collected spectra of **1e**, taken as a typical example of the series, at different pH values. In each run 10–15 pH readings were taken and the value of pK_a was calculated from each reading using the relation. $pK_a = pH + \log(A_\infty - A_i)/(A_i - A_\infty)$, where A_i is the absorbance of the test solution at pH, and A_∞ and A_∞ are the absorbance values of the strongly alkaline and acid solutions of **1** respectively. Each compound was subjected to three pK_a determinations, and the average values, given in Table 3, are within ±0.01–0.03 pK unit.

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