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Structure and Stability Relationship of 1,1-Dimethyl-2-[β-(α-aroylstyryl)]hydrazine Derivatives

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Aroylphenylacetylenes (I) reacted with N,N-dimethylhydrazine (II) to give 1,1-dimethyl-2-[β-(α-aroylstyryl)]hydrazine (III). The structure and configuration of the products are based on chemical and spectroscopic evidence.

The protonation constants of these compounds were calculated in 60 wt % dimethylformamide–water media. The effects of substituents on the protonation equilibria are discussed. The log β values were linearly correlated with Hammett substituent constant. The equation of the straight line: $\log \beta = (-0.52 \pm 0.049)\sigma + (3.86 \pm 0.02)$.

Keywords——1,1-dimethyl-2-[β-(α-aroylstyryl)]hydrazine; β-diketones; synthesis; protonation constant; linear free energy relationship

Introduction

The reactions of acetylenic ketones with amines,[2–7] hydrazine,[8–10] monosubstituted hydrazine, N,N-dimethylhydrazine, N-methyl-N′-phenylhydrazine,[11,12] as well as ethyl- and phenyl-hydrazinecarboxylate[13] have been reported. The present investigation was intended to study the reaction of aroylphenylacetylenes (I) with N, N-dimethylhydrazine (II) and to account for the manipulated methods and reasoning in establishing the mechanism of this reaction as well as the structure and configuration of the products. The protonation constants of these compounds were also calculated.

Experimental

Preparation of Aroylphenylacetylenes (Ia—f)

Aroylphenylacetylenes (Ia—f) were prepared from the corresponding aldehydes according to the method outlined by Parker, *et al.*[14] Benzoylphenylacetylene (Ia), mp 49—50°;[15] yield, 86%; *p*-toluylphenylacetylene (Ib), mp 71—72°;[16] yield, 86%; *m*-chlorobenzoylphenylacetylene (Ic), mp 90—91°;[17] yield, 80%; *p*-chlorobenzoylphenylacetylene (Id), mp 107—108°;[10] yield, 86%; *p*-methoxybenzoylphenylacetylene (Ie), mp 99—100°:[2] yield, 92%; *p*-nitrobenzoylphenylacetylene (If), mp 161—162°;[16] yield, 88%.

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1,1-Dimethyl-2-[β-(α-aroylstyryl)]hydrazine (IIIa—f)

General Procedure——A mixture of the aroylphenylacetylene (I) (0.015 mol) and N,N-dimethylhydrazine (2 ml) in EtOH (50 ml) was refluxed on a boiling water-bath for 5 hr. Evaporation of the alcohol, left a residual yellow solid which was crystallized from a suitable solvent to give the corresponding 1,1-dimethyl-2-[β-(α-aroylstyryl)]hydrazine (III) as yellow crystals. The results are reported in Table I.

TABLE I. 1,1-Dimethyl-2-[β-(α-aroylstyryl)]hydrazine (IIIa—f)

Compound	Yield (%)	mp[a] (°C)	Formula	Analysis (%) Calcd. C	H	N	Cl	Found[b] C	H	N	Cl
IIIa	92	114—115[c]	$C_{17}H_{18}ON_2$	76.66	6.81	10.52		76.71	6.75	10.42	
IIIb	96	138—139[d]	$C_{18}H_{20}ON_2$	77.11	7.19	9.99		77.32	7.41	10.11	
IIIc	89	58— 59[c]	$C_{17}H_{17}ON_2Cl$	67.88	5.70	9.31	11.79	68.10	5.81	9.23	12.02
IIId	83	128—129[d]	$C_{17}H_{17}ON_2Cl$	67.88	5.70	9.31	11.79	67.62	5.62	9.10	11.92
IIIe[e]	78	99—100[f]	$C_{18}H_{20}O_2N_2$	72.95	6.80	9.45		73.15	6.87	9.61	
IIIf	96	170—171[g]	$C_{17}H_{17}O_3N_3$	65.58	5.50	13.50		65.91	5.72	13.55	

a) Melting points are uncorrected.
b) Microanalyses were determined by Alfred Bernhardt, West Germany.
c) crystallized from cyclohexane
d) crystallized from methyl alcohol
e) OCH_3%: Calcd. for =10.47; Found=10.23
f) crystallized from petroleum ether (40—60°)
g) crystallized from benzene–methyl alcohol

Reaction of N,N-Dimethylhydrazine with Dibenzoylmethane——A mixture of the dibenzoylmethane (0.015 mol) and N,N-dimethylhydrazine (4 ml) was heated on a boiling water-bath for 10 hr. The product was crystallized from petroleum-ether (40—60°) to give 1,1-dimethyl-2-[β-(α-benzoylstyryl)]hydrazine (IIIa) as yellow crystals, mp and mixed mp 114—115°, yield, 82%.

Hydrolysis of 1,1-Dimethyl-2-[β-(α-aroylstyryl)]hydrazine (III) to the corresponding β-Diketone (VII)——A mixture of the hydrazine derivative (III) (0.5 g) and 30% H_2SO_4 (15 ml) was heated under reflux for 30 min. The reaction mixture was then cooled and the precipitated solid was crystallized from petroleum-ether (40—60°) to give the corresponding β-diketones (VIIa) and (VIIc) as colorless crystals. Authentic specimens of (VIIa, c) were prepared from the reaction of acetylenic ketone with 30% H_2SO_4 under the above mentioned conditions. Dibenzoylmethane (VIIa), mp and mixed mp 79—80°; yield, 97%, *m*-chlorodibenzoylmethane (VIIc), mp and mixed mp 71—72°; yield, 98%.

Infrared (IR) spectra were recorded using a pye–Unicam Sp 1000 and Beckman IR 12 Spectrophotometers (KBr). Electronic spectra were taken on a pye–Unicam Sp 8000 spectrophotometers. The instrument was calibrated as previously described.[18]. Nuclear magnetic resonance (NMR) spectra were measured on a Varian T-60A spectrometer using tetramethylsilane as internal standard.

A radiometer pH-meter model 63 fitted with a combined glass electrode type GK 2301 C was used for determination of pH. The instrument was accurate to ±0.01 pH unit. It was calibrated using two standard Radiometer buffer solutions at pH 4.01 and 7.00. The pH meter readings (B) recorded in 60 wt % dimethylformamide–water solutions were converted to hydrogen ion concentration [H⁺] by means of the widely known relation of Van Uitert and Haas,[19]

$$-\log[H^+] = B \pm \log U_H \qquad (1)$$

where U_H is the correction factor for the solvent composition and ionic strength for which β is read. For this purpose, readings were made on a series of solutions containing known amounts of hydrochloric acid and sodium chloride such that the ionic strength is equal to 0.10 in 60 wt % dimethylformamide–water medium. The intercept, obtained from the linear plot of pH *vs.* β, corresponding to log U_H was found equal to 0.30±0.01 at 25°.

For spectrophotometric determination of the dissociation constants of compounds (III), an aliquot of the stock solution, made by dissolving a known weight of 1,1-dimethyl-2-[β-(α-aroylstyryl)]hydrazine (III) in dimethylformamide to give an 1.0×10^{-2}M solution, was diluted with aqueous hydrochloric acid and dimethylformamide. The final solution contains accurately about 4.0×10^{-5}M of the compound (III), and 0.10M HCl in 60 wt % dimethylformamide–water. The absorption spectra of the solution (at constant temperature of

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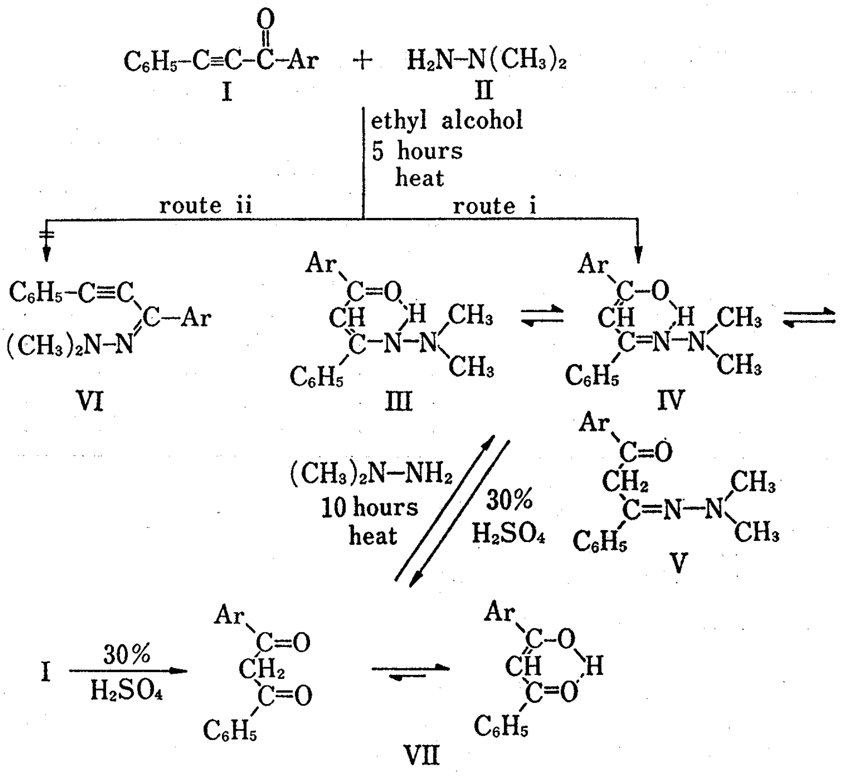
25°) were then taken at different pH's by adding carbonate free sodium hydroxide and/or hydrochloric acid in small amounts. Since the total change in volume did not exceed 1.0%, no correction was made for the concentration of the compounds. The ionic strength was kept constant at 0.10 M HCl/NaCl.



a: Ar=$C_6H_5\cdot$ b: Ar=p-$CH_3\cdot C_6H_4\cdot$
c: Ar=m-$Cl\cdot C_6H_4$ d: Ar=p-$Cl\cdot C_6H_4\cdot$
e: Ar=p-$CH_3O\cdot C_6H_4\cdot$ f: Ar=p-$NO_2\cdot C_6H_4\cdot$

Chart 1

Results and Discussion

When benzoyl-(Ia), *p*-toluyl-(Ib), *m*-chlorobenzoyl-(Ic), *p*-chlorobenzoyl-(Id), *p*-methoxybenzoyl-(Ie) and *p*-nitrobenzoyl-(If)-phenylacetylenes were refluxed with N,N-dimethylhydrazine (II) in ethanol, they gave the corresponding 1,1-dimethyl-2-[β-(α-aroylstyryl)]hydrazine (III). The reaction seems to proceed by Michael addition of N,N-dimethylhydrazine to the triple bond of acetylenic ketone [*cf.* Chart 1; route (i)] leading ultimately to the product (III). This mechanism is similar to that reported for the reaction of primary and secondary amines with acetylenic ketones[2-7].

The structure and configuration of the reaction products (III) were established by both spectroscopic and chemical evidence.

(i) Spectroscopic Evidence for the Structure of 1,1-Dimethyl-2-[β-(α-aroylstyryl)]hydrazine (III)

The infrared spectra of these compounds (Table II) were devoide of $\nu_{C\equiv C}$ which excluded the existence of structure (VI), formed by route (ii) (*cf.* Chart 1). It is noteworthy to mention that the product can exist in three tautomeric forms (III, IV and V) (*cf.* Chart 1).[20,21] However, by using TLC the product proved to be homogeneous (*i. e.* only one component).

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[20] H.F. Holtzclam, J.P. Collman, and R.M. Alire, *J. Am. Chem. Soc.*, **80**, 1100 (1958).
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Table II. Physical Data for Compounds (IIIa—f)

Compound	NMR ($CDCl_3$)		Infrared spectra (KBr)	
	δa)	Assignments (No. of protons)	cm^{-1} b)	ν
IIIa	11.78 (s)	(1) $\mathrm{C{=}O\cdots\underline{H}{-}N}$c)	1590(s)	$\mathrm{C{=}O\cdots H}$
	8.27—6.73(m)	(10) $\mathrm{Ar\underline{H}}$	1580(s)	$\mathrm{C{=}C}$
	5.75 (s)	(1) $\mathrm{{-}C\underline{H}{=}}$	1570(s)	
	2.47 (s)	(6) $\mathrm{{-}N(C\underline{H}_3)_2}$	in $CHCl_3$	
			1596(s)	$\mathrm{C{=}O\cdots H}$
			1587(s)	$\mathrm{C{=}C}$
			1570(s)	
IIIb	11.76 (s)	(1) $\mathrm{C{=}O\cdots\underline{H}{-}N}$c)	1593(s)	$\mathrm{C{=}O\cdots H}$
	8.0—7.1 (m)	(9) $\mathrm{Ar\underline{H}}$	1570(s)	$\mathrm{C{=}C}$
	5.73 (s)	(1) $\mathrm{{-}C\underline{H}{=}}$		
	2.53 (s)	(6) $\mathrm{{-}N(C\underline{H}_3)_2}$		
	2.38 (s)	(3) $\mathrm{Ar{-}C\underline{H}_3}$		
IIIc	11.87 (s)	(1) $\mathrm{C{=}O\cdots\underline{H}{-}N}$c)	1595(s)	$\mathrm{C{=}O\cdots H}$
	8.07—7.47(m)	(9) $\mathrm{Ar\underline{H}}$	1570(s)	$\mathrm{C{=}C}$
	5.70 (s)	(1) $\mathrm{{-}C\underline{H}{=}}$	1560(s)	
	2.50 (s)	(6) $\mathrm{{-}N(C\underline{H}_3)_2}$		
IIId	11.80 (s)	(1) $\mathrm{C{=}O\cdots\underline{H}{-}N}$c)	1592(s)	$\mathrm{C{=}O\cdots H}$
	8.00—7.33(m)	(9) $\mathrm{Ar\underline{H}}$	1578(s)	$\mathrm{C{=}C}$
	5.72 (s)	(1) $\mathrm{{-}C\underline{H}{=}}$		
	2.53 (s)	(6) $\mathrm{{-}N(C\underline{H}_3)_2}$		
IIIe	11.53 (s)	(1) $\mathrm{C{=}O\cdots\underline{H}{-}N}$c)	1590(s)	$\mathrm{C{=}O\cdots H}$
	8.13—6.8 (m)	(9) $\mathrm{Ar\underline{H}}$	1578(s)	$\mathrm{C{=}C}$
	5.72 (s)	(1) $\mathrm{{-}C\underline{H}{=}}$		
	3.77 (s)	(3) $\mathrm{Ar{-}OC\underline{H}_3}$		
	2.53 (s)	(6) $\mathrm{{-}N(C\underline{H}_3)_2}$		
IIIf	12.00 (s)	(1) $\mathrm{C{=}O\cdots\underline{H}{-}N}$c)	1580(s)	$\mathrm{C{=}O\cdots H}$
	8.53—7.33(m)	(9) $\mathrm{Ar\underline{H}}$	1560(s)	$\mathrm{C{=}C}$
	5.73 (s)	(1) $\mathrm{{-}C\underline{H}{=}}$	1520(s)	NO_2
	2.57 (s)	(6) $\mathrm{{-}N(C\underline{H}_3)_2}$		

a) abbreviation: s=singlet; m=multiplet
b) abbreviation: s=strong
c) exchanged with D_2O

Further insight concerning the exact structure of the reaction product may be gleaned out from the consideration of the spectral data. The IR spectra showed no absorption in the region around 1700 cm^{-1}, the free carbonyl group, and hence structure (V) was ruled out.[20] The presence of strong bands at 1595—1580 cm^{-1} and 1580—1560 cm^{-1} as well as the absence of any absorption in the region 4000—3100 cm^{-1} indicated that these compounds are present in chelated forms (III) or (IV)[20,22,23] in which the ν_{NH} or ν_{OH} absorption may be lowered by hydrogen bonding and lie masked under the C–H absorption.[23] The spectrum of IIIa, in chloroform solution, shows only a strong band at 1596 cm^{-1}, which is in good agreement with the suggested strong intramolecular (chelate) hydrogen bonding system.[24] The electronic spectra of compounds (IIIa—f) (60 wt% dimethylformamide–water solution at pH $>$6.0) are very similar (*cf.* Table III) and show two absorption bands in the ranges 348—380 nm and 261—268 nm[4] indicating their structural analogy. The wavelengths and the intensities of these bands are not changed by increasing the pH of the solution above 6.0. This is possibly accounted for by the fact that these compounds exist in the ketamine form (III).

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22) L.J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1966, p. 144.

23) N.H. Cromwell, F.A. Miller, A.R. Jonson, R.L. Frank, and D.J. Wallace, *J. Am. Chem. Soc.*, **71**, 3337 (1949).

24) R.D. Campbell and H.M. Gilow, *J. Am. Chem. Soc.*, **82**, 5426 (1960).

TABLE III. Electronic Spectra for Compounds (IIIa—f) in 60 wt% Dimethylformamide–Water Mixture at pH>6.0

Compound	λ_{max}	$\varepsilon \times 10^{-4}$	λ_{max}	$\varepsilon \times 10^{-3}$
IIIa	349	2.00	263	7.63
IIIb	352	1.94	263	9.35
IIIc	355	1.94	261	8.53
IIId	348	2.15	262	12.60
IIIe	356	2.30	268	11.59
IIIf	380	1.52	268	15.00

Confirmation of the above conclusion is forthcoming from the NMR spectra of the products (IIIa—f) ($CDCl_3$) (Fig. 1 for IIIa) (*cf.* Table II). They show a signal in the regions δ 12—11.53(NH), which disappeared when the deuteriochloroform solution was shaken with D_2O.[21] The position and the integration of the (NH) signal do not change by dilution. The above spectra show other signals in the regions δ 5.75—5.70 (s, 1, =CH–)[21] and δ 2.57— 2.47[s, 6, $N(CH_3)_2$].[25] The appearance of an NH signal and the absence of any signal which can be assigned to the ($-CH_2-$) group give a further support to the exclusion of structure (V). The chemical shifts of the (–CH=) group show almost the same values (*cf.* Table II) in all the hydrazine derivatives (IIIa—f) indicating that this group is not affected by the different substituents, a fact which can be only accounted for on the basis of structure (III).

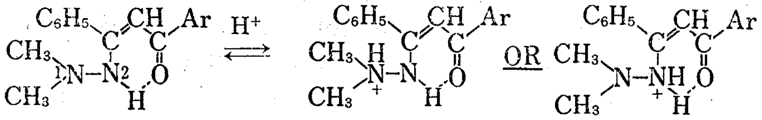
(ii) Chemical Evidence

Compelling evidence for the structure (IIIa) was obtained from the reaction of dibenzoylmethane (VIIa) and N,N-dimethylhydrazine (II), which gave similar product to IIa (*cf.* Chart 1). Furthermore, compounds (IIIa and IIIc) were easily hydrolyzed with 30% H_2SO_4 to the corresponding β-diketones (VIIa and c), indicating that they exist in the ketamine form.[26] Other evidence can be adduced in favour of the ketamine form (III) from the fact that the products (IIIa—f) gave no positive ferric chloride test and showed no propensity to react with diazomethane, even in the presence of methyl alcohol. The latter observation can not be attributed to strong chelation of the enol form (IV), since methyl alcohol solvates the enol to break up the chelate ring, and permits reaction with the enolic hydrogen.[27]

The structure of the above β-diketones (VIIa and VIIc) was established by preparing authentic samples from the reaction of the corresponding acetylenic ketones with 30%H_2SO_4[28] (*cf.* Chart 1).

(iii) Determination of the Protonation Constants of 1,1-Dimethyl-2-[β-(α-aroylstyryl)]-hydrazine (IIIa—f)

The acid-base equilibria of the compounds in 60 wt % dimethylformamide–water medium may be represented as follows (*cf.* Chart 2):



(LH⁺)

Chart 2

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25) N.S. Bhacca, D.P. Hollis, L.F. Johnson and E.A. Pier, "High Resolution NMR Spectra Catalog," Volume 2, No. 480, Varian Associates, 1962.

26) N.H. Cromwell, *Chem. Revs.*, **38**, 83 (1946).

27) B. Eistert, R. Arndt, L. Lowe, and E. Eyca, *Ber.*, **84**, 156 (1951).

28) Ch. L. Bickel, *J. Am. Chem. Soc.*, **69**, 73 (1947).

Where (L) and (LH^+) are the unprotonated and the protonated species of the compound.

Figure 2 shows the spectra of 1,1-dimethyl-2-[β-(α-benzoylstyryl)]hydrazine (IIIa) at different pH values. The dependence of absorbance on pH is shown in Figure 3 for the compound (IIIa) at λ 349 nm. The spectral changes which were observed at various pH values may indicate that either nitrogen (1 or 2) may be protonated or nitrogen 2 is deprotonated (*cf*, Chart 2). Although the latter may proceed through the formation of the enolic species, yet this was inconsistent with NMR and ultraviolet (UV) studies and the inability of these compounds to form the characteristic color of ferric chloride. Moreover, the p*K* value of β-ketoimine system (IV) usually has high value.[29] By assuming that the only absorbing species are the set of species H_nL, $H_{n-1}L$, ..., L, and the application of Beer–Lambert Law, the appropriate mass balance equation and the expression for the protonation constant,

$$\left(\beta_n = \frac{[H]^n[L]}{[H_nL]}\right)$$

equation (2) can be derived

$$\bar{\varepsilon} = \frac{As}{lT_L} = \frac{\sum_0^N E_n\beta_n[H]^n}{\sum_0^N \beta_n[H]^n} \qquad (2)$$

where; $\bar{\varepsilon}$ is the average molar absorptivity at a given wavelength, E_n is the molar absorptivity of the n^{th} species, T_L is the total compound concentration and *As* is the absorbance at a given wavelength.

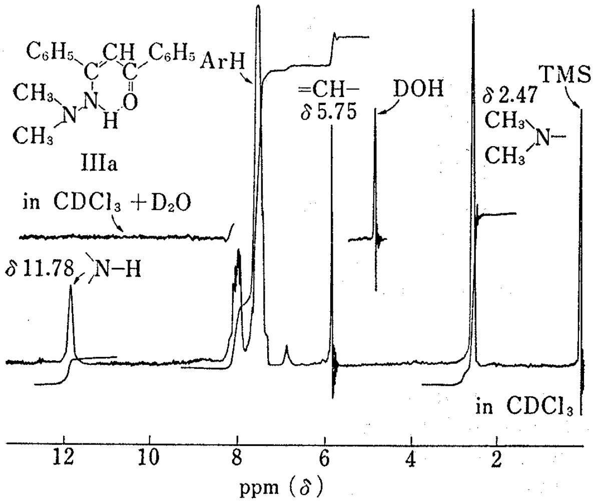

Fig. 1. NMR Spectra of IIIa In $CDCl_3$

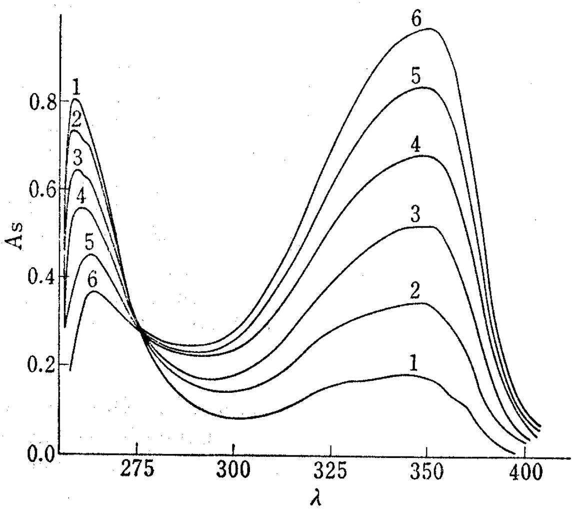

Fig. 2. Spectra of IIIa at Different pH Values

	B		B		B
1	1.65	2	3.80	4	4.12
4	4.48	5	4.97	6	6.63

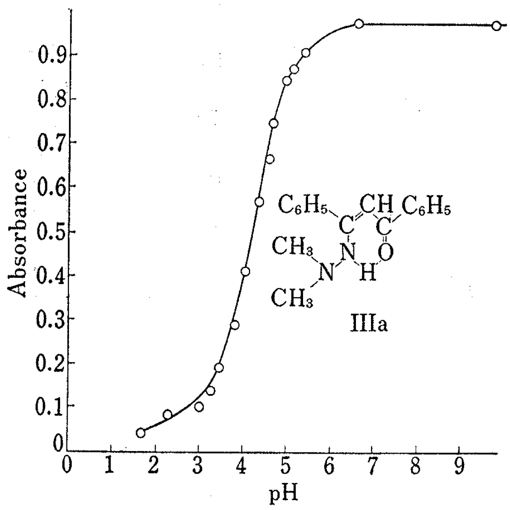

Fig. 3. Absorbance as Function of pH for IIIa

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[29] D.F. Martin, G.A. Janusonis, and B.B. Martin, *J. Am. Chem. Soc.*, **83**, 73 (1961).

Table IV. The Protonation Constants of 1,1-Dimethyl-2-[β-(α-aroylstyryl)]hydrazine (IIIa—f) at 25°, $\mu=0.10$ M HCl/NaCl in 60 wt% Dimethylformamide–Water Solvent

Compound	β_1	$\log \beta_1$	σ Value[a]
IIIa	$(8.19\pm0.13)^{b)}\ 10^3$	3.91	0.00
IIIb	$(9.37\pm0.24)^{b)}\ 10^3$	3.97	−0.17
IIIc	$(4.49\pm0.05)^{b)}\ 10^3$	3.65	+0.37
IIId	$(5.65\pm0.07)^{b)}\ 10^3$	3.75	+0.23
IIIe	$(8.78\pm0.14)^{b)}\ 10^3$	3.94	−0.27
IIIf	$(2.77\pm0.05)^{b)}\ 10^3$	3.44	+0.78

a) C. G. Swain and E. C. Lupton, *J. Am. Chem. Soc.*, **90**, 4328 (1968)
b) limits of error ±1s

Table V. Observed and Calculated Values of $\bar{\varepsilon}$ at a Given Wavelength for 1,1-Dimethyl-2-[β-(α-aroylstyryl)]hydrazine (IIIa—f) at Different pH Values

Compound	pH	$\bar{\varepsilon}_{\text{obs.}}\times10^{-3}$(wavelength)	$\bar{\varepsilon}_{\text{calc.}}\times10^{-3}$
IIIa	3.45	5.77 (349 nm)	5.80
	4.35	14.85 (349 nm)	14.86
IIIb	3.20	3.96 (352 nm)	3.96
	4.20	12.67 (352 nm)	12.71
IIIc	3.45	8.53 (355 nm)	8.51
	4.70	17.90 (355 nm)	17.91
IIId	3.30	6.92 (348 nm)	6.90
	4.20	16.32 (348 nm)	16.31
IIIe	2.70	3.10 (356 nm)	3.09
	4.30	16.58 (356 nm)	16.62
IIIf	3.20	6.76 (380 nm)	6.73
	4.20	12.25 (380 nm)	12.24

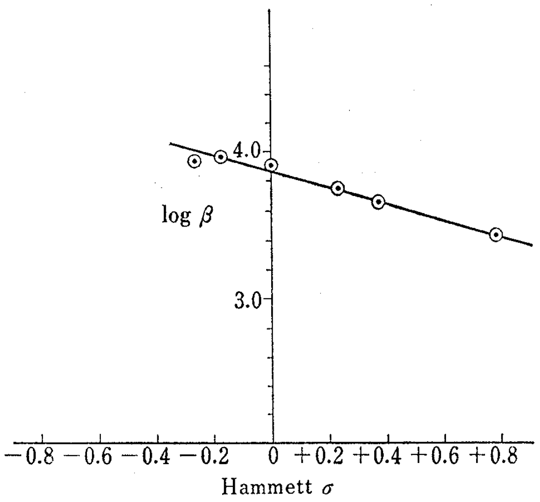

Fig. 4. log β_1 as Function, σ, Hammet Constant

First approximations to β_1 and E_1 (at 350 nm) were obtained at pH's near absorbance saturation. E_0 can be obtained from the constant absorbance value at pH's greater than 6.0. First approximations to β_2 and E_2 at the same wavelength were evaluated using equation (3),

$$Y=\frac{\bar{\varepsilon}-E_0}{[H^+]^2}+\beta_1\frac{\bar{\varepsilon}-E_1}{[H^+]}=E_2\beta_2-\bar{\varepsilon}\beta_2 \quad (3)$$

and were employed to refine β_1 and E_1 by the application of equation (4).

$$Z=\frac{\bar{\varepsilon}-E_0}{[H^+]}+\beta_2[H^+](\bar{\varepsilon}-E_2)$$
$$=E_1\beta_1-\bar{\varepsilon}\beta_1 \quad (4)$$

The results indicated that β_2 and E_2 have very small magnitudes with respect to β_1 and E_1 so that the former can be ignored with no serious error. One can conclude that equilibrium reaction in Chart 2, actually prevailed in the pH range considered. Table IV depicts the values of β_1 for the different hydrazine derivatives used in this study. Observed and calculated values of $\bar{\varepsilon}$ are shown in Table V

The application of Hammett equation to the log β values obtained is shown in Figure 4. The σ value obtained from the regression analysis of the straight line has the value (-0.57 ± 0.05). This value is substantially different from that reported for $ArN^+(CH_3)_2H$ (3.56) in water.30) This may be attributed to the solvent effect and to the weak electron transmission through the conjugated system.

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30) R.R. Wells, "Linear Free Energy Relationship," Academic Press, N.Y., 1968, p. 12.