Substituent effects on azo coupling of indoles

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Received March 10, 1993

Hassan A. Albar, Ahmad S. Shawali, and Magda A. Abdallah. Can. J. Chem. 71, 2144 (1993).

The kinetics of the azo coupling of eight *para*-substituted benzenediazonium tetrafluoroborates $2a-h$ with indole and its 1-, 2-, and 3-methyl derivatives $1a-d$, respectively, were studied in acetonitrile at 25°C under pseudo-first-order conditions. The relation $k_1(\text{obs}) = k_2[\text{diazonium salt}]$ was found applicable in all cases. The logarithms of the rate constants k_2 for each reaction series were correlated by the Hammett equation. A plot of the values of the reaction constant, ρ, obtained against the acidity constants pK_a of $1a-d$ gave a straight line: $\rho = 2.97 - 0.15\ pK_a$. These results indicate that the azo-coupling reactions of indoles $1a-d$ follow one general mechanism involving rate-limiting initial electrophilic attack at the 3-position for all four compounds, contrary to the previous conclusion of Jackson and Lynch that the final deprotonation step is rate limiting.

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Opérant dans l'acétonitrile, à 25°C, dans des conditions de pseudo premier ordre, on a étudié la cinétique du couplage azo de huit tétrafluoroborates de benzènediazonium *para*-substitués, $2a-h$, avec l'indole et ses dérivés 1-, 2- et 3-méthylés, $1a-d$. On a trouvé que, dans tous les cas, la relation $k_1(\text{obs}) = k_2$ [sel de diazonium] peut s'appliquer. L'équation de Hammett permet d'établir une corrélation entre les logarithmes des constantes de vitesse k_2 de chaque série de réactions. Une courbe des valeurs de la constante de la réaction, ρ, en fonction des constantes d'acidité, pK_a, des composés $1a-d$ donne une ligne droite, $\rho = 2.97 - 0.15\ pK_a$. Ces résultats indiquent que les réactions de couplage azo des indoles $1a-d$ se produisent par un mécanisme général impliquant une attaque électrophile initiale limitant la vitesse qui se produit en position 3 de chacun de ces composés; ce mécanisme est en désaccord avec les conclusions proposées antérieurement par Jackson et Lynch selon lesquelles la déprotonation finale serait l'état limite.

[Traduit par la rédaction]

Introduction

The mechanism of azo-coupling reactions of indole and its 1-, 2-, and 3-methyl derivatives $1a-d$ has been studied by several investigators (Scheme 1) (1–5). However, little is known about the substituent effects on the reaction rate. So far only Challis and Rzepa (3) have reported the rates of azo coupling of $1c$ with a series of five *para*-substituted benzenediazonium ions in aqueous dioxane. Here, we wish to report the results of our kinetic investigation of the azo-coupling reactions of $1a-d$ each with a series of eight *p*-substituted benzenediazonium tetrafluoroborates $2a-h$ in dry acetonitrile at 25°C (Chart 1). The goal of this study is the determination of the Hammett reaction constants (ρ) for the four reaction series in question under similar conditions and the correlation of the values of these constants with the acidity constants, pK_a, of $1a-d$ (6–9). The knowledge of such data is necessary to support or to invalidate the recently reported mechanism for the reaction of $1d$ with *p*-nitrobenzenediazonium ion $2h$ in acetonitrile (Scheme 1) (4), and to cast light on the rate-limiting step in the reactions studied.

Results and discussion

Coupling of indole and its 1- and 2-methyl derivatives $1a-c$ each with the diazonium salts 2 in dry acetonitrile at 25°C yielded the corresponding 3-arylazoindole derivatives $3-5$, respectively (Scheme 1). 3-Methyl indole $1d$ couples with 2 under similar conditions to give 2-arylazo-3-methylindoles 6 (Scheme 1). The structures of the new products $3-6$ (each

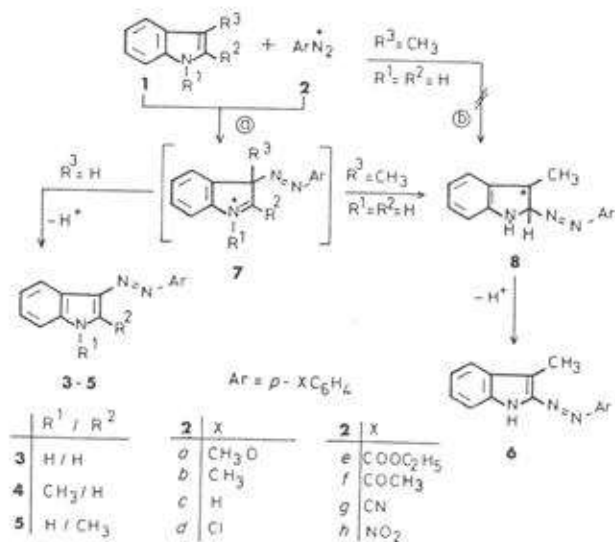[1]Author to whom correspondence may be addressed.

$a-g$) were corroborated by their elemental analyses and spectral (¹H NMR and UV) data (Tables 1–4). Furthermore, the mass spectra of the products $3-6$ were consistent with their assigned structures. Thus, each of the products $4-6$ showed, in addition to the molecular ion (M^+) peak, two characteristic peaks at m/e 158 and 130. Such peaks correspond to the fragments $(M^+ - Ar)$ and $(M^+ - Ar - N_2)$, respectively. The mass spectra of the products 3 showed the peaks of the latter fragments at m/e 144 and 116, respectively. It is worth noting that the base peak in the spectra of the products $3-5$ corresponds to the fragment $(M^+ - Ar - N_2)$, whereas for the products 6 it corresponds to the molecular ion species (M^+). This observation suggests that the radical cation of 2-arylazo-3-methylindole 6 is more stabilized than that of the corresponding 3-arylazoindoles $3-5$.

The kinetics of the reactions of $1a-d$ each with tenfold excess or more of $2a-h$ in dry acetonitrile at 25°C were followed by the rate of appearance of the corresponding azoindole derivatives at their characteristic wavelengths (Table 5). In all cases good first-order plots of $\log(D_\infty - D_t)$ against time, t, were obtained. The pseudo-first-order rate constants, k_1 (obs), were calculated from the slopes of such plots by using the least-squares method. The plots of k_1 (obs) against [diazonium salt] were, in each case, linear, indicating that the azo-coupling reactions of the indoles $1a-d$ follow the equation

$$k_1(\text{obs}) = k_2 [\text{diazonium salt}]$$

Table 6 lists the k_2 values, calculated by the least-squares method, from the slopes of such plots. The correlation coefficients were in the range 0.986–0.990.

Scheme 1

R^1 / R^2

3	H / H
4	CH_3 / H
5	H / CH_3

2	X
a	CH_3O
b	CH_3
c	H
d	Cl

2	X
e	$COOC_2H_5$
f	$COCH_3$
g	CN
h	NO_2

$Ar = p\text{-}XC_6H_4$

Chart 1

1

$p\text{-}XC_6H_4\overset{+}{N}_2BF_4^-$

2

a, $R^1 = R^2 = R^3 = H$
b, $R^1 = CH_3$, $R^2 = R^3 = H$
c, $R^1 = R^3 = H$, $R^2 = CH_3$
d, $R^1 = R^2 = H$, $R^3 = CH_3$

2	X
a	CH_3O
b	CH_3
c	H
d	Cl

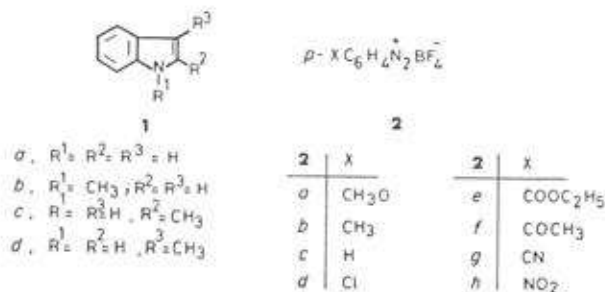| 2	X
e	$COOC_2H_5$
f	$COCH_3$
g	CN
h	NO_2

The results in Table 6 show that the azo-coupling reactions of 1a–d are affected by the substituent present in the diazonium salt, the reaction being retarded by electron-donating and enhanced by electron-withdrawing substituents. Figure 1 shows the plots of log k_2 values against the Hammett substituent constant σ (10). As shown, the relations are linear, following the equation: log $(k/k_0)_2 = \rho\sigma$. The results of such correlations are summarized in Table 7. The lower susceptibility to substituent effects ($\rho = 3.0$) found in this work for the diazo coupling to 2-methylindole 1c in acetonitrile as compared to that ($\rho = 3.3$) reported for the same reaction in 20% (v/v) aqueous dioxane at pH 4.0 (3) seems to be due to solvent effects. It has been reported that in polar aprotic solvents the diazo-coupling reactions proceed faster than in protic solvents (13) and thus ρ decreases in the former solvents.

An examination of these data shows that the sensitivity of the reactions of 1a–d each with 2a–h decreases in the order: $1d > 1a > 1b > 1c$. This is opposite to the order of the pK_a values reported for 1a–d (6–9), that is, the azo coupling with the less basic 1d is much more susceptible to polar requirements than the reaction of the stronger base 1c. This can also be seen by the excellent linear plot of the ρ values versus the pK_a values of the indoles studied, 1a–d (Fig. 2). The equation of the regression line is $\rho = 2.97 - 0.15$ pK_a, with $r = 0.998$; $s = \pm 0.016$ and $S_\rho = \pm 0.005$.

This correlation seems to indicate that the nucleophilicity of the indoles studied, 1a–d, towards the diazonium cation is closely related to their pK_a values. In fact the plots of the log k_2 values of the reactions of 1a–d with a given diazonium salt against the pK_a values were linear in all cases examined. A similar relationship between the reactivity of

Table 1. 1-Arylazoindoles 3a–h

Compound no.	Melting point, °C (Lit. mp)	Molecular formula	Anal. found (calcd.), %			IR, v cm⁻¹ NH, N=N, (C=O or C≡N)	¹H NMR, δ, ppm
			C	H	N		
3a	133–135	C₁₅H₁₂N₄O	71.5 (71.70)	5.1 (5.22)	16.6 (16.72)	3383,1460	3.10(3H,s,CH₃O), 8.50(1H,s,NH)
3b	170–172	C₁₅H₁₃N₃	76.1 (76.58)	5.6 (5.57)	17.6 (17.85)	3380,1460	2.44(3H,s,CH₃), 8.51(1H,s,NH)
3c	132–135	C₁₄H₁₁N₃	76.1 (76.01)	5.3 (5.01)	18.7 (18.98)	3385,1460	8.58(1H,s,NH)
3d	161–164	C₁₄H₁₀ClN₃	65.7 (65.75)	3.7 (3.94)	16.1 (16.42)	3396,1465	8.58(1H,s,NH)
3e	183–184	C₁₇H₁₅N₃O₂	69.3 (69.61)	5.1 (5.16)	14.2 (14.32)	3225,1465, (1695)	1.45(3H,t,CH₃), 4.41(2H,q,CH₂), 8.71(1H,s,NH)
3f	188–189	C₁₆H₁₃N₃O	72.8 (72.99)	4.8 (4.98)	15.7 (15.95)	3358,1463, (1672)	2.67(3H,s, CH₃CO), 8.78 (1H,s,NH)
3g	209–210	C₁₄H₁₀N₄	72.9 (73.17)	3.8 (4.09)	22.4 (22.74)	3285,1469, (2215)	8.74(1H,s,NH)
3h	196–199 (195–197)(4)	C₁₄H₁₀N₄O₂	63.2 (63.16)	3.8 (3.79)	20.9 (21.03)	3290,1468	8.88(1H,s,NH)

ªAll ¹H NMR spectra of 3a–h revealed an aromatic proton multiplet in the region 7.00–8.18 ppm.

Table 2. 3-Arylazo-1-methylindoles 4a–h

Compound no.	Melting point, °C (Lit. mp)	Molecular formula	Anal. found (calcd.) %			IR cm⁻¹ N=N (=O or C≡N)	¹H NMR δ ppm
			C	H	N		
4a	111–112	C₁₆H₁₅N₃O	72.3 (72.43)	5.4 (5.70)	15.6 (15.84)	1465	3.88(3H,s, N-CH₃),3.90 (3H,s,CH₃O)
4b	148–149	C₁₆H₁₅N₃	76.8 (77.08)	5.8 (6.06)	16.5 (16.85)	1465	2.40(3H,s,CH₃) 3.89(3H,s,N-CH₃)
4c	90–92	C₁₅H₁₃N₃	76.7 (76.57)	5.5 (5.57)	18.0 (17.86)	1465	3.88(3H,s,N-CH₃)
4d	124–126	C₁₅H₁₂ClN₃	67.3 (66.80)	4.6 (4.48)	15.4 (15.58)	1465	3.88(3H,s,N-CH₃)
4e	168–171	C₁₈H₁₇N₃O₂	70.8 (70.34)	5.7 (5.58)	13.4 (13.67)	1465 (1710)	1.24(3H,t,CH₃), 3.88(3H,s, N-CH₃),4.40(2H, q,CH₂)
4f	140–142	C₁₇H₁₆N₃O	73.4 (73.63)	5.2 (5.45)	14.9 (15.15)	1465 (1680)	2.66(3H,s, COCH₃),3.90 (3H,s,N-CH₃)
4g	172–174	C₁₆H₁₂N₄	73.6 (73.82)	4.5 (4.65)	21.2 (21.52)	1465 (2220)	3.90(3H,s,N-CH₃)
4h	188–191 (188–191)(4)	C₁₅H₁₂N₄O₂	64.2 (64.28)	4.60 (4.32)	20.2 (19.99)	1465	3.92(3H,s,N-CH₃)

ªAll ¹H NMR spectra of 4a–h revealed an aromatic proton multiplet in the region 7.00–8.54 ppm.

phenols was found in the coupling reaction of p-substituted phenols with diazobenzene-4-sulfonic acid (11).

Evidently, on the basis of (i) the similarity between protonation of 1a–d and the initial step in their azo-coupling reactions and (ii) the fact that the basicity pattern of 1a–d has been shown to be consistent with the concept of preferred protonation at the 3-position (6–9), it is not unreasonable to conclude that the azo-coupling reactions of the indoles 1a–d proceed in all cases by initial electrophilic attack of the diazonium cation at the 3-position as outlined in Scheme 1.

TABLE 3. 3-Arylazo-2-methylindoles 5a–h

Compound no.	Melting point, °C (Lit. mp)	Molecular formula	Anal. found (calcd.), %			IR, ν cm⁻¹ NH, N=N (C=O or C=N)	¹H NMR, δ ppm
			C	H	N		
5a	137–139	C₁₆H₁₃N₃O	72.0 (72.43)	5.4 (5.70)	15.9 (15.84)	3260,1465	2.83(3H,s,2-CH₃), 3.89(3H,s,CH₃O), 8.22(1H,s,NH)
5b	180–181	C₁₅H₁₃N₃	77.1 (77.08)	6.2 (6.06)	16.6 (16.85)	3210,1465	2.41(3H,s,CH₃), 2.81(3H,s,2-CH₃), 8.2(1H,s,NH)
5c	122–123	C₁₅H₁₃N₃	76.5 (76.57)	5.2 (5.57)	17.5 (17.86)	3310,1465	2.86(3H,s,2-CH₃), 8.26(1H,s,NH)
5d	162–163	C₁₅H₁₂ClN₃	66.8 (66.80)	4.4 (4.48)	14.9 (15.58)	3250,1465	2.82(3H,s,2-CH₃), 8.29(1H,s,NH)
5e	221–222	C₁₈H₁₇N₃O₂	70.0 (70.34)	5.6 (5.58)	13.4 (13.67)	3270,1465, (1695)	1.43(3H,t,CH₃), 2.88(3H,s,2-CH₃), 4.42(2H,q,CH₂), 8.43(1H,s,NH)
5f	179–180	C₁₇H₁₅N₃O	73.0 (73.63)	5.4 (5.45)	14.8 (15.15)	3200,1465, (1675)	2.67(3H,s, CH₃CO),2.88 (3H,s,2-CH₃), 8.47(1H,s,NH)
5g	226–227	C₁₅H₁₂N₄	73.6 (73.82)	4.7 (4.65)	23.4 (23.52)	3315,1465, (2220)	2.88(3H,s,2-CH₃), 8.49(1H,s,NH)
5h	229–230 (228–230)(4)	C₁₅H₁₂N₄O₂	64.6 (64.28)	4.5 (4.32)	20.0 (19.99)	3300,1465	2.89(3H,s,2-CH₃), 8.54(1H,s,NH)

ᵃAll ¹H NMR spectra of 5a–h revealed an aromatic proton in the region 7.00–8.54 ppm.

TABLE 4. 2-Arylazo-3-methylindoles, 6a–h

| Compound no.	Melting point, °C (Lit. mp)	Molecular formula	Anal. found (calcd.), %			IR, ν cm⁻¹ NH, N=N (C=O or C=N)	¹H NMR, δ ppm
			C	H	N		
6a	146–147	C₁₆H₁₅N₃O	72.3 (72.43)	5.8 (5.70)	15.7 (15.84)	3318,1465	2.71(3H,s,3-CH₃), 3.9(3H,s,CH₃), 8.85(1H,s,NH)
6b	168–170	C₁₆H₁₅N₃	76.9 (77.08)	6.0 (6.06)	16.5 (16.85)	3320,1465	2.24(3H,s,CH₃), 2.72(3H,s,3-CH₃), 8.86(1H,s,NH)
6c	111–112	C₁₅H₁₃N₃	76.2 (76.57)	5.5 (5.57)	17.7 (17.86)	3320,1465	2.74(3H,s,3-CH₃), 8.88(1H,s,NH)
6d	149–150	C₁₅H₁₂ClN₃	66.7 (66.80)	4.3 (4.48)	15.3 (15.58)	3325,1465	2.73(3H,s,3-CH₃), 8.85(1H,s,NH)
6e	194–196	C₁₈H₁₇N₃O₂	70.2 (70.34)	5.4 (5.58)	13.4 (13.67)	3318,1468, (1700)	1.44(3H,t,CH₃), 2.76(3H,s,3-CH₃), 4.21(2H,q,CH₂), 8.88(1H,s,NH)
6f	228–229	C₁₇H₁₅N₃O	73.4 (73.63)	5.2 (5.45)	15.0 (15.15)	3315,1465, (1675)	2.67(3H,s,CH₃), 2.77(3H,s,3-CH₃), 8.88(1H,s,NH)
6g	186–187	C₁₅H₁₂N₄	73.7 (73.82)	4.5 (4.65)	21.3 (21.52)	3390,1465, (2220)	2.75(3H,s,3-CH₃), 8.85(1H,s,NH)
6h	218–219 (217–220)(4)	C₁₅H₁₂N₄O₂	64.1 (64.28)	4.1 (4.32)	19.8 (19.99)	3330,1465	2.76(3H,s,3-CH₃), 8.87(1H,s,NH)

ᵃAll ¹H NMR spectra of 6a–h revealed an aromatic proton in the region 7.00–8.37 ppm.

TABLE 5. Characteristic electronic absorption maxima of 3-arylazo indoles 3–5 (a–h) and 2-arylazoindoles 6a–h in acetonitrile

Compound no.	λ_{max} (log ϵ), nm			
	3	4	5	6
a	361 (4.47)	363 (4.46)	365 (4.51)	389 (4.56)
b	364 (4.53)	386 (4.47)	370 (4.53)	390 (4.53)
c	365 (4.45)	369 (4.45)	372 (4.50)	392 (4.49)
d	372 (4.49)	368 (4.44)	380 (4.44)	394 (4.54)
e	405 (4.51)	382 (4.45)	382 (4.50)	394 (4.50)
f	328 (4.46)	387 (4.50)	372 (4.48)	395 (4.49)
g	375 (4.49)	386 (4.44)	387 (4.54)	396 (4.57)
h	419 (4.44)	421 (4.48)	432 (4.48)	426 (4.48)

TABLE 6. Second-order rate constants (k_2) of azo-coupling reactions of 1a–d each with 2a–h in acetonitrile at 25°C[a]

2	$10^3 k_2$ (1a)	$10^2 k_2$ (1b)	k_2 (1c)	$10^3 k_2$ (1d)
a	0.0249	0.246	0.250	0.004
b	0.0562	0.580	0.620	0.011
c	0.224	2.57	1.92	0.048
d	1.437	11.75	15.14	0.310
e	8.551	64.57	37.16	2.400
f	12.83	158.50	56.23	3.00
g	46.90	372.00	177.80	9.70
h	124.05	660.70	427.00	30.20

[a] k_2 in L mol^{-1} s^{-1}.
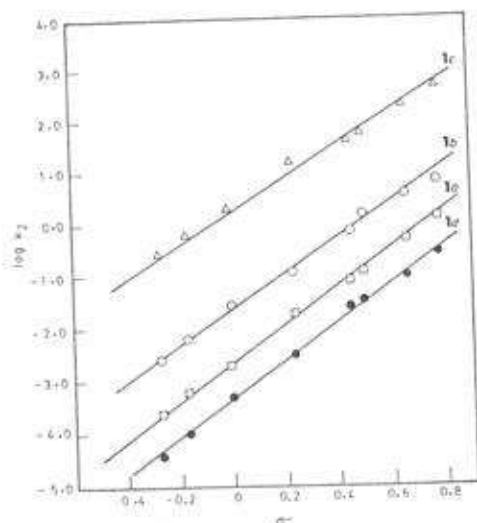
FIG. 1. Correlations of the second-order rate constants of the azo-coupling reactions of indoles 1a–d with p-substituted benzenediazonium ions 2a–h in acetonitrile at 25°C with the Hammett substituent constants σ.

Furthermore, the close similarity of the ρ value for 3-methylindole to those for indole and 1- and 2-methylindoles implies that the initial step must be the rate-limiting step for the reaction of all four compounds. This conflicts with the claim of Jackson and Lynch (4) that H$^+$-expulsion from the 2-position is rate limiting for diazo coupling of 3-methylindole 1d. The fact that ρ values correlate with the indole pK_a values also implies a common rate-limiting step for all four substrates 1a–d. This finding was also evident in Jackson and Lynch's study (4) but they chose to ignore its consequence in favour of a small positive isotope effect (ca. 2) for reactions with 2-[^{2}H$_1$]-3-methylindole.

Experimental

Indole, 2-methylindole, and 3-methylindole were Aldrich reagents and were crystallized from light petroleum ether (60–80°C) before use in the kinetic experiments: indole, mp 51–52°C; 2-methylindole, mp 61°C; and 3-methylindole, mp 94–95°C. 1-Methylindole was prepared by methylation of indole using a literature procedure (4).

The diazonium salts 2 were prepared according to a previously described method (12) using amyl nitrite instead of tert-butyl nitrite. The purity of the salts was checked by ^{1}H NMR analyses (12).

Kinetics

The reactions were carried out in 1-cm ground-glass stoppered, fused-silica, absorption cells. The reactions were followed by rate of appearance of the azoindole absorption maximum (Table 5). Stock solutions of the diazonium tetrafluoroborate 2a–h, usually 10^{-2} M, were prepared in acetonitrile. Stock indole solutions, usually 10^{-3} M, were also prepared in the same solvent. Appropriate concentrations of the diazonium salts 2 and indole 1 were prepared by dilution of the stock solutions with acetonitrile. All indole concentrations were 5×10^{-5} M. All solutions were thermostated at 25 ± 0.1°C.

Reactions were followed up to 95% completion under pseudo-first-order conditions in which at least a tenfold excess of the diazonium salt over indole was used. Duplicate or triplicate runs were performed for each concentration and readings taken in any kinetic run cover a range of 96% transmittance. The pseudo-first-order

TABLE 7. Results of linear free energy correlations of the second-order rate constants of azo coupling of indoles 1a–d with diazonium salts 2a–h in acetonitrile at 25°C[a]

Rx series	$\log k_2 = \rho\sigma + \log k_0$	r	$+S_{xx}$	$+S_\rho$	pK_a
1a + 2a–h	$\log k_2 = 3.52\sigma - 2.651$	0.999	0.001	0.002	-3.63
1b + 2a–h	$\log k_2 = 3.34\sigma - 1.654$	0.997	0.010	0.018	-2.32
1c + 2a–h	$\log k_2 = 3.00\sigma + 0.288$	0.997	0.047	0.084	-0.28
1d + 2a–h	$\log k_2 = 3.65\sigma - 3.351$	0.999	0.055	0.034	-4.55

[a]Abbreviations: r = correlation coefficient, S_{xx} = deviation, S_ρ = error estimate in ρ, pK_a = acidity constant of indole.
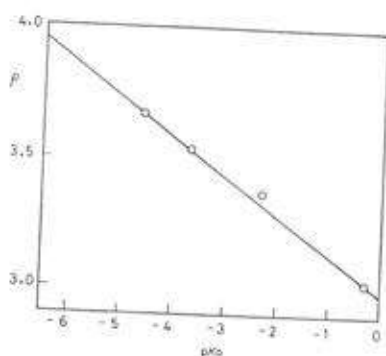

FIG. 2. Correlation of the reaction constants (ρ) of the azo-coupling reactions of indoles 1a–d with their acidity constants (pK_a).

rate constants, k_2(obs), were calculated from $\log (D_x - D_t)$ against time, t, data using the least-squares method. D_t and D_x are the absorbance values of the reaction mixture at time, t, and infinite time, respectively. The average deviation from the mean value of the rate constant in duplicate or triplicate experiments was ±5% or less.

Isolation of products

To a solution of the appropriate indole 1 (0.001 mol) in acetonitrile (20 mL) was added a solution of the appropriate diazonium tetrafluoroborate (0.01 mol) in the same solvent (10 mL), with stirring, at room temperature. After 36 h, the solvent was evaporated under reduced pressure, the crude oil left was triturated with an ethanol–water mixture, and the solid formed was collected and crystallized from aqueous ethanol. The physical constants of azo-coupling products 3–6 are listed in Tables 1–4 together with their spectral data.

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