

Benzoquinone Imines. Part XI.¹ Mechanism and Kinetics of the Reaction of *p*-Benzoquinone Di-imines with Aniline and its Derivatives

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Indamine [Phenylene Blue, *N*-(4-aminophenyl)-*p*-benzoquinone di-imine] and some *C*-alkyl derivatives have been characterised, for the first time, as the products of the oxidative coupling of *p*-phenylenediamines with anilines. The coupling reaction involves electrophilic attack of the conjugate acid of the *p*-benzoquinone di-imine at the 4-position of the neutral aniline, to give 4,4'-diaminodiphenylamine, which undergoes rapid oxidation to the indamine. The reactivity of anilines is increased by electron-donating substituents, while that of the di-imines is increased by electron-withdrawing substituents. The effect of substituents on the rate of the coupling reaction is cumulative.

The visible spectra of the indamine dyes indicate that in unsymmetrically substituted derivatives, the most alkylated ring is quinonoid, while the most chlorinated ring is benzenoid.

Hydrolysis of indamines gives indoanilines, and the pH dependence of the rate of hydrolysis indicates that hydrolysis of the neutral species is more rapid than is that of the conjugate acid. Data is given for the oxidation potential of indamine over the pH range 3.9–5.9.

THE reaction of *p*-phenylenediamine with aniline under oxidising conditions is believed to be the first step in the formation of phenosafranin (3,7-diamino-5-phenylphenazinium chloride).² By analogy with the similar reaction of *p*-phenylenediamine with *m*-diamines,³ it seems likely that the initial reaction would involve the oxidation of *p*-phenylenediamine to *p*-benzoquinone di-imine (I) and the coupling of the latter with aniline to give 4,4'-diaminodiphenylamine (II) which, on oxidation, would yield indamine (III). The present

work was undertaken to establish the detailed mechanism of this reaction, preliminary to defining the mechanism of the formation of safranin dyes.

The parent indamine (III), 'Phenylene Blue', was first obtained, but not isolated, by Nietzki⁴ by the oxidation of a mixture of *p*-phenylenediamine and aniline with dichromate in neutral solution. Nietzki demonstrated the structure by reduction of the dye to

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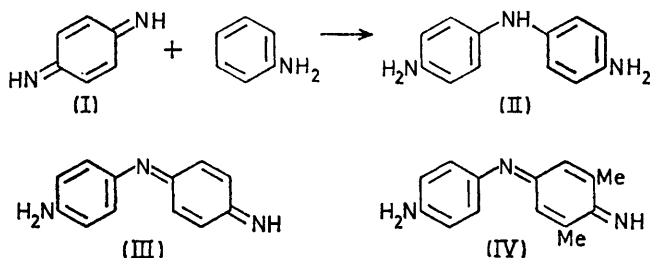
¹ Part X, J. F. Corbett, *J.C.S. Perkin II*, 1972, 999.

² G. A. Swan and D. G. I. Felton, 'The Chemistry of Heterocyclic Compounds—Phenazines,' Interscience, New York, 1957, p. 119.

³ J. F. Corbett, *J. Chem. Soc. (B)*, 1968, 827.

⁴ R. Nietzki, *Ber.*, 1883, **16**, 464.

the known triamine (II).⁵ Merz and Kammerer⁶ make the only recorded claim to have isolated Phenylene Blue. These authors oxidised a mixture of *p*-phenylenediamine dihydrochloride and aniline hydrochloride in water with potassium peroxydisulphate, and isolated



material to which they assigned the formula $C_{24}H_{23}N_5O$, suggesting it to be a mixture of the meroquinones of indamine and indoaniline. We have repeated their preparation and found that the mixture had a pH of 1.3 and, by t.l.c., that the product contained only a trace of indamine together with some indoaniline and a variety of other dyes. On the other hand, oxidation of 4,4'-diaminodiphenylamine under similar conditions gave the indamine as the major product. It seems likely that, at pH < 2, considerable hydrolysis of some of the benzoquinone di-imine to the corresponding mono-imine occurs. Coupling of the latter with aniline would give indoaniline.

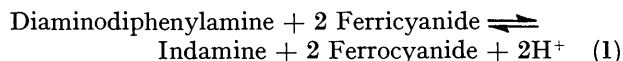
We have now found that the indamines are most readily prepared by the oxidation of equimolar mixtures of a *p*-diamine and an aniline derivative, having no *para* substituent, with potassium ferricyanide at pH 6–7. The dyes separate as crystalline ferrocyanide salts. The free bases are not readily obtained due to their propensity to undergo hydrolysis, in aqueous solvents, and self-addition, leading to complex safranin dyes, in concentrated solutions or on chromatographic plates.

Slow oxidation of mixtures of *p*-diamines and anilines, with oxygen or hydrogen peroxide, cannot be used in the preparation of indamines since hydrolysis of the intermediate di-imine is significant at high pH and low reactant concentrations, while reaction of indamine with unoxidised amines, to give safranines, occurs at near neutral pH and at high reactant concentrations.

Physical Properties and Structure of Indamines.—For spectroscopic purposes, the indamine dyes may be prepared by oxidation of a mixture of the *p*-diamine and excess of the aniline or, better, oxidation of the corresponding 4,4'-diaminodiphenylamine with a slight excess of ferricyanide. We have found that the presence of traces of unoxidised diphenylamine result in the rapid formation of safranines even in $5 \times 10^{-5}M$ solutions. Additionally, the spectra of the solutions should be determined within 2 min to avoid significant hydrolysis of the indamine. The spectrum of the parent indamine, as a function of pH, is shown in Figure 1. At high pH, the red neutral dye is the major species but, as pH

decreases, the blue conjugate acid is formed. From the spectral data the pK_a was estimated to be 7.55.

At pH < 6 the intensity of the peak at 670 nm decreases with decreasing pH due to a shift in the equilibrium (1). From spectral data over the pH range 3.80–6.0, it was possible to calculate the redox potential



of the indamine in the manner described earlier for benzoquinone imines.⁷ Data are given in Table 1.

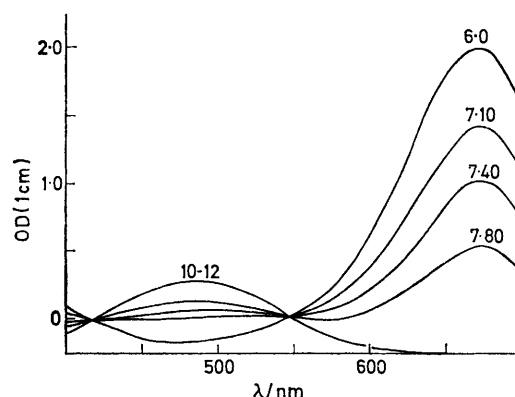


FIGURE 1 The visible spectrum of indamine ($4.1 \times 10^{-5}M$) in phosphate buffers

TABLE 1

Ionisation potential of indamine as a function of pH at 30 °C

pH (± 0.01)	Indamine ^a (%)	[Indamine]/[DADPA]	E_n/V ^b
5.83	90	0.111	0.333
5.46	81	0.235	0.363
4.82	61	0.640	0.403
4.51	43	1.32	0.431
4.33	31	2.23	0.451
3.92	16	5.25	0.485

^a Data refers to the equilibrium established on mixing equal volumes of $5 \times 10^{-5}M$ 4,4'-diaminodiphenylamine (DADPA) and $10^{-4}M$ potassium ferricyanide. ^b Calculated from $E_n = 0.420 - (3RT/2F)\ln\{[DADPA]/[Indamine]\}$ (J. F. Corbett, ref. 7).

The effect of pH on the oxidation potential is shown by equation (2)⁷ where K_{o1} , K_{o2} , K_{r1} , and K_{r2} are the first and second acid-dissociation constants of the diprotonated indamine and diaminodiphenylamine respectively, E° is the standard potential, and E_n is the potential at the designated value of $[H^+]$. If, in the present case, we take $K_{r1} = 1.6 \times 10^{-5}$ and $K_{r2} = 5 \times 10^{-7}$, $K_{o2} = 6.53 \times 10^{-8}$, and assume $K_{o1} > 10^{-2}$, equation (2) predicts that a plot of E_n versus pH should

$$E_n = E^\circ - (RT/F)\ln(1/[H^+]) - (RT/2F)\ln\left\{\frac{(K_{o1}K_{o2} + K_{o1}[H^+] + [H^+]^2)/(K_{r1}K_{r2} + K_{r1}[H^+] + [H^+]^2)}{[H^+]^2}\right\} \quad (2)$$

be linear and gave a slope of -0.09 (i.e., $-3RT/2F$) over the pH range 4–5 and that the slope should de-

⁵ R. Nietzki and O. N. Witt, *Ber.*, 1879, **12**, 1402.

⁶ K. W. Merz and A. Kammerer, *Arch. Pharm.*, 1953, **286**, 139.

⁷ J. F. Corbett, *J. Chem. Soc. (B)*, 1969, 207.

crease to -0.06 (*i.e.*, $-RT/F$) at higher pH. The data in Table 1 are in excellent agreement with this conclusion.

Table 2 gives spectral data for a number of substituted indamine dyes. It can be seen that *C*-methylation of one of the rings results in a small bathochromic

indoaniline. Thus, at pH 8.07 (Figure 2) the two indamine peaks at 484 and 672 nm are gradually replaced by the indoaniline peak at 550 nm. The final spectrum, after 4 h, indicates quantitative conversion. Similar observations were made over the pH range 4–9. At higher pH, the indoaniline undergoes further

TABLE 2
Spectra of indamine dyes

Reactants		Cation $\lambda_{\max.}/\text{nm}$ (log ϵ)	$\Delta\lambda^a$		Free base $\lambda_{\max.}/\text{nm}$ (log ϵ)	$\Delta\lambda^a$		Structure of indamine
Di-imine	Aniline		B	Q		B	Q	
Parent	Parent ^c	672(4.6)			484(3.91)			parent
Parent	2-Me ^c	674(4.5)		2	486(3.84)		2	2
Parent	3-Me ^c	676(4.4)		4	482(3.68)		-2	3
Parent	2,5-Me ₂	676(4.3)		2,0	486		4,0	2,5
Parent	2,6-Me ₂	677(4.4)		3	474(3.86)		-12	2,6
Parent	2-MeO	653		(-19)	470		(-5)	(3)
Parent	2-MeO				508(3.5)		(24)	(2)
2-Me	2-Me	683	9		496(3.81)	10		<i>d</i>
2-Me	3-Me	685	9		482	0		<i>d</i>
2-Me	2,5-Me ₂	686	10	1,3	484(3.58)	-2	2, -12	2,2',5 ^e
2-Me	2,6-Me ₂	686	9	3	482(3.75)	8	-14	2,2',6 ^e
2-Me	3-MeO	669	16		486	10	(-12)	2',(3) ^e
2-Me	2-MeO				520(3.5)	10	(26)	2',(2) ^e
2-Cl	2-Me	662	-12		475(3.70)	-11		2,2'
2-Cl	2,5-Me ₂	666	-10	4	468(3.52)	-18	-7	2,2',5
2-Cl	2,6-Me ₂	668	-9	6	470(3.68)	-4	-5	2,2',6
2,5-Cl ₂	2-Me				474(3.68)	-1		2,2',5'
2,5-Cl ₂	2,6-Me ₂				460(3.62)	-8	-14	2,2',5',6
2,6-Cl ₂	Parent				468(3.52)	-16/2		2',6'
2,6-Cl ₂	2-Me				463(3.50)	-12	-5	2,2',6'
2,6-Cl ₂	2,5-Me ₂				455(3.42)	-13	-8	2,2',5,6'
2,6-Cl ₂	2,6-Me ₂				455(3.43)	-15	-8	2,2',6,6'
2,6-Cl ₂	3-Cl				465(3.60)	-3		2',3,6'

^a Shift (nm) produced by the introduction of a substituent into the benzenoid ring (column B) or quinonoid ring (column Q). Values in parenthesis refer to methoxy-groups, values in italics to chloro-, and other values to methyl groups. ^b Positions of methyl and chloro- (italicised) substituents. ^c Spectral data from oxidation of the corresponding 4,4'-diaminodiphenylamine. All other data from oxidation of a mixture of the *p*-diamine and an excess of the aniline. ^d Data does not indicate which ring is quinonoid. ^e The studied solution probably contains the indicated 2'-methyl compound and the isomer in which the methyl group is in the 3'-position of the benzenoid ring.

shift (0–6 nm) while *C*-chlorination of one of the rings results in a hypsochromic shift (1–15 nm), and *C*-methoxylation in a hypsochromic shift of 19 nm. Furthermore *C*-methylation of the unmethylated ring of a *C*-methoxy- or *C*-methylindamine results in a relatively large bathochromic shift (8–16 nm). On the basis of the arguments used in the case of the indophenol dyes,⁸ these results indicate that in unsymmetrically substituted indamines, the ring bearing the most methyl groups will be quinonoid and the ring containing the most chloro-groups will be benzenoid. Thus, oxidation of a mixture of *p*-phenylenediamine and 2,6-xylydine, or 2,6-dimethyl-*p*-phenylenediamine and aniline, would give rise to the same indamine (IV).

It should be noted that Table 2 does not contain data for the conjugate acids of the dichloro-indamines since under the conditions of generation reversal of the redox equilibrium [equation (1)] occurs prior to or simultaneously with protonation when the pH is lowered. Chloro-groups evidently increase the oxidation potential of the indamine.

Hydrolysis of Indamine—When a dilute aqueous solution of indamine is stored, spectral changes occur which are consistent with its undergoing hydrolysis to

indophenol, a new peak being observed at 630 nm. Indophenol is itself unstable at these high pH levels.

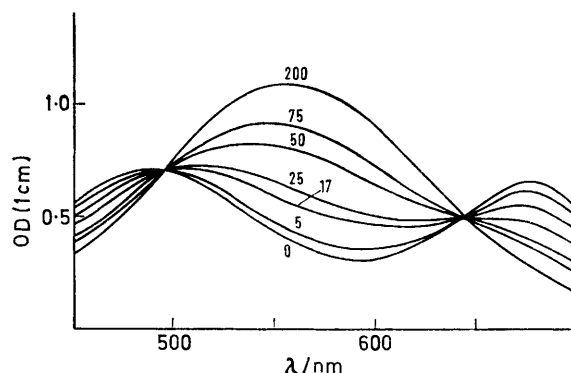


FIGURE 2 The spectrophotometric course of the hydrolysis of indamine ($1.0 \times 10^{-4}\text{M}$) at pH 8.07 and 30° , t/min

The rate of hydrolysis of indamine was measured spectrophotometrically over the pH range 4–9 and was estimated at higher pH values from initial rates. Hydrolysis was found to fit a first-order rate plot and to be dependent, at pH > 5.5, on the nature of the buffer (see Figure 3). At pH > 8 the rate is independent of

⁸ J. F. Corbett, *J. Chem. Soc. (B)*, 1970, 1418.

pH, while in the region 5.5–8 the rate decreases with decreasing pH and then becomes pH independent at pH < 5.5. At pH > 5.5, the rate of hydrolysis is greater in phosphate buffer than it is in acetate or hydrogen

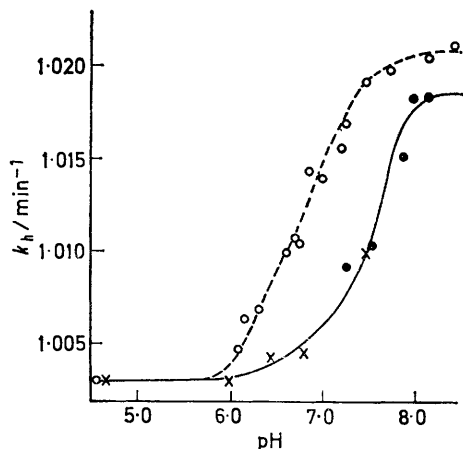


FIGURE 3 The effect of pH on the rate of hydrolysis of indamine at 30° in phosphate (○), acetate (×), and hydrogen carbonate (●) buffers. The full line represents the theoretical curve calculated from equation (3)

carbonate buffers of similar ionic strength. There is thus a specific catalysis by phosphate as was observed for the hydrolysis of *p*-benzoquinone monoimine.⁹

Considering the data for the uncatalysed hydrolysis, the pH-independent portions are consistent with hydroxide ion-catalysed hydrolysis of the conjugate acid of indamine at high pH and uncatalysed hydrolysis of the same species at low pH. Thus, the observed rate constant k_h is given by equation (3), in which k_a and k_b are the specific rate constants for the two processes given above and α is the fraction of indamine present as the conjugate acid at the pH to which k_h

$$k_h = k_a\alpha[\text{OH}^-] + k_b \quad (3)$$

pertains. Using the values $k_a = 1.2 \times 10^6 \text{ l mol s}^{-1}$, $k_b = 0.05 \text{ s}^{-1}$, and $\text{p}K_a = 7.55$, the theoretical curve in Figure 3 is obtained and can be seen to give a good fit with the experimental data.

Mechanism of the Reaction of *p*-Benzoquinone Di-imines with Aniline Derivatives.—As indicated before, indamines are formed when mixtures of a *p*-diamine and an aniline, having no 4-substituent, are oxidised by ferricyanide. It has been shown previously⁷ that, above pH 8, *p*-phenylenediamine is oxidised quantitatively and instantaneously to *p*-benzoquinone di-imine. The observed relatively slow development of the indamine colour must therefore be due to a reaction between the di-imine and the aniline.

Preliminary experiments with *p*-benzoquinone di-imine and an excess of aniline indicated that, over the pH range 6–9, significant phenosafranin formation occurred as the indamine was formed. Thus, at a fixed pH, when the colour development is followed spectrophotometrically at 672 nm (see Figure 4), the initial

rate is proportional to the aniline concentration, the maximum optical density is independent of aniline concentration, and the time taken for achievement of maximal optical density is inversely proportional to the aniline concentration. These observations pertain at other pH values and show that the rate of formation of indamine and of its subsequent consumption are first-order in aniline concentration. Additionally, it was noted that the maximum amount of indamine formed never exceeded 50–60%. In view of this, and of the interference by safranin formation it was not possible to make a study of the detailed mechanism for this pair of reactants. Similar conclusions were reached for reactions of *C*-methylated *p*-benzoquinone di-imines with aniline.

On the other hand it was found that reaction of the parent di-imine, or its *C*-methyl derivatives, with *o*-toluidine, 2,5- or 2,6-xylydine, or *m*-anisidine, and that of *C*-chlorinated di-imines with a variety of aniline derivatives, resulted in almost quantitative formation of the corresponding indamine before significant formation of safranin occurred.

A detailed study was made of the reaction of *p*-benzoquinone di-imine with *o*-toluidine and with 2,6-xylydine. Owing to the low reactivity of anilines, reactions had to be carried out with a large excess of arylamine in order to avoid significant hydrolysis of the di-imine.^{3,9} Studies of the stoichiometry showed that the formation of one molecule of indamine requires two molecules of di-imine (either pure di-imine or from *p*-diamine and

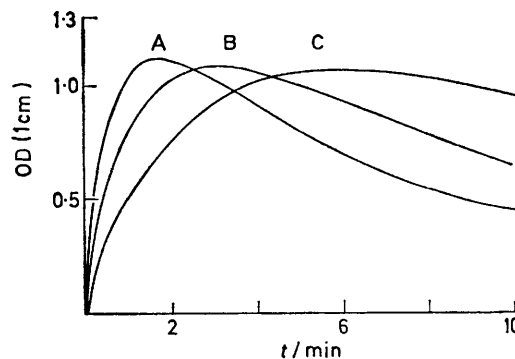
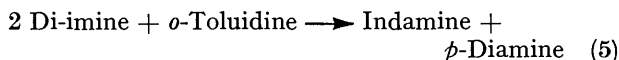
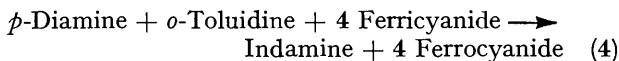


FIGURE 4 Optical density (670 nm) versus time curves for the reaction of *p*-benzoquinone di-imine ($5.0 \times 10^{-5} \text{ M}$) with aniline, at $\text{pH } 7.80 \pm 0.01$ and 30°, in the presence of an excess of ferricyanide. Aniline concentrations: A, $1.6 \times 10^{-2} \text{ M}$; B, $8.0 \times 10^{-3} \text{ M}$; C, $4.0 \times 10^{-3} \text{ M}$

2 mol. equiv. of ferricyanide), or one molecule of *p*-diamine and 4 mol. equiv. of ferricyanide. Thus *o*-toluidine is a 4-equivalent coupler and the reaction can be represented as in equations (4) or (5). In all experiments the rate of colour development followed a first-order kinetic law and the rate, at a fixed pH, was



⁹ J. F. Corbett, *J. Chem. Soc. (B)*, 1969, 213.

found to be proportional to the initial concentration of *o*-toluidine. Thus the rate controlling step involves the reaction of one molecule of the di-imine with one molecule of *o*-toluidine.

Rate data, calculated using the appropriate rate equation,¹⁰ are given in Tables 3 and 4. The second-

TABLE 3

Rate data for the reaction of *p*-benzoquinone di-imine with *o*-toluidine at 30 °C

pH (±0.01)	Di-imine (10 ⁴ M)	<i>o</i> -Toluidine (10 ³ M)	<i>k</i> ₁ /s ⁻¹	<i>k</i> ₂ /l mol ⁻¹ s ⁻¹
6.08	2.0 ^a	0.1		317
6.55	2.0 ^a	0.1		127
8.08	1.0	2.0	0.088	43.8
8.24	1.0	4.0	0.113	2.83
8.38	1.0	5.0	0.108	2.17
8.56	1.0	10.0	0.147	1.47
8.56	1.0	20.0	0.287	1.43
8.78	1.0	20.0	0.165	0.825
9.18	1.0	20.0	0.057	0.283
9.73	1.0	40.0	0.042	0.105
10.07	1.0	80.0	0.060	0.050

^a Using pure di-imine, others used *p*-diamine with 2 molar proportions of ferricyanide.

TABLE 4

Rate data for the reaction of *p*-benzoquinone di-imine with 2,6-xylylidine at 30 °C

pH (±0.01)	Di-imine ^a (10 ⁻⁵ M)	2,6-Xylylidine (10 ⁻³ M)	<i>k</i> ₂ /l mol ⁻¹ s ⁻¹
7.92	5.0	1.0	18.2
8.14	5.0	10.0	11.1
8.46	5.0	10.0	5.20
8.53	5.0	10.0	4.62
8.83	10.0	10.0	2.37

^a Using *p*-diamine and 4.4 molar proportions of ferricyanide.

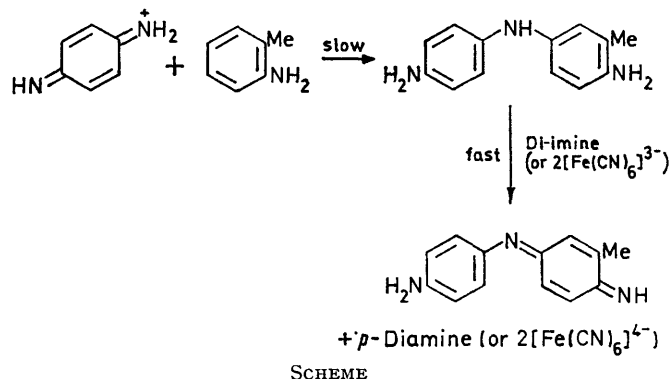
order rate constants, *k*₂, are calculated from the experimentally-determined first-order rate constants, *k*₁, by the equation $k_2 = k_1/[\text{aniline derivative}]$. From Tables 3 and 4 it can be seen that the rate constant for indamine formation increases with increasing pH, and it can be shown that *k*₂ is given by equation (6), where *k*_a is the specific second-order rate constant for the reaction between the conjugate acid of the di-imine (DH⁺) and the neutral aniline derivative (A), and α_{DH⁺} and α_A are the fractions of the reactants which exist as these respective species at the pH to which *k*₂ pertains. The good fit to this equation, where $pK_a =$

$$k_2 = k_a \alpha_{\text{DH}^+} \alpha_A \quad (6)$$

5.75 for the di-imine,⁹ and for *o*-toluidine, $pK_a = 4.04$,¹¹ and $k_a = 9.30 \times 10^2 \text{ l mol}^{-1} \text{ s}^{-1}$ and, for 2,6-xylylidine, $pK_a = 3.55$,¹¹ and $k_a = 2.75 \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$, is seen in Figure 5.

From these results, the mechanism shown in the Scheme is proposed. The rate-controlling step is the electrophilic attack of the conjugate acid of the di-imine on the 4-position of the aniline derivative to give the 4,4'-diaminodiphenylamine, which then undergoes

rapid oxidation, either by a second molecule of di-imine or by excess of ferricyanide to give the indamine. This mechanism is analogous to that deduced for the reaction of di-imines with *m*-diamines.³



In order to establish the effect of substituents on the reactivity of the di-imine and of the aniline, kinetic experiments were performed with a variety of reactant pairs. The results are shown in Table 5. For the less reactive pairs (numbers 3, 5, and 17), initial rates were obtained assuming quantitative

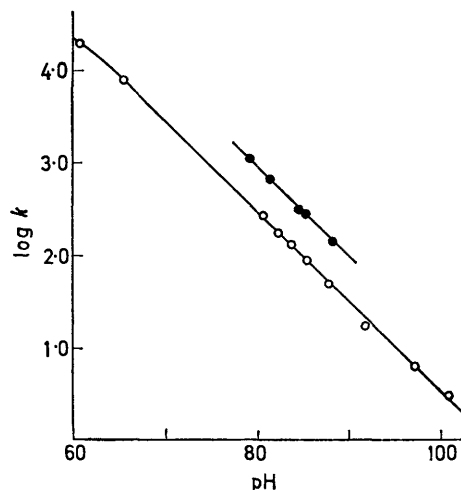


FIGURE 5 The effect of pH on the rate of reaction of *p*-benzoquinone di-imine with *o*-toluidine (○), and with 2,6-xylylidine (●) at 30°. The full lines are theoretical curves calculated from equation (6).

conversion of the di-imine into indamine. In the case of the parent reactants (number 1), it was evident that some side-reaction occurred. The extent of indamine formation was deduced from the yield of phenosafranine and the rate constant was evaluated from the initial rate corrected for the fraction of indamine formed.

Since the pK_a of substituted di-imines was not known, a comparison of reactivities was made at fixed pH; the constant k'_2 relates to pH 9.0 and was calculated from equation (7) where *k*₂ and pH relate to the experimental values, on the basis that at pH > 8, a plot of log *k*₂ versus pH is linear with a slope of -1. It can be

$$\log k'_2 = \log k_2 + \text{pH} - 9.0 \quad (7)$$

¹⁰ J. F. Corbett, *J. Chem. Soc. (B)*, 1970, 1502.

¹¹ N. I. Kudryashova and N. V. Khromov-Borisov, *Zhur. org. Khim.*, 1966, 2, 578.

seen that alkylation of the di-imine decreases the rate while alkylation of the aniline increases the rate. Conversely, chlorination of the di-imine increases the rate while chlorination of the aniline decreases the rate. These results are consistent with the proposed mechanism.

In other studies of di-imine reactions,^{3,8} substituent effects have been found to be cumulative. In the present case, such cumulative effects would be represented by equation (8) where a and b are the factors

$$k'_2 = (a^m b^n c^o d^p) k \quad (8)$$

by which 2- and 3-methylation of aniline increase the rate, and c and d are the factors by which chlorination

Table 5. The results, $a = 4.84$, $b = 8.94$, $c = 1.98$, $d = 0.234$, and $k = 0.104 \text{ l mol}^{-1} \text{ s}^{-1}$ indicate approximate cumulativeness of substituent effects with a multiple correlation coefficient of 0.9860. It is particularly interesting to note that the computed value of k is very close to the experimentally estimated value of 0.095 $\text{l mol}^{-1} \text{ s}^{-1}$. A complete list of substituent effects is given in Table 6.

In the course of the present work it was necessary to prepare some 4-amino-4'-nitrodiphenylamines as intermediates in the synthesis of 4,4'-diaminodiphenylamines. Adaptations of published methods¹² for the synthesis of diphenylamine derivatives were unsuccessful. Thus, for example, heating 4-fluoronitrobenzene and

TABLE 5

Rate data for the reaction of *p*-benzoquinone di-imines with anilines to give indamines at 30 °C

No.	Di-imine ^a	Aniline		pH (±0.01)	10 ² k ₁ /s ⁻¹	k ₂ /l mol ⁻¹ s ⁻¹	k' ₂ /l mol ⁻¹ s ⁻¹ ^b
		Subst.	Concn. (mmol)				
1	Parent						0.095 ^c
2	Parent	2-Me	5	8.38	1.08	2.16	0.520
3	Parent	3-Me	4	8.40	1.75 ^d	4.18	1.05
4	Parent	2,6-Me ₂	10	8.46	5.20	5.20	1.49
5	2-Me	2-Me	40	8.55	1.65 ^d	4.12	0.146
6	2-Me	2,6-Me ₂	10	8.64	1.21	0.121	0.542
7	2-Me	2,5-Me ₂	9.6	8.33	4.06	4.23	0.905
8	2-Cl	2-Me	10	8.40	5.77	5.77	1.45
9	2-Cl	2,6-Me ₂	10	9.43	2.10	2.10	5.65
10	2-Cl	2,5-Me ₂	9.6	9.29	5.33	5.55	10.8
11	2,5-Cl ₂	2-Me	10	9.10	1.88	1.88	1.50
12	2,5-Cl ₂	2,6-Me ₂	10	9.54	3.96	3.96	13.8
13	2,6-Cl ₂	Parent	10	8.21	2.18	2.18	0.353
14	2,6-Cl ₂	2-Me	10	9.44	0.640	0.640	1.73
15	2,6-Cl ₂	2,6-Me ₂	10	10.40	0.383	0.383	9.65
16	2,6-Cl ₂	2,5-Me ₂	9.6	9.40	5.86	6.12	15.3
17	2,6-Cl ₂	3-Cl	10	8.12	1.15 ^d	1.15	0.152
18	Parent	3-MeO	2	8.56	1.81	9.05	3.30
19	2-Me	3-MeO	5	8.55	1.36	2.72	0.961
20	Parent	2-MeO	5	8.52	0.121	2.42	0.800
21	2-Me	2-MeO	20	8.56	0.988	0.495	0.180

^a From $5 \times 10^{-5} \text{ M}$ -*p*-diamine and $2 \times 10^{-4} \text{ M}$ -ferricyanide. ^b At pH 9.00. ^c Estimated as described in text. ^d Calculated from initial rate.

and methylation of the di-imine alter the rate, m , n , o , and p are the number of such substituents present, and k is the rate constant for the reaction of the parent di-imine with aniline. Owing to the uncertainty of the value of k , equation (8) was solved by a computer, as a

TABLE 6

The mean effect of substituents on the rate of coupling of *p*-benzoquinone di-imine and aniline at 30 °C and fixed pH

Di-imine		Aniline	
Substituent	Factor	Substituent	Factor
Me	0.234	2-Me	4.84
Cl	1.98	3-Me	8.94
		2-MeO	7.5
		3-MeO	35
		3-Cl	0.37

logarithmically-transformed multiple linear regression, for a , b , c , d , and k using the data for numbers 2—16 in

¹² I. Goldberg, D.R.P. 187,870 (*Chem. Zentr.*, 1907, **II**, 1465); U.S. Rubber Co., B.P. 839,420 (*Chem. Abs.*, 1960, **54**, 24,549); F. Ullmann and R. Dahmen, *Ber.*, 1980, **41**, 3751.

2,5-diaminotoluene in dimethylformamide gave a good yield (80%) of *NN*-dimethyl-4-nitroaniline. The reaction of 2-chloro-5-nitrobenzenesulphonic acid with 2,5-diaminotoluene is of no value since it would not yield an unambiguous product. Attempts to react the former with nitrotoluidines were unsuccessful. However, we have obtained adequate yields of the desired products by reaction of *p*-fluoronitrotoluenes with *p*-phenylenediamines in hot dimethyl sulphoxide. This solvent has recently been shown to enhance the rate of reaction of halogenonitroarenes with aromatic amines.¹³

EXPERIMENTAL

Materials.—The *p*-diamines and anilines were all commercial samples which were purified by recrystallisation or distillation. 4,4'-Diaminodiphenylamine sulphate was a commercial sample purified by recrystallisation from dilute sulphuric acid.

¹³ L. A. Suchcova and S. M. Shein, *Reakts. spos. org. Soedinenii*, 1969, **6**, 586 (*Chem. Abs.*, 1970, **72**, 2791); G. Ulluminati, G. Sleiter, and M. Speranza, *J. Org. Chem.*, 1971, **36**, 1723.

4'-Amino-3-methyl-4-nitrodiphenylamine.— 5-Fluoro-2-nitrotoluene (1.6 g), *p*-phenylenediamine (5.4 g), sodium hydrogen carbonate (1.0 g), and dimethyl sulphoxide (50 ml) were heated for 23 h at 125°. The cooled mixture was poured into water (500 ml) and the crude product was filtered off, washed with water, and dried. The solid was extracted with dichloromethane, and hexane was added to the extract to precipitate the *nitro-amine* (1.2 g), m.p. 137.5–139° (Found: C, 64.0; H, 5.50; N, 17.3. $C_{14}H_{13}N_3O_2$ requires C, 64.2; H, 5.35; N, 17.3%).

4'-Amino-2-methyl-4-nitrodiphenylamine.— 2-Fluoro-5-nitrotoluene (1.5 g) was reacted for 4 h with *p*-phenylenediamine (5.4 g) as described before to give the *nitro-amine* (1.7 g), m.p. 119–121° (Found: C, 64.1; H, 5.51; N, 17.5%).

4,4'-Diamino-2-methyldiphenylamine.—This compound was prepared by catalytic reduction of the aminonitrodiphenylamine (H₂-4% Pt-C) and isolated as the *dihydrochloride* (Found: C, 54.9; H, 5.98; N, 14.9. $C_{13}H_{15}Cl_2N_3$ requires C, 54.9; H, 5.28; N, 14.9%).

4,4'-Diamino-3-methyldiphenylamine.—This compound was obtained as before as the *dihydrochloride hydrate* (Found: C, 52.4; H, 5.69; N, 14.1. $C_{13}H_{17}Cl_2N_3O$ requires C, 51.6; H, 5.45; N, 13.9%).

Indamines.—(i) *p*-Phenylenediamine (2.4 g) and 2,6-xylydine (2.9 g) in water (100 ml) was added, with stirring, to a solution of potassium ferricyanide in 0.5M-sodium acetate (350 ml). Black crystals with a green reflex separated and were shown to be *3,5-dimethylindamine ferrocyanide* (Found: C, 62.5; H, 4.73; Fe, 6.0; N, 22.3. $(C_{14}H_{16}N_3)_3[Fe(CN)_6] \cdot 2H_2O$ requires C, 62.2; H, 5.73; Fe, 6.0; N, 22.3%). Similarly were prepared indamine salts from *p*-phenylenediamine and aniline and *o*-toluidine. T.l.c. showed these indamines to be free from significant impurities.

(ii) A $5 \times 10^{-5}M$ solution (9.9 ml) of the appropriate 4,4'-diaminodiphenylamine in aqueous buffer was injected with $1.2 \times 10^{-2}M$ -potassium ferricyanide (0.1 ml) and the visible spectrum was recorded immediately.

(iii) A $5 \times 10^{-5}M$ solution (9.9 ml) of the appropriate *p*-phenylenediamine in aqueous buffer containing an excess of the appropriate aniline was injected with $2.2 \times 10^{-2}M$ -potassium ferricyanide (0.1 ml) and the visible spectrum was recorded at intervals to determine the indamine spectrum before the onset of safranin formation.

Dissociation Constants.—The acid dissociation constant of indamine was determined spectrophotometrically, while those of 4,4'-diaminodiphenylamine were determined by potentiometric titration of a solution of the sulphate with sodium hydroxide, under an atmosphere of nitrogen.

Kinetics.—Kinetic experiments at $30 \pm 0.1^\circ$ were performed as described previously. Buffer solutions were prepared from AnalaR grade materials. Individual kinetic runs were reproducible to within $\pm 3\%$ and it is estimated that the rate constants are accurate to within $\pm 10\%$. Typical experimental data is given in Table 7.

TABLE 7

Experimental rate data for the reaction of *p*-benzoquinone di-imine with 2,6-xylydine at $30.0 \pm 0.1^\circ$

pH = 8.14 ^a			
Optical density ^b	Reaction (%)	t/s	k ₁ /s ⁻¹
0.36	25	2.50	0.114
0.72	50	6.25	0.110
1.08	75	12.5	0.110
1.26	87.5	19.0	0.109
1.44	100		
pH = 8.53 ^a			
0.36	25	6.0	0.047
0.72	50	15.0	0.046
1.08	75	30.5	0.045
1.44	100		

^a [*p*-Phenylenediamine] = $5 \times 10^{-5}M$; [Ferricyanide] = $2.2 \times 10^{-4}M$; [2,6-xylydine] = $1.0 \times 10^{-2}M$. ^b In a 4-cm cell at 474 nm.

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