

Colour and Constitution of the Nitro- and Dinitro-*p*-phenylenediamines and their *N*-Methyl Derivatives

By Kwong-Yung Chu and John Griffiths,* Department of Colour Chemistry, The University, Leeds LS2 9JT

The syntheses of new violet to blue-green dinitro-*p*-phenylenediamines are described. The visible absorption spectra are compared with those of the mononitro-analogues, and the light absorption characteristics have been examined by the PPP-MO procedure. Good agreement between the theoretical predictions and experiment was observed for those derivatives with minimal steric crowding. Bathochromic shifts of up to 100 nm result from the introduction of a second nitro-group into the nitro-*p*-phenylenediamine chromogen.

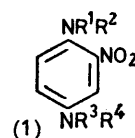
NITRO-*p*-PHENYLENEDIAMINE and various *N*-alkyl derivatives have found extensive use as low molecular-weight dyes for the colouration of hair,¹ and range from orange to violet in colour. Recently we reported the synthesis of the previously unknown 2,3- and 2,5-dinitro-*p*-phenylenediamines, and also described a convenient route to the difficultly accessible 2,6-dinitro-isomer.² The large bathochromic shifts resulting from the introduction of a second nitro-group into nitro-*p*-phenylenediamine prompted an investigation of the *N*-alkylated dinitro-compounds, to see how far the colour range of these dyes could be extended, and to examine the light absorption characteristics of these systems.

For comparison purposes we have examined the related *N*-methylated nitro-*p*-phenylenediamines. Although Corbett has discussed the absorption spectra of these compounds from an empirical viewpoint,³ no theoretical treatments have been reported. Thus we have used the PPP-SCF-MO procedure to calculate the visible absorption maxima of the mononitro-compounds, and have extended the calculations to include the dinitro-analogues. Substituent, solvent, and steric effects have been interpreted with the aid of these computations.

RESULTS AND DISCUSSION

N-Methylated Nitro-*p*-phenylenediamines.—The eight *N*-methyl derivatives (1b–i) of nitro-*p*-phenylenediamine (1a) were prepared by literature methods, or modifications of these. *N*¹,*N*⁴,*N*⁴-Trimethyl-2-nitro-*p*-phenylenediamine (1h) and the *N*¹,*N*¹,*N*⁴,*N*⁴-tetramethyl-compound (1i) have been prepared by condensation of 4-chloro-3-nitro-*N,N*-dimethylaniline at 180 °C

in a sealed tube with methylamine and dimethylamine respectively.⁴ These compounds were prepared more conveniently, and in higher yields, by condensation of the appropriate amines with 4-fluoro-*N,N*-dimethyl-3-nitroaniline in boiling ethanol. The *N*¹-methyl- and *N*¹,*N*¹-dimethyl-2-nitro-*p*-phenylenediamines, (1b) and (1d) respectively, were prepared similarly from 4-fluoro-3-nitroaniline and the appropriate amines.



	R ¹	R ²	R ³	R ⁴
a;	H	H	H	H
b;	Me	H	H	H
c;	H	H	H	Me
d;	Me	Me	H	H
e;	H	H	Me	Me
f;	H	Me	H	Me
g;	Me	Me	Me	H
h;	H	Me	Me	Me
i;	Me	Me	Me	Me

N-Methylated Dinitro-*p*-phenylenediamines.—The syntheses of 2,3-, 2,5-, and 2,6-dinitro-*p*-phenylenediamine (2a), (3a), and (4a), respectively, by nitration and subsequent hydrolysis of *N*¹,*N*⁴-bis(phenylsulphonyl)-*p*-phenylenediamine have been reported recently.² In an attempt to prepare the *N*¹,*N*⁴-dimethylated derivatives, nitration of *N*¹,*N*⁴-dimethyl-*N*¹,*N*⁴-bis(phenylsulphonyl)-*p*-phenylenediamine was examined. The latter compound proved unreactive, however, and prolonged reaction times at 100 °C afforded only starting materials. The cause of this inertness is probably steric, and similar

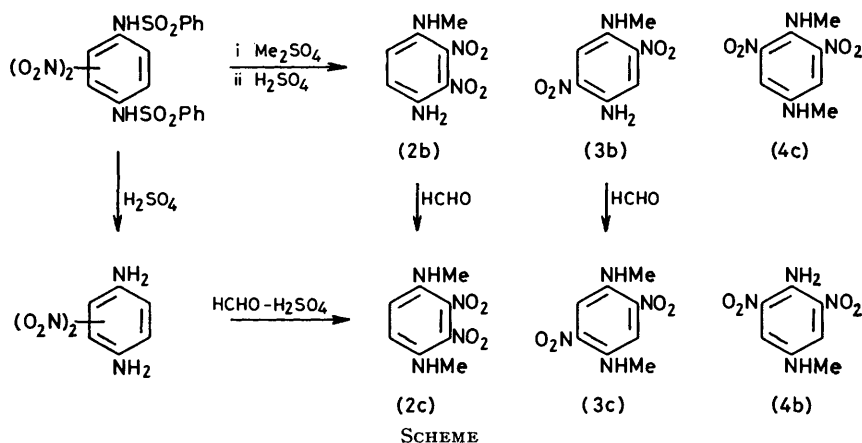
¹ J. F. Corbett, 'The Chemistry of Synthetic Dyes,' Vol. V, ed. K. Venkataraman, Academic Press, New York, 1971, pp. 508–510.

² K. Y. Chu, and J. Griffiths, *J.C.S. Perkin I*, 1978, 406.

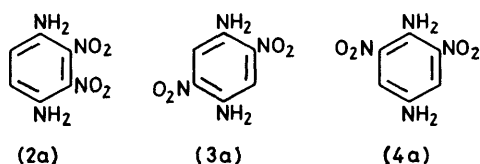
³ J. F. Corbett, *J. Soc. Dyers and Colourists*, 1967, **83**, 273; *Spectrochim. Acta*, 1967, **23A**, 2315.

⁴ J. F. Corbett and A. G. Fooks, *J. Chem. Soc. (C)*, 1967, 1136.

difficulties have been reported for the nitration of N^1, N^4 -diacetyl- N^1, N^4 -dimethyl-*p*-phenylenediamine.⁴ It was found, however, that 2,6-dinitro- N^1, N^4 -bis(phenylsulphonyl)-*p*-phenylenediamine could be dimethylated, and removal of the protective phenylsulphonyl groups afforded N^1, N^4 -dimethyl-2,6-dinitro-*p*-phenylenediamine (4c) (Scheme). Curiously, methylation of the 2,3-, and 2,5-dinitrobis(phenylsulphonyl)-compounds



gave only monomethylation, and thus the monomethylamines (2b) and (3b) were obtained after hydrolysis in concentrated sulphuric acid (see Scheme). More severe methylation conditions, using methyl iodide or dimethyl sulphate and potassium hydroxide in boiling acetone, failed to give any dimethyl derivatives, and resulted only in decomposition of starting material.



The required N^1, N^4 -dimethyl derivatives of 2,3- and 2,5-dinitro-*p*-phenylenediamine were obtained by direct methylation of the free amines with formaldehyde in sulphuric acid at 50 °C.⁵ Thus the red (2c) and blue (3c) were obtained in 59 and 89% yields respectively (see Scheme). Interestingly, methylation of the 2,6-dinitro-amine by this procedure afforded only a monomethyl-derivative, and on steric grounds this was presumed to be the N^4 -methyl compound (4b). It was found that hydrolysis of the protected bis(phenylsulphonyl) derivatives and subsequent methylation with formaldehyde could be achieved in one reaction sequence, thus greatly simplifying the preparation of the methyl-derivatives (2c), (3c), and (4b).

Electronic Absorption Spectra.—The visible absorption spectra of the mono- and di-nitro compounds were measured in cyclohexane, dichloromethane, and absolute

ethanol, and the extinction coefficients for the longest wavelength band were determined in the first solvent.

The absorption spectra were calculated by the PPP-SCF-MO method, using a limited configuration interaction treatment including the first nine singly excited singlet states. The success of this procedure in handling related donor-acceptor substituted benzene chromophores⁶ indicates its general usefulness and, provided

strictly planar structures are considered, the results of such calculations can be as useful as the considerably more lengthy all-valence electron procedures. An empirical procedure was adopted for the evaluation of suitable parameters, and it was found that published values⁷ for the nitro-group did not give satisfactory results for the nitroanilines, which were used as model compounds. Better nitro-parameters are listed in Table I, and these gave excellent agreement between the predicted and experimental absorption maxima of the nitroanilines. Parameters for the amino- and dimethylamino-group have been described elsewhere,⁸ and those for the methylamino-group were evaluated empirically (Table I). For all the compounds studied a planar

TABLE I

New parameters used in the PPP calculations					
Bond type X-Y	Z_Y^a	β_{XY}/eV	$VSIP_Y/\text{eV}^b$	A_Y/eV^c	$r_{XY}/\text{Å}^d$
C-N (methylamino)	2	-2.75	18.5	9.26	1.38
C-N (nitro)	2	-2.0	24.8	12.5	1.49
N-O	1	-3.05	16.3	1.8	1.21

^a Number of π electrons contributed by the atom. ^b Valence state ionisation potential. ^c Electron affinity. ^d Bond length.

geometry was assumed, although certain of these are known to deviate appreciably from molecular coplanarity. Hydrogen bonding between mutually *ortho* amino- and nitro-groups was neglected in these calculations, as this should have only a relatively minor effect on the absorption spectra.

⁵ A. Halasz, *Chem. and Ind.*, 1969, 1701.

⁶ J. Griffiths, M. Lockwood, and B. Roozpekar, *J.C.S. Perkin II*, 1977, 1608.

⁷ H. Labhart and G. Wagnière, *Helv. Chim. Acta*, 1963, **46**, 1314.

⁸ J. Griffiths and M. Lockwood, *J.C.S. Perkin I*, 1976, 48.

Corbett has examined the electronic absorption spectra of the mononitro-*p*-phenylenediamines,³ and by relating the two longest wavelength bands to those of nitrobenzene a set of empirical relationships have been derived for predicting the λ_{\max} values of these and other

evident from a consideration of absorption intensities that mono-methylation of an amino-group causes little steric interaction with an adjacent nitro-group. The hydrogen bond existing between the two groups may serve to preserve molecular coplanarity.

TABLE 2
Experimental and calculated spectral data for the mononitro-*p*-phenylenediamines (1)

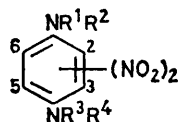
Compd.	R ¹	R ²	R ³	R ⁴	$\lambda_{\max}(\text{exp.})/\text{nm}$			$\frac{\epsilon_{\max}}{\text{l mol}^{-1} \text{cm}^{-1}}$ (C ₆ H ₁₂)	$\lambda_{\max}(\text{calc.})$ nm	f^a (calc.)
					C ₆ H ₁₂	EtOH	CH ₂ Cl ₂			
(1a)	H	H	H	H	441	473	465	3 900	461	0.18
(1b)	Me	H	H	H	472	498	500	5 100	473	0.18
(1c)	H	H	H	Me	459	498	485	3 790	468	0.17
(1d)	Me	Me	H	H	429	440	461	1 400	485	0.17
(1e)	H	H	Me	Me	461	484	491	3 300	474	0.16
(1f)	H	Me	H	Me	489	520	520	4 800	480	0.17
(1g)	Me	Me	Me	H	435	451	479	1 100	492	0.16
(1h)	H	Me	Me	Me	489	505	522	4 500	487	0.16
(1i)	Me	Me	Me	Me	423	445	468	1 200	501	0.16

^a Oscillator strength.

amino- and hydroxy-substituted nitrobenzenes. Examination of the PPP calculations for the nitro- and dinitro-*p*-phenylenediamines show, however, that the visible absorption bands are complex transitions, involving predominantly electron-density migration

It is interesting that the bathochromic shift accompanying methylation, which is due to the increase in electron donating strength of the amino-group, depends critically on the position of the amino-group involved. Thus methylation of an amino-group *ortho* to nitro gives

TABLE 3
Experimental and calculated spectral data for the dinitro-*p*-phenylenediamines



Compd.	R ¹	R ²	R ³	R ⁴		$\lambda_{\max}(\text{exp.})/\text{nm}$			$\frac{\epsilon_{\max}}{\text{l mol}^{-1} \text{cm}^{-1}}$ (C ₆ H ₁₂)	$\lambda_{\max}(\text{calc.})$ nm	f (calc.)
						C ₆ H ₁₂	EtOH	CH ₂ Cl ₂			
2,3-Dinitro	H	H	H	H	(2a)	472 ^a	491	474	4 200 ^a	455	0.31
	Me	H	H	H	(2b)	499	512	507	6 300	465	0.32
	Me	H	Me	H	(2c)	530	539	539	6 900	478	0.32
2,5-Dinitro	H	H	H	H	(3a)	518	560	540	4 600	489	0.29
	Me	H	H	H	(3b)	558	592	588	4 950	506	0.28
	Me	H	Me	H	(3c)	596	624	632	5 050	520	0.27
2,6-Dinitro	H	H	H	H	(4a)	498	516	512	3 280	464	0.33
	H	H	H	Me	(4b)	519	548	540	6 760	476	0.32
	Me	H	Me	H	(4c)	504	532	525	5 060	489	0.32

^a Measured in benzene because of low solubility in cyclohexane.

from the amino- to the nitro-group(s). Thus additive wavelength correlations with nitrobenzene probably have little theoretical significance.

The experimental and calculated spectral data for the mononitro-*p*-phenylenediamines (1) are summarised in Table 2. The predicted wavelength values are in good agreement with the experimental values measured in cyclohexane, with the exception of those compounds possessing an *N,N*-dimethylamino-group *ortho* to the nitro-group. The latter compounds, *i.e.* (1d), (1g), and (1i), will possess steric crowding, causing the amino- and nitro-groups to rotate out of full conjugation with the benzene ring. Thus hypsochromic shifts occur, and the theoretical λ_{\max} values are overestimated. The deviations from planarity are clearly indicated by the low extinction coefficients of these compounds. It is also

greater shifts than for methylation of a *meta*-amino-group. This suggests that the 1-amino-group is the dominant auxochrome, and the theoretical treatment predicts this effect well. The most bathochromic member of the nitro-series is the *N*¹,*N*⁴,*N*⁴-trimethyl derivative (1h) [λ_{\max} (CH₂Cl₂) 522 nm] which is violet. The red tetramethyl compound (1i) absorbs at shorter wavelengths (468 nm) because of steric crowding, and its absorption intensity is correspondingly low.

The experimental and calculated spectral data for the dinitro-*p*-phenylenediamines are given in Table 3. The introduction of a second nitro-group into the mononitro compounds (1) produces a general bathochromic shift of the visible band and the magnitude of the shift is dependent on the relative orientation of the two nitro-groups. Thus when the two nitro-groups are mutually

para (i.e. 2,5) the shift in cyclohexane is of the order of 77–107 nm, whereas for the *meta* (2,6) orientation this is 15–57 nm, and for the *ortho* (2,3) orientation 27–41 nm. Thus for any given series of dinitro-derivatives the λ_{max} values generally follow the order 2,5 > 2,6 > 2,3. For the N^1, N^4 -dimethyl compounds, however, the order is 2,5 > 2,3 > 2,6, and this can be attributed to the anomalous 2,6-isomer (4c) which has a bulky methyl-amino-group between two *ortho* nitro-groups. In this derivative only will loss of planarity occur, thus causing it to absorb at shorter wavelengths. This dependence of wavelength on the relative orientation of the nitro-groups is predicted accurately by the MO calculations (Table 3). Absolute agreement between the theoretical λ_{max} values and experiment is not as good as in the mononitro-series, however.

The most bathochromic member of the dinitro-series, i.e. N^1, N^4 -dimethyl-2,5-dinitro-*p*-phenylenediamine (3c), is predicted correctly, and this compound is blue-green in colour. The dinitro-compounds in general augment the shades provided by the mononitro-compounds, and give violet to blue-green colours on polymeric substrates.

All the nitro-dyes show a positive solvatochromism between cyclohexane as solvent and dichloromethane or ethanol, and it is evident that the shifts are dependent on the hydrogen bonding characteristics of the solvent. For example, many of the higher alkylated mononitro-compounds show smaller shifts in ethanol than in dichloromethane. In the dinitro-series the solvatochromic shifts are more consistent, and are always greater in dichloromethane. The charge-transfer character of the visible transition of the nitro-*p*-phenylenediamines results in an excited state of greater polarity than the ground state, and thus a positive solvatochromism is to be expected.

EXPERIMENTAL

N^1, N^4, N^4 -Trimethyl-2-nitro-*p*-phenylenediamine (1h).—4-Fluoro-*NN*-dimethyl-3-nitroaniline (1.1 g) and methylamine (33% ethanolic solution, 10 ml) in ethanol (30 ml) were heated under reflux for 24 h. Water (15 ml) was added and the ethanol removed under reduced pressure to give black crystals, which were filtered off and dried (0.95 g, 81.5%). Recrystallisation from a mixture of benzene-petroleum (b.p. 80–100 °C) gave (1h) as very dark, lustrous crystals, m.p. 97–98 °C (lit.,⁴ 100 °C).

N^1, N^1, N^4, N^4 -Tetramethyl-2-nitro-*p*-phenylenediamine (1i).—4-Fluoro-3-nitro-*NN*-dimethylaniline (0.8 g) was treated with dimethylamine (33% ethanolic solution, 12 ml) in ethanol (20 ml) as described for (1h). The product (1i) (0.76 g, 84%) was obtained as a dark red oil, homogeneous by t.l.c. analysis. The physical properties and absorption spectrum in ethanol were identical to those reported by Corbett.⁴

N^4, N^4 -Dimethyl-2-nitro-*p*-phenylenediamine (1e).—4-Fluoro-*N, N*-dimethyl-3-nitroaniline (0.55 g) and aqueous ammonia (d 0.88; 10 ml) were heated in ethanol (100 ml) at 110–120 °C for 24 h in a steel autoclave. The red solution was evaporated to near dryness and diluted with water (30 ml). The precipitated solid was purified by chromatography (alumina; benzene-dichloromethane 1 : 1), giving

very dark red crystals of (1e) (0.31 g, 56%), m.p. 108–110 °C (lit.,⁹ 112 °C).

N^1 -Methyl-2,5-dinitro-*p*-phenylenediamine (3b).—2,5-Dinitro- N^1, N^4 -bis(phenylsulphonyl)-*p*-phenylenediamine ² (0.2 g) was dissolved in sodium hydroxide solution (1*N*; 100 ml) and stirred vigorously with an excess of dimethyl sulphate at room temperature. The pH of the mixture was kept above 8–9 by the addition of more sodium hydroxide as required. After 15 h the precipitate was filtered off, washed with water, and dried, giving the lemon yellow monomethylated derivative (0.17 g, 84%), m.p. 273–274 °C (decomp.). The methyl derivative was dissolved in concentrated sulphuric acid (25 ml) and kept at 15 °C for 30 h. When the mixture was poured into water a blue precipitate formed, which was filtered off and recrystallised from benzene, giving N^1 -methyl-2,5-dinitro-*p*-phenylenediamine (3b) as blue crystals (0.053 g, 72%), m.p. 216 °C (Found: C, 39.6; H, 4.0; N, 26.4. $C_7H_8N_4O_4$ requires C, 39.6; H, 3.8; N, 26.4%), ν_{max} (KBr) 3 390, 3 425, and 3 500 cm^{-1} .

N^1 -Methyl-2,3-dinitro-*p*-phenylenediamine (2b).—2,3-Dinitro- N^1, N^4 -bis(phenylsulphonyl)-*p*-phenylenediamine ² (0.3 g) was methylated as described for the 2,5-dinitro-isomer. Hydrolysis of the monomethylated derivative in concentrated sulphuric acid gave N^1 -methyl-2,3-dinitro-*p*-phenylenediamine (2b) as dark red plates (0.051 g, 48%), m.p. 187 °C (M^+ 212; calc. for $C_7H_8N_4O_4$, M 212).

N^1, N^4 -Dimethyl-2,6-dinitro-*p*-phenylenediamine (4c).—2,6-Dinitro- N^1, N^4 -bis(phenylsulphonyl)-*p*-phenylenediamine ² was methylated with an excess of dimethyl sulphate as described for the 2,5-dinitro-isomer. The N^1, N^4 -dimethyl derivative (0.13 g, 75%) was hydrolysed in concentrated sulphuric acid to give N^1, N^4 -dimethyl-2,6-dinitro-*p*-phenylenediamine (4c) as very dark red, lustrous needles (0.056 g, 94%), m.p. 120 °C (M^+ 226; calc. for $C_8H_{10}N_4O_4$, M 226), ν_{max} (KBr) 3 340 and 3 437 cm^{-1} .

N^1, N^4 -Dimethyl-2,5-dinitro-*p*-phenylenediamine (3c).—(a) 2,5-Dinitro-*p*-phenylenediamine ² (0.10 g) was dissolved in concentrated sulphuric acid (10 ml) and treated with methanolic formaldehyde solution (37%, 2 ml) at ca. 50 °C. After 3 h at this temperature, the mixture was poured onto ice, neutralised with ammonium hydroxide solution, and the blue precipitate filtered off. Recrystallisation from benzene gave N^1, N^4 -dimethyl-2,5-dinitro-*p*-phenylenediamine (3c) as lustrous black plates (0.102 g, 89%), m.p. 277 °C (dec.) (Found: C, 42.2; H, 4.5; N, 25.0. $C_8H_{10}N_4O_4$ requires C, 42.5; H, 4.4; N, 24.8%), ν_{max} (KBr) 3 420 cm^{-1} .

(b) 2,5-Dinitro- N^1, N^4 -bis(phenylsulphonyl)-*p*-phenylenediamine ² (0.1 g) was dissolved in concentrated sulphuric acid (10 ml), and after 30 h at 15 °C further sulphuric acid (3 ml) and methanolic formaldehyde solution (37%; 1 ml) were added. The temperature was raised to 50 °C for 4.5 h, and the mixture poured over ice. The blue precipitate, after purification by column chromatography (alumina; benzene) gave (3c) as black plates (0.034 g, 72%), identical to the product from (a).

N^1, N^4 -Dimethyl-2,3-dinitro-*p*-phenylenediamine (2c).—2,3-Dinitro- N^1, N^4 -bis(phenylsulphonyl)-*p*-phenylenediamine ² (0.1 g) was hydrolysed in concentrated sulphuric acid (10 ml) at 15 °C for 30 h. Sulphuric acid (3 ml) and methanolic formaldehyde solution (37%, 1 ml) were added, and the mixture heated at 50 °C for 45 min. The mixture was

⁹ H. H. Hodgson and J. H. Crook, *J. Chem. Soc.*, 1932, 2976.

poured over ice and neutralised with ammonium hydroxide solution to give a purple solution which was extracted with ether. Removal of the solvent from the ethereal extracts gave a dark solid, homogenous by t.l.c. Recrystallisation from benzene-petroleum (b.p. 80—100 °C) gave *N*¹,*N*⁴-dimethyl-2,3-dinitro-*p*-phenylenediamine (2c) as black leaflets (0.028 g, 59%), m.p. 171—172 °C (Found: C, 42.7; H, 4.4; N, 24.3. C₈H₁₀N₄O₄ requires C, 42.5; H, 4.4; N, 24.8).

*N*⁴-Methyl-2,6-dinitro-*p*-phenylenediamine (4b).—2,6-Dinitro-*p*-phenylenediamine² (0.1 g) was methylated with formaldehyde-sulphuric acid as described for the preparation of (3c). Recrystallisation of the crude product from benzene-petroleum (b.p. 80—100 °C) gave *N*⁴-methyl-2,6-

dinitro-p-phenylenediamine (4b) as black needles with a metallic lustre (0.085 g, 79%), m.p. 200—201 °C (Found: C, 40.2; H, 4.0; N, 26.2. C₇H₈N₄O₄ requires C, 39.6; H, 3.8; N, 26.4%), ν_{\max} (KBr) 3 350, 3 395, and 3 465 cm⁻¹. The same compound was formed in 56% yield by hydrolysis of 2,6-dinitro-*N*¹,*N*⁴-bis(phenylsulphonyl)-*p*-phenylenediamine and subsequent methylation in concentrated sulphuric acid as described for (3c).

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