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Azo Pigments and their Intermediates. Effect of Substitution on the Diazotization and Coupling Reactions of *o*-Hydroxyanilines

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ABSTRACT

The effects of substituents on the diazotization and coupling reactions of o-*hydroxyanilines have been studied. When the substituent is a strong electron-withdrawing group, e.g.* NO_2*, the resulting substituted 2-hydroxy-1-benzenediazonium chloride is highly acidic, even in aqueous hydrochloric acid solution. It deprotonates and forms the corresponding substituted 1,2-benzoquinone-1-diazide. For less electron-withdrawing or even electron-releasing substituents, the so-generated diazonium chlorides are soluble in the aqueous hydrochloric acid solution. These diazotized products are isolated as hexafluorophosphate salts. The coupling reactions between various diazotized products of* o-*hydroxyanilines and 2-hydroxy-3-naphthanilide are shown to proceed through the 1,2-benzoquinone-1-diazide intermediate, regardless of their original structure. Synthetic results show that the substituted 1,2-benzoquinone-1-diazide intermediate is only reactive when it is activated by a substituent that is more electron-withdrawing than the chloro group.*

1 INTRODUCTION

*C*harge *c*ontrol *a*gents (CCA) are additives that are used in a dry toner to maintain and regulate the charge level of a toner in the developer.[1] For negative black toner application, acidified carbon blacks have been found to serve a dual function in toners.[2] They are black colorants as well as negative

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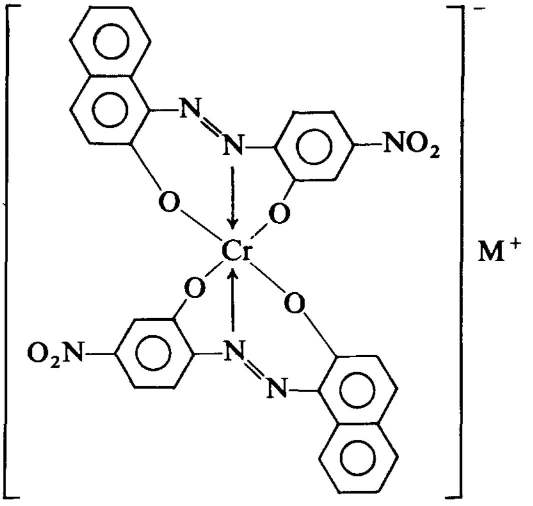
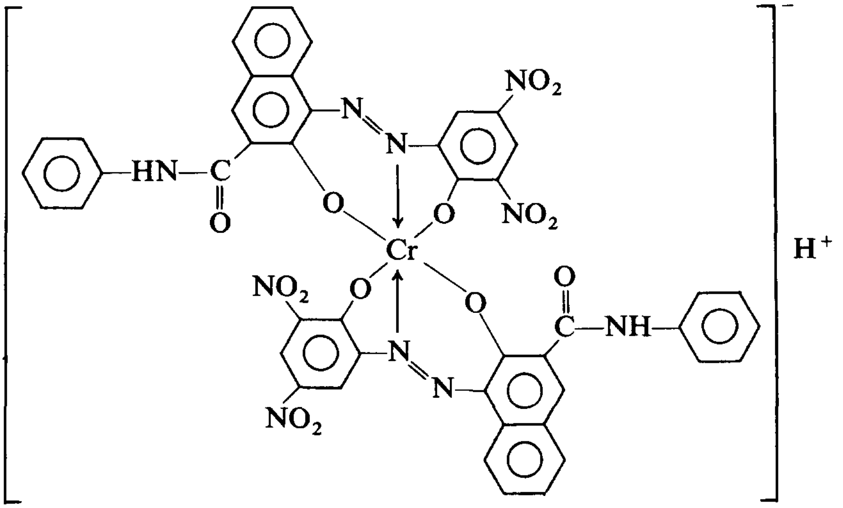


CI Acid Black (Bontron S31)



Aizen Spilon Black TRH

Formula 1

CCAs. Recent work by Birkett and Gregory as well as researchers at Hodogaya showed that 1:2 Cr/azo complexes, such as Bontron S31 and Aizen Spilon Black TRH (Formula 1), are effective negative CCAs. They not only enhance the negative charging in toners, but also improve the copy quality.[3-5] Macholdt and Sieber[6,7] further showed that, among the 6–7 different chemical classes that were examined in their CCA study, azo pigments and their chromium complexes were the most potent negative CCA classes found. Prompted by these findings, we felt that a structure–property relationship study on the charging characteristic of Cr/azo complexes was warranted. Only with such knowledge can the rational design and synthesis of materials with improved charging properties be achieved. We therefore initiated a systematic effort to synthesize a number of azo ligands by coupling substituted *o*-hydroxyanilines with 2-hydroxy-3-naphthanilide. Strong substituent effects on both diazotization and coupling reactions were observed. The subsequent effects are discussed in terms of an electronic effect.

2 EXPERIMENTAL

2.1 Materials

Picramic acid was purchased as the sodium salt from Sigma; it was converted to the free acid with hydrochloric acid and then purified by solvent extraction. 2-Amino-4-nitrophenol (96%), 2-amino-5-nitrophenol (99%), 5-chloro-2-hydroxyaniline (97%), 2-aminophenol (99%), 2-amino-*p*-cresol (97%), anhydrous sodium acetate (gold label) and ammonium hexafluorophosphate (99%) were obtained from Aldrich. *N*,*N*-Dimethylformamide (DMF), acetone, concentrated hydrochloric acid, sodium nitrite and diethyl ether (anhydrous) were reagent certified grade from Fisher. All these materials were used as received. 2-Hydroxy-3-naphthanilide was bought from Aldrich. It was recrystallized from a mixture of DMF and water before use.

2.2 General techniques

Melting points were taken on a capillary melting point apparatus (Thomas Hoover) and were uncorrected. Infrared spectra were determined on a Perkin–Elmer model 1750 FTIR. ^{13}C NMR spectra were recorded in DMSO-d_6 (from Merck) on a Bruker AM 360 spectrometer. Elemental analyses were performed by Galbraith laboratories.

2.3 Diazotization of substituted *o*-hydroxyanilines

A dispersion of the hydrogen chloride salt of a substituent σ-hydroxyanaline was prepared by stirring 0·02 mol of the *o*-hydroxyaniline in an aqueous solution containing 8 ml of concentrated HCl and 80 ml of water. The dispersion was then cooled to 0–5°C by an ice-water bath. An aqueous $NaNO_2$ solution (2 g in 5 ml of water) was added dropwise over about 30 min. When the substituent was a NO_2 group, the diazotized product precipitated out of the solution as a yellow solid. In this case, the product was isolated by filtration and purified by washing with cold water and cold methanol. When the substituent was Cl, H or CH_3, the diazotized solution was dark brown. A concentrated aqueous solution of ammonium hexafluorophosphate (0·04 mol) was added and the precipitated hexafluorophosphate salt was isolated by filtration.

2.4 Coupling reactions between the diazotized products of substituted *o*-hydroxyanilines and 2-hydroxy-3-naphthanilide

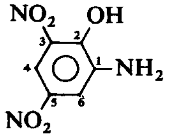
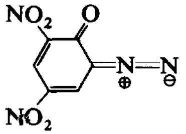
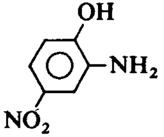
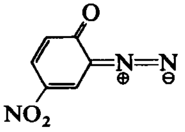
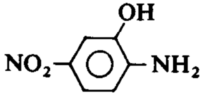
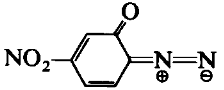
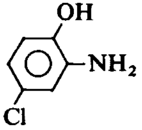
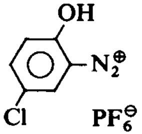
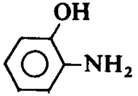
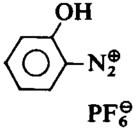
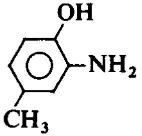
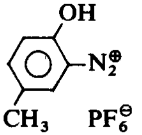
The above diazotized products were dissolved in ~80 ml of cold DMF in a 500 ml three-neck flask, which was surrounded by an ice-water bath. A cold DMF solution containing 5·3 g of 2-hydroxy-3-naphthanilide in ~80 ml of DMF was introduced over a period of ~30 min. A brown solution was obtained. A cold solution containing 10 g of NaOAc in 150 ml of water was added into the DMF mixture over 30 min. After the addition was completed, the product mixture was stirred at room temperature overnight. The coupling product, if formed, was isolated by filtration. It was then purified by washing with warm water (2 × 250 ml, at ~80°C), acetone (3 × 250 ml) and ether. After vacuum drying, a purified monoazo compound was obtained. The synthetic data and the spectroscopic properties of these materials are tabulated in Tables 1 and 2.

3 RESULTS AND DISCUSSION

3.1 Effect of substitution on the diazotization of *o*-hydroxyanilines

Substituted *o*-hydroxyanilines could be diazotized in an aqueous hydrochloric acid solution at 0–5°C. When the substituent was a nitro group, the diazotized products precipitated out of the reaction liquor and were isolated by filtration as yellow or orange solids. When the substituent was less electron-withdrawing than a nitro group, such as Cl, H and CH_3, the diazotized products were soluble in the reaction mixture and were isolated as hexadluorophosphate salts using ammonium hexafluorophosphate as precipitating agent. The isolated products were yellow or orange yellow solids. The reactions are summarized in Scheme 1. The yields and the spectroscopic properties of these materials are given in Table 1.

TABLE 1
Synthesis and Characterization of the Diazotized Products from *o*-Hydroxyanilines

	o-*Hydroxyaniline*	*Structure of diazotized product*	*Yield*[a]	*IR*[b]	^{13}C *chemical shift*[c]					
					C1	*C2*	*C3*	*C4*	*C5*	*C6*
I			~94%	2 220 (s), 2 230 (w)	99·3	164·3	129·2	129·2	148·8	134·6
II			~95%	2162 (m), 2190 (s)	90·7	174·8	124·1	132·1	132·6	129·7
III			85%	2150 (s), 2190 (s)	92·8	174·9	106·0	155·4	117·8	129·5
IV			89%	2203 (s)	90·8	173·0	116·8	140·3	124·1	124·2
V			81%	2220 (m), 2230 (m), 2248 (s)	94·7	169·6	117·9	141·0	120·1	128·6
VI			78%	2240 (s)	94·9	167·5	119·5	143·4	128·0	126·0

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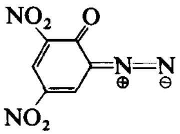
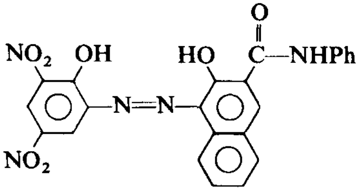
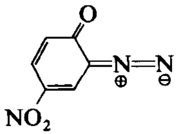
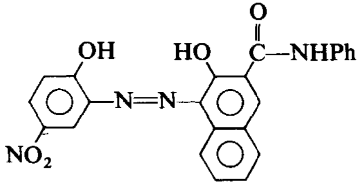
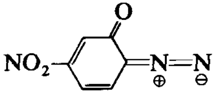
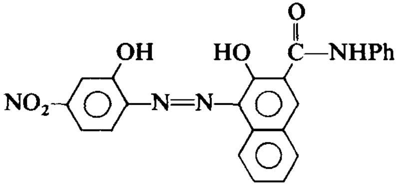
[a] Isolated yield.

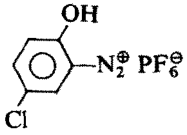
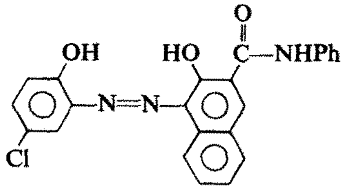
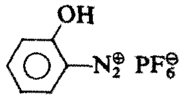
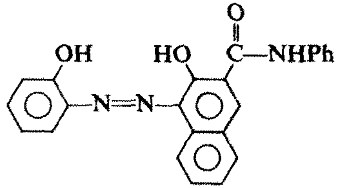
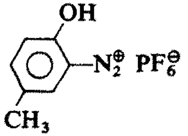
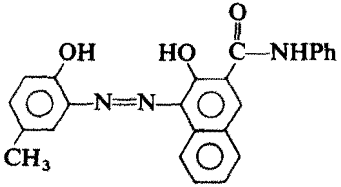
[b] In KBr, in cm^{-1}; s, m and w denote strong, medium and weak, respectively.

[c] In DMSO-d_6, ppm from TMS; the labelling system is given in Structure 1.

TABLE 2

Coupling Reactions between the Diazotized Products of Substituted *o*-Hydroxyanilines and 2-Hydroxy-3-naphthanilide

Starting material	*Structure of monoazo dye*	*Yield*	*M.p.*[a]	*IR*[b]	*Elemental analysis*			
						C	*H*	*N*
		95%	>310°C	1678 cm^{-1}	Calc'd:[c] Found:	56·21 56·40	3·49 3·16	14·25 13·91
		80%	291–293°C	1660, 1670 cm^{-1}	Calc'd:[c] Found:	61·88 62·31	4·06 4·01	12·55 12·08
		65%	>310°C	1660 cm^{-1}	Calc'd: Found:	64·48 64·22	3·76 4·02	13·08 12·77

		70%	282°C (dec)	1658 cm^{-1}	calcd Found:	66·11 65·53	3·86 4·05	10·05 10·01
		Trace	—	—	—	—	—	—
		Trace	—	—	—	—	—	—

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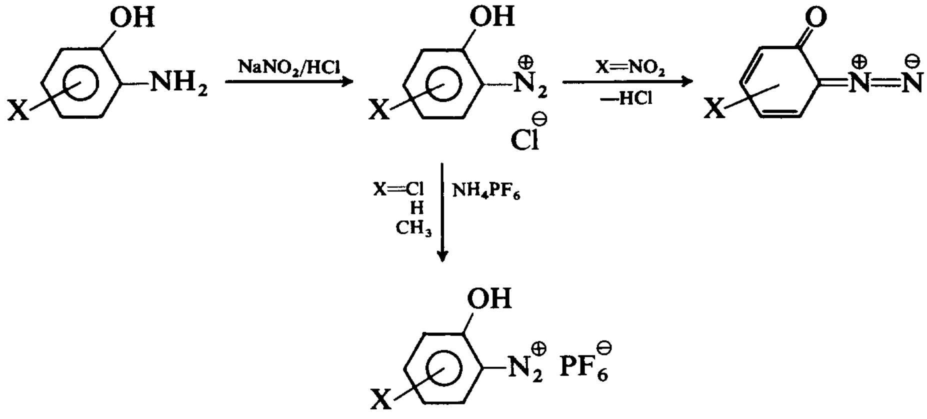
[a] Melting point (°C).

[b] In KBr pellet, amide carbonyl stretchings.

[c] Monohydrate of the dye.



Scheme 1

The diazotized products were characterized by IR and solution ^{13}C NMR spectroscopy (Table 1). In the IR spectra, none of them exhibited any N—H stretchings that are characteristic of the starting *o*-hydroxyanilines. In addition to the aromatic C—H stretches at 3100 ± 20 cm^{-1}, very characteristic bands, attributable either to a diazo ($C{=}\overset{+}{N}{=}\bar{N}$) or a diazonium ($\overset{+}{N}{\equiv}\bar{N}$) group, are observed at 2150–2250 cm^{-1}.[8-12] Although there is a trend (except Structure I) that this band shifts to higher frequencies, from 2200 to 2250 cm^{-1}, as the substituent becomes increasingly electron-releasing, the IR data along do not allow a clear distinction between the diazo and diazonium functions.

The ^{13}C NMR spectra of all diazotized products were studied in DMSO-d^6. All the compounds showed a characteristic upfield carbon resonance at 90–100 ppm, attributable to the carbon adjacent either to a diazonium or a diazo group.[13,14] Chemical-shift assignments were first made with the diazotized product of *o*-hydroxyaniline. The chemical shifts of all other compounds were assigned based on known substituent induced shifts.[15] The data are tabulated in Table 1. Due to the strong substituent effect on the chemical shift of C1, a clear distinction between a diazo or a diazonium functionality again cannot be made from the ^{13}C NMR data.

Anderson *et al.*[16,17] reported the determination of the dipole moment of the diazotized product of 2-hydroxy-3,5-dibromoaniline and they concluded from the low dipole moment that the diazotized product is 3,5-dibromo-1,2-benzoquinone-1-diazide. Without product isolation, they further generalized that the structure of the diazotized product of *o*-hydroxyaniline is 1,2-benzoquinone-1-diazide. As shown later in this paper, this generalization is incorrect. The diazotized product from *o*-hydroxyaniline as a diazonium salt.

When the *o*-hydroxyaniline was substituted with a nitro group, the diazotized product precipitates out of the aqueous hydrochloric acid solution (Scheme 1). One the other hand, when the substituent is Cl or CH_3 or H, the diazotized product remained in the aqueous hydrochloric acid solution. The diazotized product was isolated as a hexafluorophosphate salt. Thus, in the case of nitro substituted *o*-hydroxyanilines, if these diazotized products are diazonium salts, the counter anion would be a choride anion. In this work, we synthesized 2-hydroxyl-1-benzenediazonium chloride in acetic acid using the *n*-amyl nitrite method.[18] This diazonium chloride and the diazotized product from 2-hydroxy-3,5-dinitroaniline (**I**) were dissolved in a mixture of water and DMF (1:1) separately. The two solutions were then titrated with an aqueous solution of $AgNO_3$. While white precipitates of AgCl with a recovery of 99·7% of theory (after vacuum drying) were obtained for the 2-hydroxy-1-benzenediazonium chloride solution, no precipitate was observed for the solution containing the diazotized product from **I**. The absence of the chloride anion leads to the conclusion that the diazotized product from **I** is 3,5-dinitro-1,2-benzoquinone-1-diazide. By analogy (Scheme 1), the diazotized products from *o*-hydroxyanilines **II** and **III** are 1,2-benzoquinone-1-diazides also. We also propose that, in the case of *o*-hydroxyanilines **IV**, **V** and **VI**, the diazotized products are the diazonium chlorides. These diazonium chlorides are soluble in aqueous solution and the products can only be isolated when precipitated as hexafluorophosphate salts.

The *o*-hydroxyanilines **I**–**III** are substituted by one or more nitro groups. The formation of *o*-benzoquinonediazides from these compounds suggests that the diazonium chlorides of **I**–**III** are actually formed. Due to the strong electron-withdrawing nature of the nitro and the diazonium[19] groups, the OH protons in these diazonium chlorides become very acidic, even in aqueous hydrochloric acid solution. These nitro substituted *o*-hydroxydiazonium salts deprotonate and form the corresponding substituted *o*-benzoquinonediazides.

When the substituent is less electron-withdrawing or even electron-releasing, the substituted *o*-hydroxydiazonium salts are presumably not as acidic and remain as diazonium chlorides in the hydrochloric acid solution. The diazonium salts become isolable when precipitated as hexafluorophosphate salts.

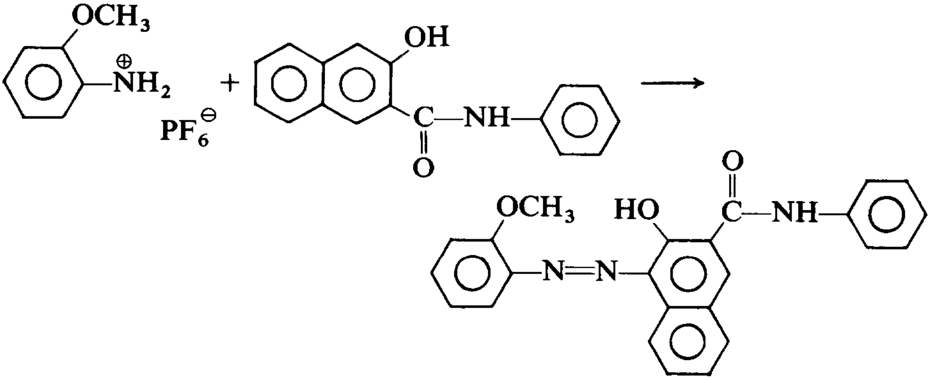
3.2 Effect of substituent on the coupling reaction

Attempts were made to couple the diazotized products from **I**–**V** with 2-hydroxy-3-naphthanilide in DMF. Sodium acetate was used as a base catalyst for the reaction. The synthetic data, along with the physical properties of the monoazo dyes are tabulated in Table 2. All synthesized dyes are high melting, red-brown solids. They exhibit characteristic carbonyl stretches between 1655 and 1678 cm^{-1}. The frequencies are higher than those in the couplers and are attributable to the amide C=O stretches in the monoazo dyes.

The synthetic data indicate that there is a strong substituent effect on the coupling reaction. For relatively electron-rich diazonium salts, such as 2-hydroxybenzene-1-diazonium and 2-hydroxy-5-methylbenzene-1-diazonium hexafluorophosphate, monoazo dyes, if formed, are probably less than 5%. Although the coupling product solutions are red in color, analyses of the recovered solids reveal that the product solutions consist primarily of the coupler. The use of higher reaction temperatures and stronger bases (NaOH and triethanolamine) did not result in any yield improvement.

The diazonium group is known to be a very powerful electron-withdrawing group.[19] The *o*-hydroxydiazonium salts in Table 1 are expected to be acidic. It is then anticipated that the addition of the aqueous sodium acetate solution to the coupling mixtures would result in deprotonation of the *o*-hydroxydiazonium salts, forming the corresponding 1,2-benzoquinone-1-diazides. Thus, substituted 1,2-benzoquinone-1-diazides are intermediates of the coupling reaction. The inability of 5-methyl-1,2-benzoquinone-1-diazide and 1,2-benzoquinone-1-diazide to couple with 2-hydroxy-3-naphthanilide to form products simply indicates that these 1,2-benzoquinone-1-diazides are not strong enough electrophiles for the coupling reaction.

To support the above model, we synthesized 2-methoxybenzene-1-diazonium hexafluorophosphate and examined its coupling reaction with 2-hydroxy-3-naphthanilide (Scheme 2). Under identical coupling conditions, a monoazo dye was isolated in 75% yield.[21] This observation suggests that the lack of coupling reactions from the diazotized products of



Scheme 2

o-hydroxyanilines **V** and **VI** is indeed due to the low reactivity of the 1,2-benzoquinone-1-diazide intermediates. We have shown above, that a diazonium salt bearing an electron-releasing substituent is still reactive in the coupling reaction.

4 CONCLUSIONS

It has been shown that there is a strong substituent effect on the diazotization of substituted *o*-hydroxylanilines in aqueous hydrochloric acid solution. When the substituent is strongly electron-withdrawing, such as a nitro group, the diazotized product, a nitro substituted 2-hydroxy-1-benzenediazonium chloride, deprotonates and forms a nitro substituted 1,2-benzoquinone-1-diazide. The nitro substituted 1,2-benzoquinone-1-diazide usually precipitates out of the product solution. For less acidic diazotized products, the diazonium chlorides are soluble in the aqueous solutions. These diazonium salts are isolable as hexafluorophosphate salts using ammonium hexafluorophosphate as a precipitating agent.

A strong substituent effect on the coupling reaction is also observed. Evidence is provided that all the coupling reactions proceed through the 1,2-benzoquinone-1-diazide intermediate. Our data show that 1,2-benzoquinone-1-diazides are reactive in the coupling reaction only when they are activated by an electron-withdrawing group that is more potent than the chloro group.

REFERENCES AND NOTE

1. Gruber, R. J. & Julien, P. C., In *Handbook of Imaging Materials*, ed. A. S. Diamond. Marcel Dekker, New York, 1991.
2. Julien, P. C., In *Carbon Black–Polymer Composites*, ed. E. K. Sichel. Marcel Dekker, New York, 1982.
3. Birkett, K. L. & Gregory, P., *Dyes Pigm.*, **7** (1986) 341.
4. Niimura, I., Imagome, H., Yamaga, H., Akuzawa, N., Yuta, K. & Kurahashi, T., US Patent 4,433,040, 1984.
5. Hsieh, B. R., *Dyes Pigm.*, **14** (1990) 287.
6. Macholdt, H. T. & Sieber, A., *J. Imaging Technol.*, **14** (1988) 89.
7. Macholdt, H. T. & Sieber, A., *Dyes Pigm.*, **9** (1988) 119.
8. Whetsel, K. B., Hawkins, G. F. & Johnson, E. F., *J. Am. Chem. Soc.*, **78** (1956) 3360.
9. Aroney, M., LeFevre, J. W. & Werner, R., *J. Chem. Soc.*, (1955) 276.
10. Crawford, B. L., Fletcher, W. H. & Ramsay, D. A., *J. Chem. Phys.*, **19** (1951) 406.
11. Fahr, E., *Liebigs Ann. Chem.*, **617** (1958) 11.
12. Yates, P., Shapiro, B. L., Yoda, N. & Fugger, J., *J. Am. Chem. Soc.*, **79** (1957) 5756.

13. Law, K. Y., Kaplan, S. & Tarnawskyj, I. W., *Dyes Pigm.*, **17** (1991) 41.
14. Olah, G. A. & Grant, J. L., *J. Am. Chem. Soc.*, **97** (1975) 1546.
15. Eyring, D. F., *Org. Magnet. Reson.*, **12** (1979) 525.
16. Anderson, J. D. C. & Le Fevre, J. W., *Nature*, **162** (1948) 449.
17. Anderson, J. D. C., Le Fever, J. W. & Wilson, J. R., *J. Chem. Soc.* (1949) 2082.
18. Saunders, K. H. & Allen, R. L. M., *Aromatic Diazo Compounds*, 3rd edn. Edward Arnold, Baltimore, MD, 1985, pp. 23–4.
19. Lewis, E. S. & Johnson, M. D., *J. Am. Chem. Soc.*, **81** (1959) 2070.
20. Law, K. Y., Kaplan, S., Crandall, R. & Tarnawskyj, I. W., *Chem. Mater.*, **5** (1993) 557.
21. Satisfactory elemental analysis and spectroscopic properties are obtained for the monoazo dye 1-(*o*-methoxyphenylazo)-2-hydroxy-3-naphthanilide: m.p.: 234–236°C; IR (KBr): 1673 cm^{-1} (amide C=O); calculated for $C_{24}H_{19}N_3O_3$: C72·53, H 4·82, N 10·57; found: C 72·02, H 4·88, N 10·42.