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Azo Pigments and their Intermediates. A New Class of Couplers for Red and Near-IR Sensitive Photogenerating Azo Pigments

Kock-Yee Law & Ihor W. Tarnawskyj

Xerox Webster Research Center, 800 Phillips Road, 0114-39D,
Webster, New York 14580, USA

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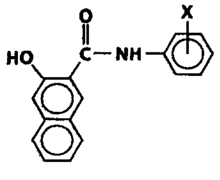
ABSTRACT

*The synthesis of azoic couplers, 2,8-dihydroxy-3-naphthanilide and its derivatives, by first converting 2,8-dihydroxy-3-naphthoic acid into its phenyl ester followed by condensing the phenyl ester with an aniline derivative, is reported. Photogenerating bisazo and trisazo pigments have been prepared by coupling 2,8-dihydroxy-3-naphthanilide with 2,7-diamino fluorenone and tris(*p*-aminophenyl)amine, respectively. The absorption spectra of these pigments are found to be red-shifted relative to analogous pigments synthesized from 2-hydroxy-3-naphthanilide. The data suggest that 2,8-dihydroxy-3-naphthanilides are new coupler components for red and near-IR absorbing photogenerating azo pigments. Evidence is provided that the red shift is a result of an intramolecular H-bonding between the 8-OH group in the coupler moiety and the nitrogen atom in the hydrazone unit of the pigment. Comparison of the pigments synthesized in this work with those from 2-hydroxy-11*H*-benzo(*a*)carbazole-3-carboxanilides suggests that the wavelength extension achieved by carbazole-couplers may also be a H-bonding effect, between the N—H group in the carbazole ring and the nitrogen in the hydrazone unit. The advantage of using the couplers described in this work for preparing red and near-IR absorbing photogenerating pigments is discussed.*

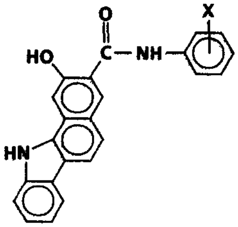
INTRODUCTION

Azo dyes and pigments are well known for their use as colorants in the dye industry. In 1969, Rau reported a study of the photocurrent generation by a thin film of 1-phenylazo-2-naphthol.[1] Subsequently, Champ and Shattuck showed that the bisazo pigment Chlorodiane Blue [4,4'-bis(1"-azo-2"-hydroxy-3"-naphthanilide)-3,3'-dichlorobiphenyl] could photogenerate electron-hole pairs in bilayer xerographic devices.[2] Due to the simplicity of the azo pigment synthesis, these earlier reports seemed to inspire and initiate a very intense subsequent effort in the xerographic photoreceptor industry. Thousands of azo pigments of different structural variations have been prepared, xerographically screened and claimed in the patent literature.[3] Among the azo pigments that have been examined for xerographic applications, (bis or tris) azo pigments synthesized from 2-hydroxy-3-naphthanilides were consistently found to exhibit moderate to high photoconductivity. Most of these pigments primarily absorb and photorespond in the visible region (400–650 nm). They are not candidates for xerographic printers, where illuminators, such as the GaAlAs diode lasers (780 nm) and the light-emitting diodes (660–680 nm), are preferred.

One of the identified approaches to extend the photoresponse of azo pigments beyond 650 nm is to use carbazole-couplers, such as anilides from 2-hydroxy-11*H*-benzo(*a*)carbazole-3-carboxylic acid, as coupler components in the photogenerating pigment synthesis. Most of the carbazole-couplers are not commercially available and in-house synthesis is needed.[4] It is also important to note that the starting 2-hydroxy-11*H*-benzo(*a*)carbazole-3-carboxylic acid itself has to be synthesized from 2,8-dihydroxy-3-naphthoic acid (**1**) via a multi-step reaction.[5] It is thus advantageous from the viewpoint of cost and synthetic simplification if one can use 2,8-dihydroxy-3-naphthoic acid directly as a precursor for the synthesis of photogenerating azo pigments. Here, we report the synthesis of a new class of anilide couplers from **1**. The optical properties of the azo pigments synthesized from these couplers are presented. Results show that the pigments resulting from **1** absorb at longer wavelengths relative to analogous structures from 2-hydroxy-3-naphthanilides. The origin of the bathochromic shift is discussed.



2-hydroxy-3-naphthanilides



carbazole-couplers

EXPERIMENTAL

Materials

2,8-Dihydroxy-3-naphthoic acid (>96%) was purchased from Rohner. Phenol (99 + %), aniline (99·5 + %), *p*-chloroaniline (98%), *p*-fluoraniline (99%), *o*-ethylaniline (98%), *N*-methyl pyrrolidinone (NMP) (99%) were brought from Aldrich. Xylenes (certified), *N*,*N*-dimethylformamide (DMF) (+99%), acetone (certified), methanol (certified), sodium nitrite, ether (anhydrous), sodium acetate (anhydrous) and fluoboric acid (48%) were obtained from Fisher and they were used as received. Phosphorous oxychloride was purchased from Aldrich and was distilled before use. 2,7-Diaminofluorenone was synthesized by reducing 2,7-dinitrofluorene (Aldrich) with stannous chloride (Fisher) using the procedure of Barker and Barker.[6] Tris(*p*-aminophenyl)amine was a sample generously provided by Dr A. Tokida of Fuji Xerox.

General techniques

Melting points were taken on a capillary melting point apparatus (Thomas Hoover) and were uncorrected. IR spectra were measured in KBr pellets on a Perkin-Elmer model 1750 FTIR. ^{13}C-NMR spectra were recorded in DMSO-d_6 (from Merck) on a Bruker AM360 spectrometer. Mass spectra were recorded on a Varian VG 7035 mass spectrometer at the University of Rochester. Elemental analyses were performed by Galbraith Laboratories.

Synthesis of phenyl 2,8-dihydroxy-3-naphthoate

A mixture of 2,8-dihydroxy-3-naphthoic acid (50 g, 0·24 mol), phenol (184·5 g, *c.* 2 mol) and phosphorus oxychloride (40 g) was stirred and heated by an oil bath (bath temperature *c.* 125°C) for 2 h under N_2 atmosphere. Thin-layer chromatography (TLC) analysis revealed that the starting acid was consumed. The product mixture was cooled to room temperature and methanol (80 ml) was added. The resulting solution was then poured into 1 liter of water and stirred for about 1·5 h. The desired product was isolated by filtration and was purified by first washing three times with water and then reprecipitating from a mixture of methanol and water (100 ml of methanol and 800 ml of water). After rinsing the solid with chloroform (2 × 150 ml) and vacuum drying, 52 g (76%) of pure phenyl 2,8-dihydroxy-3-naphthoate was obtained. Analysis gave the following:

m.p.	172–1735°C
IR (KBr)	1691 cm^{-1} (C=O)
^{13}C-NMR (DMSO-d_6)	106·4, 110·7, 116·2, 119·8, 121·9, 124·4, 126·1, 128·1, 129·0, 129·6, 132·6, 150·4, 151·7, 154·3 and 166·6 ppm
MS (*m/z*)	280
Calc. for $C_{17}H_{12}O_4$	C 72·86, H 4·31
Found	C 72·91, H 4·59

Synthesis of 2,8-dihydroxy-3-naphthanilide (3a)

A mixture of phenyl 2,8-dihydroxy-3-naphthoate (5·6 g, 0·02 mol), aniline (11·2 g, 0·12 mol) and 10 ml of NMP was stirred and heated to reflux at a bath temperature of *c.* 250°C under a N_2 atmosphere. After 2 h, TLC analysis revealed that all the starting phenyl ester was consumed. The mixture was cooled to room temperature and poured into *c.* 300 ml of ice cold 5% HCl. The yellow precipitate obtained was isolated by filtration. After washing with water and vacuum drying, *c.* 5·5 g of crude product resulted. It was then recrystallized from a mixture of DMF/methanol/H_2O, yielding 4·99 g (89%), a yellow solid, which was subsequently identified as 2,8-dihydroxy-3-naphthanilide (**3a**).

Anilides **3b–3d** were synthesized analogously. The synthetic data, the physical properties and the spectroscopic properties of these compounds are summarized in Tables 1 and 2.

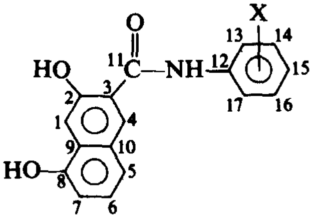
TABLE 1
Synthesis, Physical Properties, IR and Mass Spectral Data of 2,8-Dihydroxy-3-Naphthanilides (**3a–3d**)

Anilide	*Yield (%)*	*m.p. (°C)*		*C*	*H*	*N*	*IR*[a]	*M+*[b]
3a (X = H)	89	258–260	Calc.	73·11	4·69	5·02	1658, 1667	279
			Found:	72·29	4·92	5·04		
3b (X = F)	96	236–239	Calc.	68·68	4·07	4·71	1657	297
			Found:	68·39	4·18	4·55		
3c (X = Cl)	97	255–257	Calc.	65·08	3·86	4·46	1658, 1666	313
			Found:	64·74	4·14	4·58		
3d (X = o-C_2H_5)	91	178–180	Calc.	74·25	5·58	4·56	1650	307
			Found:	75·25	5·91	4·74		

[a] Amide C=O (in cm^{-1}).
[b] Molecular ion (in *m/z*).

TABLE 2

^{13}C-NMR Chemical Shift Data (in DMSO-d_6) of **3a–3d**



Anilide	*Chemical shift (ppm)*
3a	105·8 (C7), 109·7 (C1), 119·4, 120·6, 121·6, 124·0, 124·1, 127·6, 128·5, 128·8, 130·4 (C4), 138·5 (C12), 151·6 (C8), 153·0 (C2), 167·7 (C11)
3b	105·6 (C7), 109·5 (C1), 115·1, 115·3, 119·2, 121·4, 122·3, 122·4, 123·9, 127·4, 128·1, 130·0 (C4), 134·7 (C12), 151·4 (C8), 152·8 (C2), 165·5 (C11)
3c	105·7 (C7), 109·7 (C1), 119·4, 121·9, 122·0, 124·1, 127·5, 127·7, 128·3, 128·7, 130·3 (C4), 137·6 (C12), 151·6 (C8), 152·7 (C2), 165·7 (C11)
3d	14·2 (CH_3), 24·1 (CH_2), 105·9 (C7), 109·7 (C1), 119·5, 120·7, 123·8, 124·2, 125·2, 126·3, 127·6, 128·5, 128·7, 131·3 (C4), 135·7, 135·8, 151·5 (C8), 152·6 (C2), 164·6 (C11)

Synthesis of 2,7-bis(1′-azo-2′,8′-dihydroxy-3′-naphthanilide)fluorenone (4)

2,7-Diaminofluorenone (1·05 g, 5 mmol) was stirred in 20 ml of 18% hydrochloric acid at 50–60°C for 1 h and then at room temperature overnight. The yellow dispersion obtained was cooled to about 0–5°C by an ice–water bath. A cold aqueous solution of $NaNO_2$ (1 g in 2·5 ml of water) was then added dropwise in about 15 min and the resulting mixture was stirred in an ice bath for 30 min. A clear dark brown solution resulted. This dark brown solution was filtered using a medium sintered glass funnel into a 250 ml precooled filtration flask. Fluoboric acid (10 ml) was added to the cold filtrate, and a yellow precipitate was formed immediately. The yellow precipitate was filtered and washed with cold water, cold methanol and ether; the product was air dried for 1 h, 1·85 g of a tetrazonium salt being obtained.

The above tetrazonium salt was then dissolved in about 40 ml of cold DMF (external ice–water bath). A cold DMF solution containing 3·46 g of 2,8-dihydroxy-3-naphthanilide in 250 ml of DMF was added to the salt solution over about 20 min; the color of the salt solution changed from orange–brown to dark purple. A cold solution of 5 g of NaOAc in 75 ml of water was added slowly to the DMF solution (in 30 min). The temperature of the DMF solution was kept below 7°C during the addition. After the addition was complete, the ice bath was removed and the mixture was stirred at room temperature overnight. The crude bisazo pigment was then washed with warm water (81°C, twice and 250 ml each), warm DMF (81°C, three times and 250 ml each). After the third DMF wash, the product was stirred in 250 ml of acetone and then 250 ml of ether to remove residual high boiling solvents. The product was then dried inside a vacuum oven at 75°C, yielding a dark blue pigment product, 0·51 g (13%). It was identified as 2,7-bis(1'-azo-2',8'-dihydroxy-3'-naphthanilide)fluorenone:

m.p.	>300°C
IR (KBr)	1720 cm^{-1} (fluorenone C=O) and 1677 cm^{-1} (amide C=O)
Calc. for $C_{47}H_{30}N_6O_7$	C 71·19, H 3·82, N 10·62
Found	C 70·19, H 4·22, N 10·31

Synthesis of tris[4-(1'-azo-2',8'-dihydroxy-3'-naphthanilide)phenyl]amine (5)

Tris(*p*-aminophenyl)amine (0·58 g, 2 mmol) was stirred in an aqueous solution containing 14 ml of 18% hydrochloric acid at about 60°C for 1 h and then 16 h at room temperature. The dispersion obtained was then cooled to 0–5°C by an ice–water bath. A cold aqueous solution of sodium nitrite (0·6 g in 1·5 ml of water) was added dropwise. After the addition, the resulting mixture was stirred in an ice bath for another 30 min. A clear brown solution resulted. The dark brown solution was filtered (by a medium sintered glass funnel) into a 250 ml precooled filtration flask. Fluoboric acid (5 ml) was added to the cold filtrate, and a yellow precipitate was formed. The yellow precipitate was collected by filtration. After washing with cold water, cold methanol, ether and air-drying, about 1·25 g of a tris(diazonium)salt was obtained.

The tris(diazonium)salt was dissolved in about 30 ml of cold DMF (external ice–water bath). A cold DMF solution containing 2,8-dihydroxy-3-naphthanilide (1·84 g, 6·6 mmol) was then added to the solution and a cold solution of 3 g of NaOAc in 45 ml of water was added over 30 min. The temperature of the DMF solution was kept below 7°C during the addition. After the addition was complete, the ice bath was removed and the product was stirred at room temperature overnight. The crude pigment was filtered (fine sintered glass funnel) and was purified as above, yielding a dark blue pigment, which was identified as tris[4-(1'-azo-2',8'-dihydroxy-3'-naphthanilide)phenyl]amine, 0·79 g (34%):

m.p.	>295°C
IR (KBr)	1677 cm^{-1} (amide C=O)
Calc. for $C_{69}H_{48}N_{10}O_9$	C 71·37, H 4·17, N 12·06
Found	C 70·97, H 4·43, N 12·08

RESULTS AND DISCUSSION

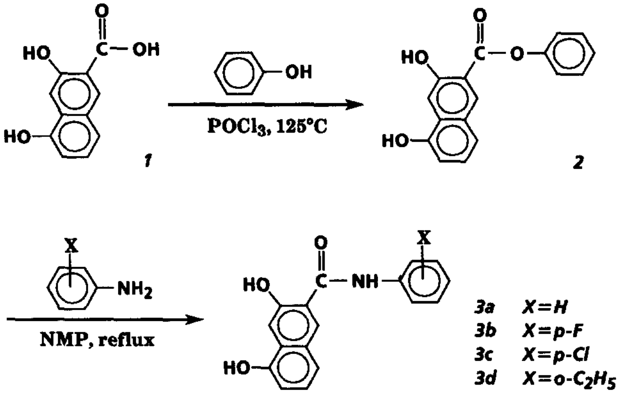
Synthesis and properties of 2,8-dihydroxy-3-naphthanilides

2,8-Dihydroxy-3-naphthanilides are synthesized by first converting 2,8-dihydroxy-3-naphthoic acid (**1**) into its phenyl ester (**2**) and then condensing **2** with an aniline derivative in a high boiling solvent such as *N*-methyl-2-pyrrolidinone (NMP). The reaction sequence is given in Scheme 1.

In the first step of the synthesis, **1** was esterified to its phenyl ester **2** using phosphorous oxychloride as a condensing agent. To minimize side reactions from the 8-OH group in **1**, phenol was used in large excess; it was a reactant as well as the reaction solvent. The yield of **2** was 76% and was chromatographically clean. The anilides were synthesized by reacting **2** with six equivalents of different aniline derivatives in NMP at reflux. The isolated yields were close to quantitative. The reaction was very general. The synthetic data and the physical properties of the synthesized anilides are summarized in Table 1.

The anilides **3a**–**3d** are yellow powders and exhibit good solubility in polar organic solvents (DMF, DMSO and NMP). In the IR spectra, very characteristic bands at 1650 ± 10 cm^{-1}, attributable to the amide C=O stretchings are observed (Table 1). It is important to note that the C=O stretchings in **3a**–**3d** are consistently at lower frequencies as compared to that of **2**, which is at 1691 cm^{-1}.

In the mass spectra, molecular ions of **3a**–**3d** are observed (Table 1). The major fragmentation process for the molecular ions is to eliminate the aniline moiety. The resulting fragment, at *m/z* 188, is the parent peak in all the mass spectra. The mass spectral reactions are similar to those of the carbazole-couplers.[4]

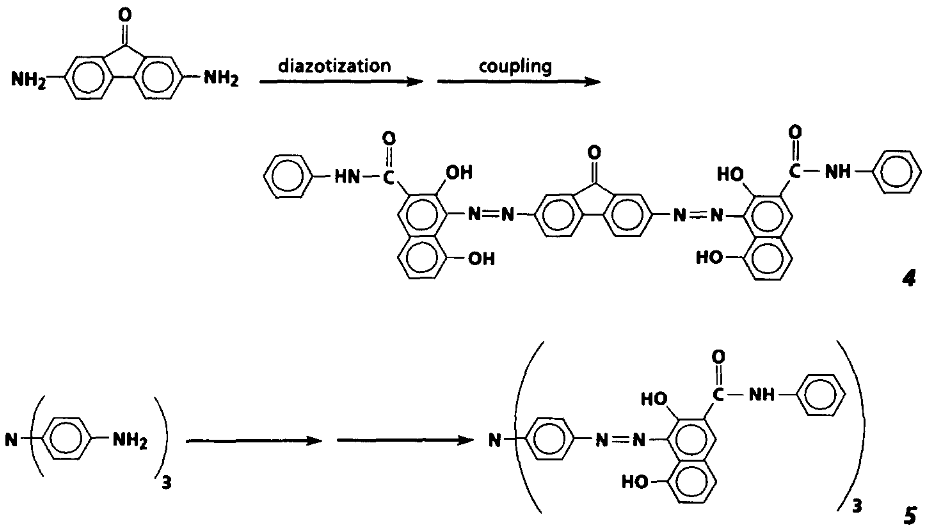


Scheme 1

All synthesized anilides exhibit well behaved ^{13}C-NMR spectra in DMSO-d_6 and peaks corresponding to individual carbon resonances are well resolved. The ^{13}C-NMR chemical shift data are summarized in Table 2. Although unambiguous assignments of individual peaks are difficult due to the similar shift among sp^2 carbons, characteristic resonances at *c.* 165, *c.* 153 and *c.* 151·5 ppm, attributed to the amide carbon (C-11) and the aromatic hydroxy carbons C-2 and C-8, respectively, are easily identified. From the chemical shift data of 2-hydroxy-3-naphthanilides[7] and the known substituent effect exerted by the 8-OH group,[8] C-1, C-4, C-7 and C-13, which are at *c.* 110, *c.* 130, *c.* 106 and *c.* 138 ppm, respectively, are distinguishable from other ^{13}C signals.

Synthesis and optical absorption of photogenerating bisazo and trisazo pigments

Bisazo pigment **4** and trisazo pigment **5** were prepared by first diazotizing the amine, 2,7-diaminofluorenone and tris(*p*-aminophenyl)amine, respectively, with a slight excess of sodium nitrite in an aqueous solution of 18% hydrochloric acid, followed by coupling the diazonium salts with 2,8-dihydroxy-3-naphthanilide (**3a**). These pigments were purified by repetitive washing in warm water and warm DMF. Details of the synthesis and purification procedures have been reported elsewhere.[9,10] The synthetic scheme for **4** and **5** is shown in Scheme 2. Both pigments are high melting, dark blue powders. They exhibit characteristic amide



Scheme 2

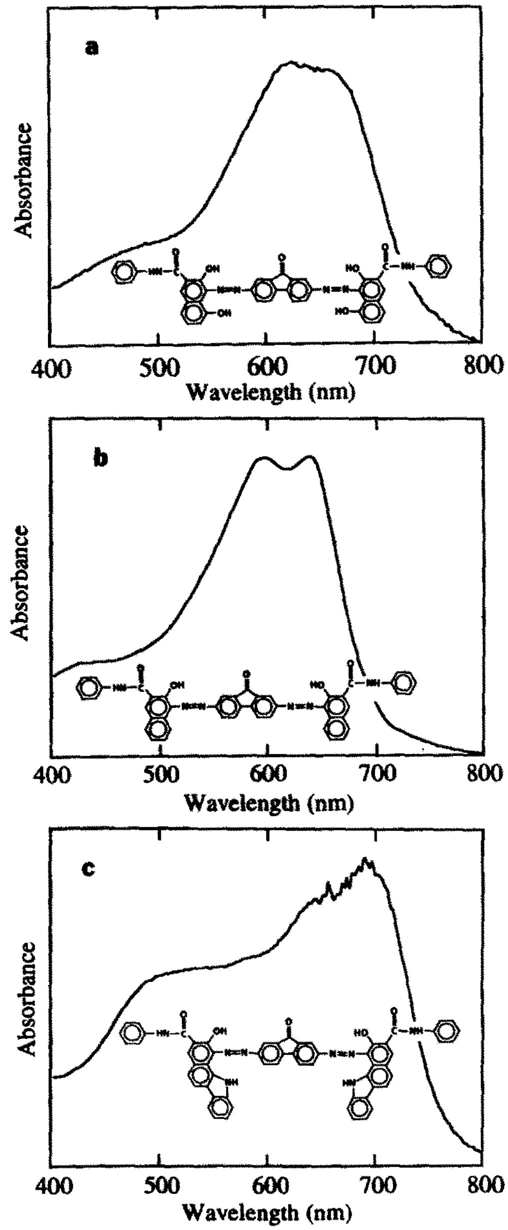


Fig. 1. Absorption spectra of bisazo pigments from 2,7-diaminofluorenone.

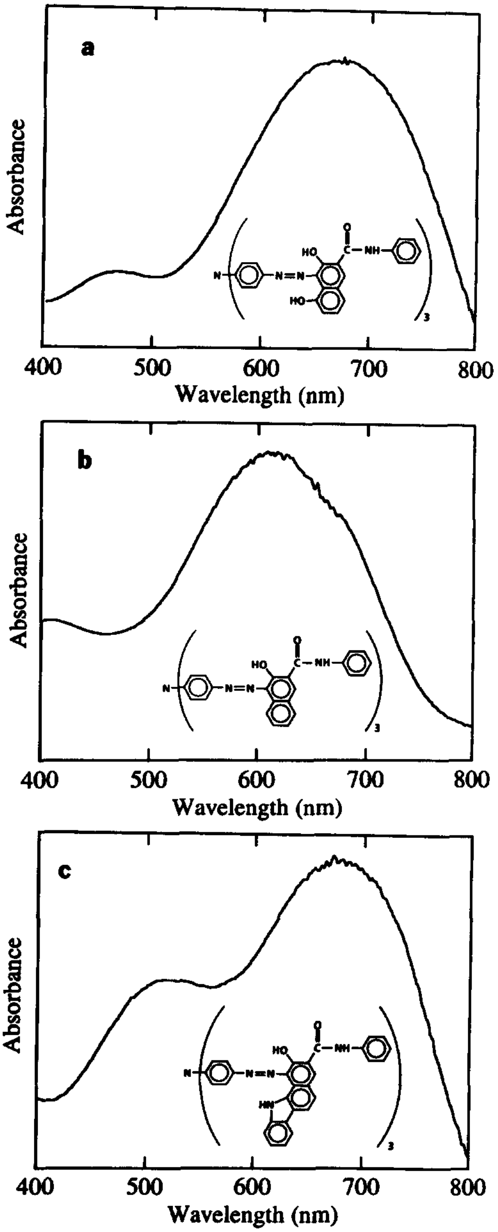


Fig. 2. Absorption spectra of trisazo pigments from tris(*p*-aminophenyl)amine.

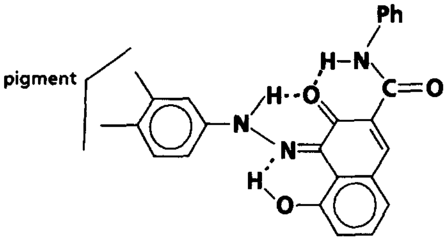
C=O stretchings that are at higher frequencies relative to the starting coupler.[7]

Figure 1(a) shows the solid state absorption spectrum of **4** in a KBr pellet. The absorption λ_{max} of **4** is centered around 640 nm and the onset is at *c.* 740 nm. The absorption band is red-shifted as compared to the absorption of a similar bisazo pigment, from which the 8-OH groups in the coupler moieties are absent (Fig. 1(b)).[10] On the other hand, the absorption of **4** is comparable to an analogous bisazo pigment synthesized by coupling 2,7-diaminofluorenone with carbazole-coupler (Fig. 1(c)).

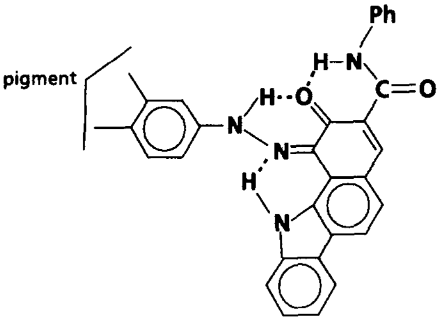
Figure 2(a) shows the solid state absorption spectrum of the trisazo pigment **5** in KBr pellet. Again the optical absorption of **5** is red-shifted relative to a similar trisazo pigment from 2-hydroxy-3-naphthanilide (Fig. 2(b)) and is comparable to that of a trisazo pigment synthesized from tris(*p*-aminophenyl)amine and a carbazole-coupler. We conclude from the absorption spectral data that the 8-OH groups in the coupler moieties are responsible for the bathochromic shifts in the bisazo pigment **4** and the trisazo pigment **5**. The magnitude of the bathochromic shifts is comparable to that achieved by the carbazole-couplers. 2,8-Dihydroxy-3-naphthanilides are, therefore, couplers for the synthesis of red and near-IR absorbing pigments. Since 2,8-dihydroxy-3-naphthoic acid is the starting material for preparing 2-hydroxy-11*H*-benzo(*a*)carbazole-3-carboxylic acid, which in turn is the precursor for carbazole-couplers,[4,5] the approach reported in this work appears to be more economical owing to the fewer steps involved in the coupler synthesis.

Origin of the bathochromic shift

We previously studied the electronic structures of many classes of photogenerating bisazo and trisazo pigments from 2-hydroxy-3-naphthanilides.[7] The results indicated that these photogenerating azo pigments are bis- and tris-(hydrazones) in the solid state, rather than the conveniently drawn azo structures. We have also shown that substituents in the anilide ring and the naphthalene ring have very little effect on the tautomeric equilibrium and the absorption of the pigment.[7,9,10] These studies included pigments from 2-hydroxy-6-methoxy-3-naphthanilides (Law & Tarnawskyj, unpublished). The electron-releasing character of the 6-OCH_3 group and the 8-OH group in the naphthalene ring should be very similar. Since no bathochromic shift was observed for pigments from 2-hydroxy-6-methoxy-3-naphthanilides, we attribute the red-shifts in **4** and **5** to an intramolecular H-bonding effect between the 8-OH group in the coupler moiety and the nitrogen in the hydrazone unit.



Carbazole-couplers are another class of couplers that are capable of extending the absorption wavelength of the synthesized azo pigments to the red (Figs 1(c) and 2(c)). The bathochromic shift resulting from the couplers described in this work suggests that a similar mechanism, i.e. an intramolecular H-bonding between the N—H group in the carbazole ring and the nitrogen in the hydrozone unit, may be operative in the carbazole-couplers.



CONCLUDING REMARKS

This work describes the synthesis of a new class of azoic couplers, 2,8-dihydroxy-3-naphthanilide and its derivatives. Photogenerating pigments synthesized from them are found to absorb at longer wavelengths (by *c.* 50 nm) as compared to analogous structures from 2-hydroxy-3-naphthanilides. Since a similar bathochromic shift is not obtained for pigments from 2-hydroxy-6-methoxy-3-naphthanilide (a coupler bearing a similar electron-releasing group), we propose that the bathochromic effect generated by 2,8-dihydroxy-3-naphthanilides is not due to the electron-releasing nature of the 8-OH group, but arises from the intramolecular H-bonding between the 8-OH group in the coupler moiety and the nitrogen atom in the hydrazone unit of the pigment.

Prior to this work, photogenerating bisazo and trisazo pigments with extended red and near-IR responses could only be prepared from 2-hydroxy-11*H*-benzo(*a*)carbazole-3-carboxanilides. We have compared the structures of these pigments with those synthesized in this work. The comparison suggests that the wavelength extension achieved by carbazole-couplers may also be an intramolecular H-bonding effect between the N—H group in the carbazole ring and the nitrogen in the hydrazone unit of the pigment.

Finally, carbazole-couplers were synthesized in a two-step reaction from 2-hydroxy-11*H*-benzo(*a*)carbazole-3-carboxylic acid, which in turn has to be prepared from 2,8-dihydroxy-3-naphthoic acid in a multi-step reaction. We have now demonstrated that extended red and near-IR absorbing photogenerating pigments can be synthesized from 2,8-dihydroxy-3-naphthanilides directly. The approach reported herein is, therefore, more economical.

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