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Azo Pigments and their Intermediates. A CP MAS ^{13}C-NMR Study of the Tetrazotized Products of 1,5-Diamino-4,8-dihydroxyanthraquinone

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ABSTRACT

*An attempt to use 1,5-diamino-4,8-dihydroxyanthraquinone (***1***) as a precursor to synthesize bisazo pigments, by an azotization-coupling reaction sequence, is reported. The tetrazotization of* **1***, by a slight excess of sodium nitrite, is effective both in concentrated hydrochloric acid and concentrated sulfuric acid. In concentrated hydrochloric acid, the tetrazonium product was isolated as the tetrafluoroborate salt,* **3***, by adding fluoroboric acid into the azotized solution. In concentrated sulfuric acid, the tetrazonium product was isolated as the sulfate salt,* **4***, by simply diluting the azotized solution with ice-water. The structures of* **3** *and* **4** *were characterized by IR and cross-polarization magic angle spinning (CP MAS) ^{13}C-NMR spectroscopy, as well as solution NMR measurements. Due to their high acidity,* **3** *and* **4** *deprotonate to form* **5***, an insoluble purple–brown solid in dilute aqueous solution or in organic solvents. Compound* **5** *only dissolves in acidic solutions and, since this involves a protonation reaction, it can only be characterized by solid-state techniques. In this work, the structure of* **5** *was established by IR and CP MAS ^{13}C-NMR spectroscopy. Two characteristic carbonyl stretchings at 1670 and 1655 cm^{-1} are observed in the IR spectrum and two carbonyl carbons at 176·8 and 178·2 ppm are observed in the solid-state ^{13}C-NMR spectrum. The protonation–deprotonation relationships between* **3***,* **4** *and* **5** *were established from their solution and solid-state NMR spectra. The facile deprotonation of* **3** *and* **4** *and the insolubility of* **5** *in any solvents are shown to be a hindered factor for the synthesis of bisazo pigments.*

INTRODUCTION

Azo dyes and pigments make up the largest chemical class in the Color Index. Their common structural characteristic is the azo chromophore connecting two-carbon systems, at least one of which is aromatic. Depending on the number of azo linkages, these compounds can be further classified into sub-groups, such as monoazo, bisazo, trisazo and polyazo. The photoconductivity of azo pigments was first recognized in 1975 by Champ and Shattuck,[1] where they 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. This disclosure, coupled with the ease of the synthesis of these materials, led to a very intense effort where thousands of azo pigments of a variety of structures were synthesized and evaluated for xerographic applications.[2] Generally speaking, azo pigments absorb only in the visible region (400–650 nm) and do not show any significant absorption at >660 nm, where light sources for printers, such as LED (680 nm) and diode laser (780 nm), emit. They are, therefore, not very useful for xerographic printer applications.

Azo pigments are generally synthesized by coupling an azonium salt of an aromatic amine. Among aromatic amines, isomeric diaminoanthraquinones have been investigated in some detail because they are commercially available, non-toxic and inexpensive.[3] Again, these bisazo pigments only absorb in the visible region and are not sensitive in the red or near-IR. The common feature of these azo pigments is their absorption edges, which are shifted to longer wavelength by 100–150 nm as compared with the solution absorption maxima of the diaminoanthraquinone precursors.[4] In an attempt to synthesize bisazo pigments that absorb beyond 650 nm, 1,5-diamino-4,8-dihydroxyanthraquinone (**1**), which exhibits a solution absorption at λ_{max} 623 nm in dimethylformamide (DMF), was chosen as a precursor for azo-pigment synthesis. An investigation on the synthesis and structural characterization of the tetrazotized products of **1** is reported here. The merit of using solid-state ^{13}C-NMR techniques to study metastable species (such as tetrazonium salts) and insoluble compounds, which cannot be characterized otherwise, is demonstrated. Pigment syntheses were attempted and factors hindering the synthesis are discussed.

EXPERIMENTAL

Materials

1,5-Diamino-4,8-dihydroxyanthraquinone (**1**) was purchased from Lancaster Synthesis (Windham, New Hampshire, USA). Sodium nitrite (certified grade), fluoroboric acid (HBF_4, purified, 48–50%), concentrated hydrochloric acid and concentrated sulfuric acid (reagent grade) were obtained from Fisher (Springfield, New Jersey, USA). Deuterated solvents were bought from Merck (St Louis, Missouri, USA). All of these materials were used as received.

Spectroscopic techniques

IR spectra were taken in potassium-bromide pellets on a Perkin-Elmer model 1750 FTIR. Solution ^1H-NMR spectra were recorded in deuterium chloride on a Bruker WP-80 spectrometer. Solution ^{13}C-NMR spectra (in DMSO-d_6 or in deuterium chloride) were obtained at room temperature with a Bruker CXP spectrometer operating at 50·3 MHz in a Cryomagnet Systems Inc. superconducting magnet system. Simple ^{13}C free induction decays using 90° carbon pulses and Waltz decoupling resulted in adequate signal-to-noise after 15 000–30 000 scans.

Cross-polarization magic angle spinning (CP MAS) solid-state ^{13}C-NMR spectra were recorded on the same CXP spectrometer. Proton-enhanced cross-polarization used 3–6-ms contact times, high-power ($H_1 = 12\,G$) proton decoupling and recycle times of 1–3 s. Magic angle spinning (4–4·5 kHz) was performed in a Doty Scientific probe with approx. 100 mg of each sample packed into 6-mm (o.d.) sapphire rotors. The TOSS technique for sideband suppression was used for all measurements. Typically, 256–10 000 scans were averaged for each spectrum. Spectral assignment is facilitated by distinguishing the protiated and non-protiated carbons using a spin temperature reversal pulse sequence.[5,6] After the cross-polarization mixing period and prior to carbon observation, proton rf phase is inverted for 100 μs. During this period the carbon spins cross-polarize in the reverse direction, protiated carbons the fastest and non-protiated carbons the slowest. Conveniently, after 100 μs, the protiated carbons are approximately nulled. The authors find this technique superior in its differentiation of protiated and non-protiated carbons to the commonly used delayed decoupling technique.[7]

Tetrazotization of **1**

Compound **1** (5·4 g, 20 mmol) in 150 ml conc. HCl was stirred magnetically in a three-necked 250-ml flask in a warm water-bath for ~90 min. The hydrochloride salt dispersion was then cooled to room temperature. A sodium-nitrite solution (5 g $NaNO_2$ in 12 ml of water) was added slowly to the salt dispersion. After 60–90 min, a dark-brown solution, presumably consisting of 4,8-dihydroxyanthraquinone-1,5-tetrazonium dichloride (**2**), was obtained. The solution was filtered through a medium, sintered glass funnel. The tetrazonium salt product was isolated as the tetrafluoroborate salt, **3**, by adding 60 ml HBF_4 to the filtrate. The precipitate was filtered, washed with cold 18% aq. HCl solution and then vacuum dried, yielding a brown solid, which was subsequently identified as 4,8-dihydroxyanthraquinone-1,5-tetrazonium-bis(tetrafluoroborate) by IR and NMR spectroscopy, 6·7 g (72%).

RESULTS AND DISCUSSION

Synthesis and IR spectra of the tetrazotized products of 1,5-diamino-4,8-dihydroxyanthraquinone

Tetrazotization of 1,5-diamino-4,8-dihydroxyanthraquinone (**1**) in concentrated hydrochloric acid with an excess amount of sodium nitrite results in dissolution of the hydrogen chloride salt of **1** and a dark-brown solution. A brown precipitate (**3**) can be isolated as soon as fluoroboric acid is introduced into the mixture. Figure 1 shows the partial IR spectra of **1** and **3** in potassium-bromide pellets. The vibrational frequency data are tabulated

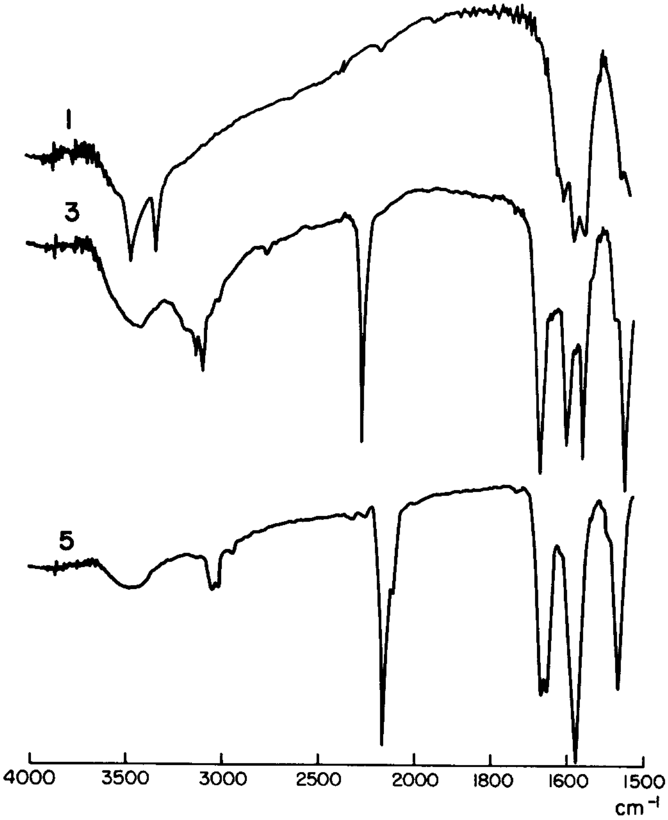


Fig. 1. IR spectra of compounds **1**, **3** and **5**.

TABLE 1
IR and ^{1}H-NMR Spectral Data of Compounds **1**, **3**, **4** and **5**

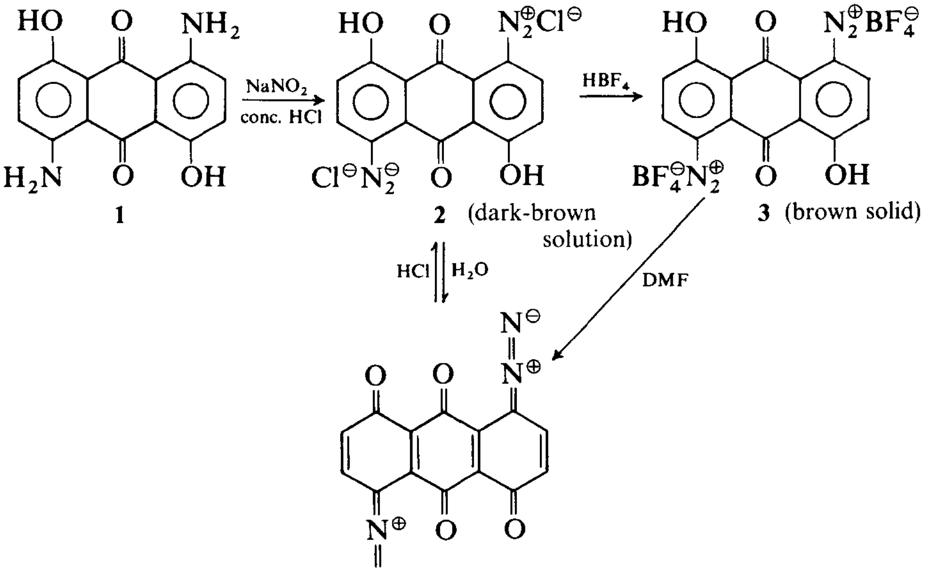
Compound	*IR* (cm^{-1})	δ (*ppm from TMS*)
1	3 328, 3 460 (N—H)	*In DMSO-d_6*: 7·28 (s, 4H, aromatic C—H), ~8·0 (s, 4H, NH exchangeable), and 14·3 (s, 2H, OH exchangeable)
3	2 263 ($-N^{\oplus}\equiv N$), 1 674 (C=O)	*In DCl*: 8·07 (d, 2H, $J = 12$ Hz) and 9·13 (d, 2H, $J = 12$ Hz)
4	2 261 ($-N^{\oplus}\equiv N$), 1 673 (C=O)	
5	2 160, 2 106 ($C=N^{\oplus}=N^{\ominus}$), 1 670, 1 655 (C=O)	*In DCl*: 8·07 (d, 2H, $J = 12$ Hz) and 9·13 (d, 2H, $J = 12$ Hz)

in Table 1. The observation of a high frequency peak at ~2260 cm^{-1}, which can be assigned to the —$N^{\oplus}\equiv N$ stretching,[8,9] accompanied by the disappearance of the N—H stretching in the spectrum of **3**, suggest that **1** was tetrazotized to 4,8-dihydroxyanthraquinone-1,5-tetrazonium dichloride (**2**). While **2** is water soluble, the tetrazonium product is isolable as the tetrafluoroborate salt, **3**, (in ~72% yield) by adding fluoroboric acid to the aqueous solution of **2**.

A similar tetrazotization reaction of **1** was also observed in concentrated sulfuric acid. In this case, the tetrazonium product was isolated as 4,8-dihydroxyanthraquinone-1,5-tetrazonium sulfate (**4**) by discharging the product solution into ice-water. The IR spectral data of **4** (Table 1) are very similar to those of **3**.

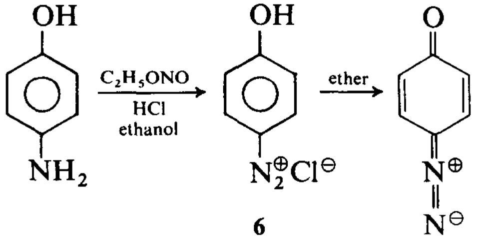
In addition to the —$N^{\oplus}\equiv N$ stretching, a carbonyl stretching at ~1673 cm^{-1} is observed in the spectra of **3** and **4**. Since the carbonyl stretching in **1** is at ~1630 cm^{-1} (Fig. 1), the observed carbonyl frequency shift, which is indicative of the removal of intramolecular hydrogen bonding between the C=O and the NH_2 groups in **1**, suggests that **1** was azotized to tetrazonium products (**3** and **4**) under present experimental conditions. As shall be seen in later sections, the structure assignments of **3** and **4** are confirmed by the solution and solid-state ^{13}C-NMR data.

In the initial stage of this investigation, cold water was frequently used to wash **3** and **4** to remove residual acids. This procedure caused partial or sometimes complete color change of the solid, from brown to purple–brown. This purple–brown solid is insoluble in water and organic solvents, but exhibits good solubility in concentrated hydrochloric acid and concentrated sulfuric acid. An identical insoluble solid can also be obtained by either diluting the product solution of **2** with water or by suspending **3** or **4** in an organic solvent (such as DMF, acetone, or pyridine). The IR spectral data of this solid, compound **5**, is included in Fig. 1 and Table 1. The results reveal that **5** exhibits high-frequency stretchings at 2160 and 2106 cm^{-1} and two carbonyl stretchings at 1670 and 1655 cm^{-1}. The vibrational stretchings at 2160 and 2106 cm^{-1} suggest that the diazonium group in **3** or **4** may be converted to a diazo group, which usually exhibits a stretching frequency between 2000 and 2100 cm^{-1}.[10-12] This observation, along with the appearance of an additional carbonyl stretching at 1655 cm^{-1}, leads to the proposal that **5** is 1,5-bis(diazo)-4,8-dioxoanthraquinone, the deprotonated product of **3** or **4**. As shall be seen in later sections, the protonation–deprotonation relationships between **3**, **4** and **5** are established by studying their solution ^{1}H- and ^{13}C-NMR spectra and the structure of **5** is confirmed by the CP MAS ^{13}C-NMR spectrum. The synthesis and the transformation of various tetrazotized products of **1** is depicted in Scheme 1.



Scheme 1

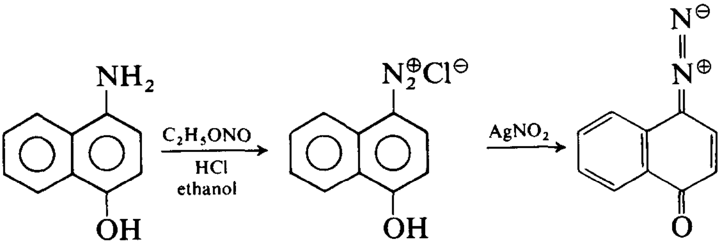
Although the deprotonation reactions of **2**, **3** or **4** to form **5** is not known, the existence of two forms of diazonium products from *p*-aminophenol is well documented in the literature. For example, in 1956, Whetsel, Hawkins and Johnson[8] reported the preparation of 1-phenol-4-diazonium chloride (**6**) from *p*-aminophenol and ethyl nitrite in an acidic ethanolic solution. Compound **6** was found to convert to another solid, compound **7**, in diethyl ether. In the IR spectra, stretchings at 2237 and 2107 cm^{-1} were observed for **6** and **7**, respectively. On the basis of the decrease in vibrational frequency, they concluded that **7** is the deprotonated form of **6** and the observed low frequency in **7** is attributable to the conversion of the diazonium group to a diazo group (Scheme 2).



6 **7**

Scheme 2

The investigation of the diazotization of 4-amino-1-naphthol is less systematic. In 1945, Anderson and Roedel[13] reported the formation of the diazonium product, **8**, a tan-colored solid obtained by azotizing 4-amino-1-naphthol with ethyl nitrite in the presence of hydrochloric acid. Compound **8** was converted to a dark-orange solid, **9**, by silver nitrite in water (Scheme 3). They assigned **9** to the deprotonated form of **8** by UV absorption. IR spectral data of **8** and **9** were not reported at that time.



8 **9**

Scheme 3

A subsequent investigation by LeFévre, Sousa and Werner[14] showed that **9** exhibits vibrational stretchings at 2014 and 1618 cm^{-1}. They assigned the stretching at 2014 cm^{-1} to diazo group and the stretching at 1618 cm^{-1} to a carbonyl group. Again, the stretching frequency of the diazo group is significantly lower than that of a diazonium group ($\sim$2150–2300 cm^{-1}).[8,9]

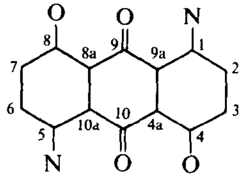
The OH proton in **1** is actually quite acidic, as judged from the chemical shift observed in the ^{1}H-NMR spectrum ($\delta \sim 14{\cdot}3$ ppm). Since Lewis and Johnson[15] showed that diazonium groups are the most powerful electron-withdrawing functionalities known, the occurrence of deprotonation reactions of **2**, **3** and **4** to **5** in water or in DMF is not unreasonable. The acid dissociation constants of the tetrazonium salts prepared in this work, however, could not be determined, due to the irreversibility of the deprotonation reaction (**5** precipitates out of the solution). On the other hand, the pK_a value of **6** was determined to be ~ −3 by UV- absorption spectroscopy.[16] Compounds **2**, **3** and **4** are expected to be more acidic than **6** because of the electron-withdrawing nature of the anthraquinone ring system. Thus, the observed facile deprotonation of the tetrazonium salts prepared in this work is rational.

Solution proton and ^{13}C-NMR spectra

The solution ^{1}H-NMR spectra of **3** and **5** were recorded in deuterium chloride. Identical ^{1}H spectra are obtained for both compounds (Table 1). The

TABLE 2

Solution and Solid-State ^{13}C-NMR Spectral Data of **1**, **3**, **4** and **5**



Compound		Chemical shift (ppm)						
		1,5	2,6	3,7	4,8	9,10	4a, 8a	9a, 10a
1	DMSO-d$_6$[a,b]	147·5	127·3	128·3	155·1	186·2	113·4	107·7
	DMSO-d$_6$[a,c]	147·4	127·2	128·3	155·1	186·3	113·5	107·8
	Solid[d]	147·2	128·3	128·3	156·6	185·9	114·4	108·3
		150·2						
3	DCl[e]	102·8	143·6	129·8	171·8	181·5	120·0	137·7
	Solid[d]	101·3	145·9	126·1	170·8	182·4	117·9	138·6
4	DCl[e]	102·8	143·6	129·8	171·8	181·5	120·0	137·7
	Solid[d]	101·9	144·1	127·9	169·3	181·4	119·3	137·9
				(125·5)[f]	(162·2)[f]	(187·2)[f]	(117·1)[f]	(134·6)[f]
5	DCl[e]	102·8	143·5	129·8	171·6	181·5	120·0	137·8
	Solid[d]	82·7	136·6	132·2	176·8	178·2	123·2	142·5

[a] Reference TMS (0 ppm).

[b] This work.

[c] From Ref. 22.

[d] Reference, methyl carbons of hexamethylbenzene (17·4 ppm).

[e] Reference, methyl carbons of the sodium salt of 3-(trimethylsilyl)-1-propane sulfonic acid (0 ppm).

[f] Sister peaks.

observation of a clean AB quartet in the aromatic region of the ^{1}H spectra of **3** and **5**, which is in contrast to the broad singlet observed in **1**, not only supports the contention that **1** was azotized to a tetrazonium product under our reaction conditions, but also suggests that ***3** and **5** exist as identical species in deuterium-chloride solution.* This, of course, implies that **5** is the deprotonated product of **3** and **4** and that the dissolution of **5** in concentrated hydrochloric acid involves protonating it to form **2**. An identical conclusion can also be reached by studying the solution (DCl) ^{13}C-NMR spectra of **3**, **4** and **5**, where, again, identical ^{13}C-NMR spectra are obtained (Table 2). Since the solution ^{13}C-NMR spectra of **3** and **4** are similar to the solid-state spectra, details of the chemical-shift assignments are discussed in the next section.

CP MAS ^{13}C-NMR spectra

Figure 2a shows the CP MAS ^{13}C-NMR spectrum of **1**. The chemical-shift data are listed in Table 2. The data reveal that the chemical shift of the carbonyl carbons (9, 10) is at its characteristic downfield position at 185·9 ppm. Carbons 1, 5 are distinguished from carbons 4, 8 by the characteristic doublet splitting due to their interactions with their neighboring quadrupolar ^{14}N nuclei.[17] Protiated carbons 2, 6, 3, 7 are at 128·3 ppm and are identified by the spin-reversal experiment (Fig. 2b). The assignments of carbons 4a, 8a and 9a, 10a are based on the chemical-shift assignments of the solution spectrum of **1** (Table 2).[18]

The CP MAS ^{13}C-NMR spectrum of **3** (Fig. 3a) shows that the chemical shift of the carbonyl carbons (9, 10) is at 182·4 ppm. Assignments of other carbons are based partly on the estimated substituent-induced chemical-shift changes from **1** to **3** and on the spin-reversal experiment. For example, assuming that the substituent additivity parameters for benzene[20] are applicable to the present system, the estimated chemical-shift changes from $\mathbf{1} \rightarrow \mathbf{3}$ would be ~ -32 ppm at carbon 1 and $\sim +19$, $\sim +5$ and $\sim +27$ ppm at the *ortho*-, *meta*- and *para*-carbons, respectively. The large upfield shift predicted for carbons 1, 5, taken together with the expected line-broadening (unresolved doublet) effect produced by the quadrupolar ^{14}N nuclei,[17] allows us to assign 101·3 ppm to these carbons unambiguously. The large downfield shift predicted for the *para*-carbons leads to the assignment of carbons 4, 8 to 170·8 ppm. The significant decrease in intensity during spin reversal (Fig. 3b) of carbons 4, 8 relative to carbons 9, 10 is consistent with carbons 4, 8 being spatially nearer to hydrogens. Since protiated and non-protiated carbons are distinguishable by the spin-reversal experiment (Fig. 3b), and since there is a predicted larger downfield shift for the *ortho*- than the *meta*-carbons, the remaining four carbon peaks can be assigned

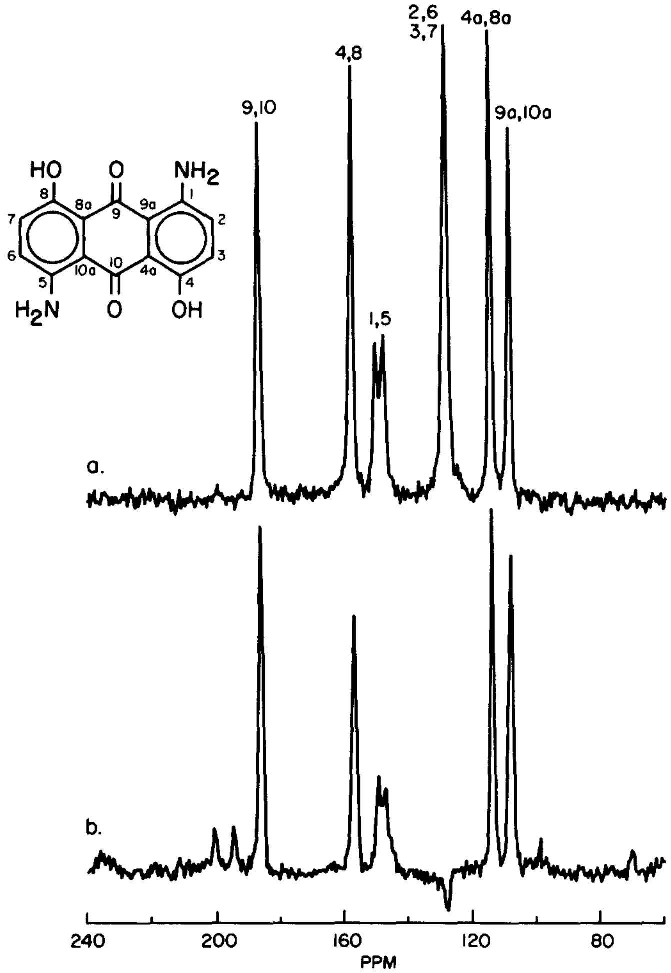


Fig. 2. CP MAS ^{13}C-NMR spectra of **1**: (a) cross-polarization time = 3 ms, spinning rate = 4300 Hz, repetition time = 3 s, number of scans = 256; (b) same as (a), except with a 100-μs spin temperature reversal time inserted between the cross-polarization and observation periods.

unambiguously as follows: carbons 2, 6 at 145·9 ppm; carbons 3, 7 at 126·1 ppm; carbons 4a, 8a at 117·9 ppm and carbons 9a, 10a at 138·6 ppm.

It is worth noting that the signals of the protiated carbons of **3** (carbons 2, 6, 3 and 7) are very broad in the CP MAS ^{13}C-NMR spectrum (Fig. 3a). The broad line-width is attributable to the un-decoupled dipolar interactions with the ^{19}F spins of the tetrafluoroborate anion,[21] and suggests that the tetrafluoroborate anions reside near these carbons. This interpretation is substantiated by the CP MAS ^{13}C-NMR spectrum of tetrazonium sulfate, **4**, (Fig. 4 and Table 2), where narrower line-widths are observed for the

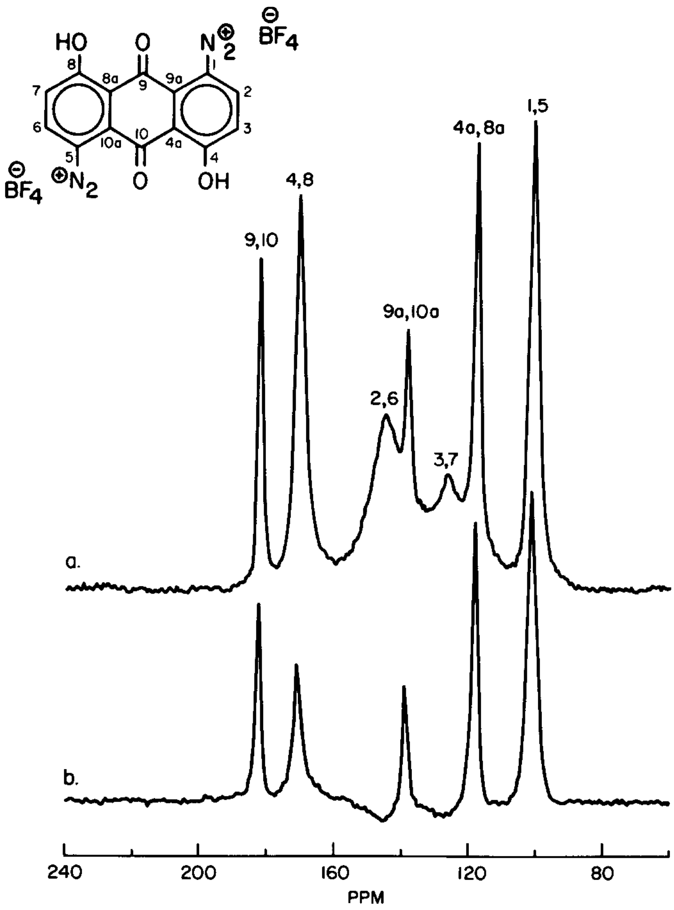


Fig. 3. CP MAS ^{13}C-NMR spectra of **3**: (a) cross-polarization time = 8 ms, spinning rate = 4700 Hz, repetition time = 4 s, number of scans = 7200; (b) same as (a), except with 100-μs spin temperature reversal.

protiated carbons. Although the chemical shifts of the carbons in **4** are very similar to those in **3**, presumably due to crystal packing, sister peaks are resolved for nearly every carbon in the ^{13}C-NMR spectrum of **4**.[22]

The CP MAS ^{13}C-NMR spectra of **5** are given in Fig. 5 and the chemical-shift data are listed in Table 2. Seven carbon peaks are observed in the ^{13}C-NMR spectrum. The spectral data reveal that **5** is a unique species in the solid state and is different from **3** or **4**, despite the fact that they all have the same solution ^{1}H and ^{13}C-NMR spectra. The presence of two carbonyl peaks at 176·8 and 178·2 ppm is in contrast to the one carbonyl carbon seen in the spectra of **3** and **4**, and is consistent with the IR spectral data of **5**, where two carbonyl stretchings are observed. Since the signal at 176·8 ppm is more attenuated under spin-reversal conditions, it is assigned to carbons

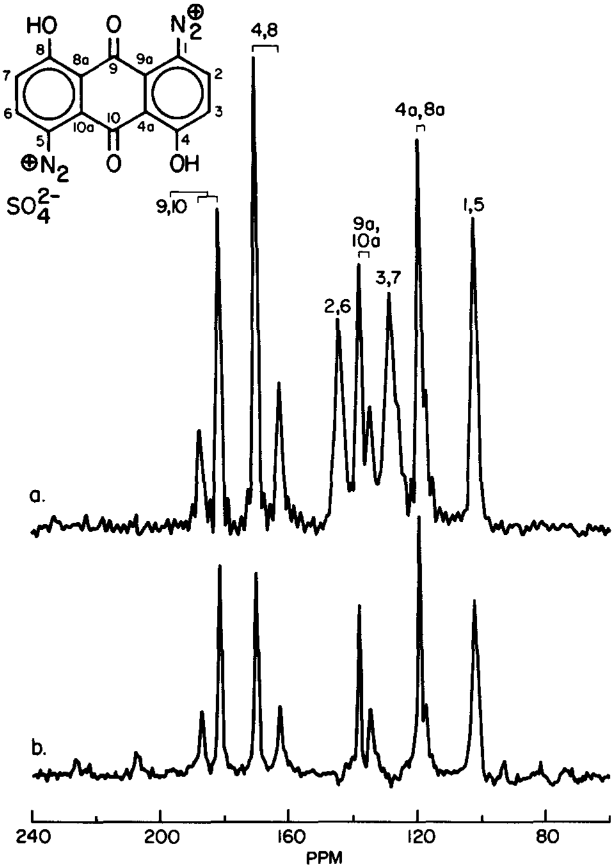


Fig. 4. · CP MAS ^{13}C-NMR spectra of **4**: (a) cross-polarization time = 3 ms, spinning rate = 4480 Hz, repetition time = 3 s, number of scans = 10 000; (b) same as (a), except with 100-μs spin temperature reversal.

4, 8. The peak at 178·2 ppm, then, is from carbons 9, 10. Thus, the CP MAS ^{13}C-NMR spectra are consistent with the proposed structure of **5**.

Another interesting result in the ^{13}C-NMR spectrum of **5** is the upfield signal at 82·7 ppm. Since the line-width of this signal is broader than all other non-protiated peaks in the spectrum, we can assign it to carbons 1, 5.[17] The anomalous upfield position of carbons 1, 5 actually gives further credential to the structure assignment of **5**. The α-carbons of diazo compounds, which are normally at 20–67 ppm, are known to be strongly shielded by the electrons in the diazo group because of a resonance effect.[23,24]

$$\rangle C{=}N^{\oplus}{=}N^{\ominus} \longleftrightarrow \rangle C^{\ominus}{-}N^{\oplus}{\equiv}N$$

The fact that the chemical shift of the diazo carbons in **5** is at ~83 ppm, >16 ppm lower-field than expected, suggests that the shielding effect

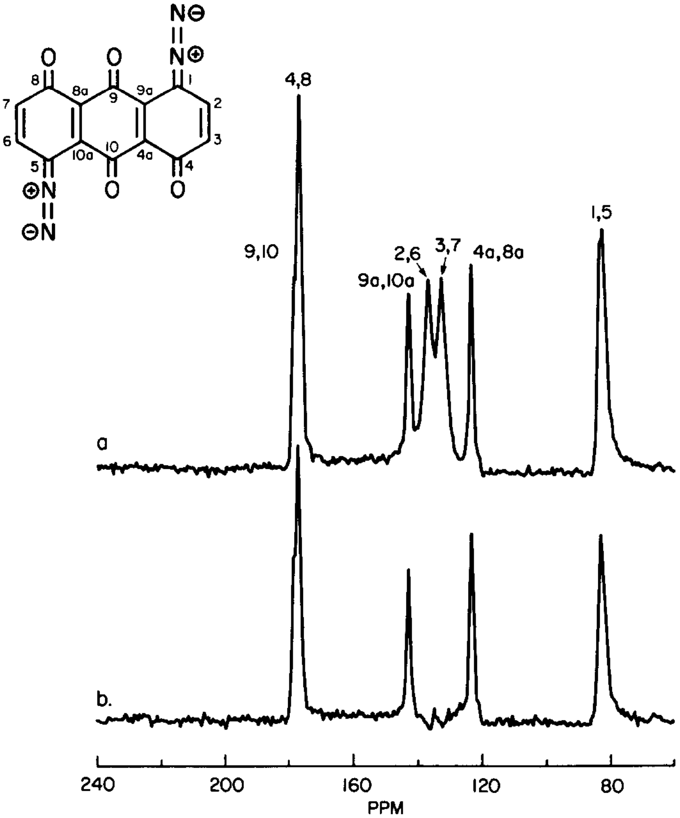
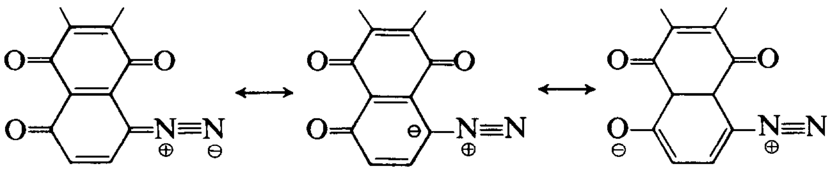


Fig. 5. CP MAS ^{13}C-NMR spectra of **5**: (a) cross-polarization time = 6 ms, spinning rate = 4200 Hz, repetition time = 3 s, number of scans = 10 000; (b) same as (a), except with 100-μs spin temperature reversal.

produced by the diazo group in **5** is reduced because of the resonance stabilization of the negative charge by the para C═O group.



The chemical shifts of the remaining carbons in **5** are assigned using the spin-reversal technique (Fig. 5b). The data are given in Table 2.

Finally, as noted earlier, **5** is insoluble in organic solvents, except in acidic solutions. However, dissolution of **5** in acid involves protonation of **5** to form **2** (in the case of hydrochloric acid). The structure of **5** is therefore not accessible by solution measurements. This work thus demonstrates the utility of solid-state ^{13}C-NMR to structurally characterize an organic solid which could not be examined in solution.

Attempted pigment synthesis

As noted in the introductory section, the objective of the present work was to synthesize bisazo pigments from **1**. While the syntheses of the tetrazonium salts, **3** and **4**, were successful, these two compounds deprotonate to form an insoluble solid, **5**, in water or in organic solvents. This rules out any neutral or alkaline conditions for the subsequent coupling reaction in which naphtholic couplers could be used. Since **3** and **4** are soluble in concentrated hydrochloric acid, and it is known that coupling reactions can also occur in acidic media if very reactive coupler components are used, the coupling of **3** with *N*,*N*-dimethylaniline in concentrated hydrochloric acid was attempted. No pigment product was observed even after prolonged stirring at room temperature. Attempts to increase the pH of the reaction medium by adding sodium-hydroxide solution into the coupling mixture, which may increase the reactivity of *N*,*N*-dimethylaniline, result in the precipitation of **5**, even at low pH (~1–2). The coupling reaction is then terminated. The facile deprotonation of **3** or **4** to **5** thus appears to be a limiting factor for the pigment synthesis.

SUMMARY

Tetrazonium salts, **3** and **4**, of 1,5-diamino-4,8-dihydroxyanthraquinone (**1**) have been prepared and structurally characterized by IR, solution ^{1}H-NMR, solution ^{13}C-NMR and CP MAS ^{13}C-NMR spectroscopy. Due to the high acidity of these tetrazonium salts, they deprotonate in water or organic solvents to form an insoluble product, **5**, characterized by IR and CP MAS ^{13}C-NMR spectroscopy. The high acidity of the tetrazonium salt and the low solubility of the deprotonated form are shown to be the primary obstacle for bisazo-pigment synthesis.

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18. The solution ^{13}C-NMR spectrum of **1** in DMSO-d_6 has been studied by Chippendale.[19] All carbon peaks were assigned (see Table 2) and the assignments of carbons 4a, 8a and 9a, 10a were reported to be only tentative. In the present work, the ^{13}C-NMR spectrum of **1** in DMSO-d_6 has been reinvestigated and the chemical-shift assignments of 4a, 8a and 9a, 10a has been clarified by selective decoupling of the OH proton.
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