Azo Pigments and Their Intermediates. Electronic Structure of "Bisazo" Pigments by Cross-Polarization Magic Angle Spinning ^{13}C NMR Spectroscopy

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The electronic structures of a number of photoconductive bisazo pigments II–VIII, synthesized by coupling 1,5-diaminonaphthalene, 2,7-diaminonaphthalene, 2,7-diaminofluorenone, 2,7-diaminodibenzothiophene sulfone, 4,4′-diamino-3,3′-dichlorobiphenyl, 4,4′-diaminoterphenyl and 4,4′-diaminoazobenzene with 2-hydroxy-3-naphthanilide couplers, respectively, have been studied by cross-polarization magic angle spinning (CP MAS) ^{13}C NMR spectroscopy. These bisazo pigments are amorphous (or microcrystalline), pigmentary powders in the solid state. Their electronic structures are neither accessible by solution spectroscopic nor X-ray powder diffraction studies. ^{13}C chemical shift data of 1,5-bis(1′-azo-2′-hydroxy-3′-naphthanilide)-naphthalene (IIa) reveal that the hydroxylic aromatic carbons present in the coupler moieties of IIa are absent. This observation, along with the appearance of a new carbonyl resonance, leads us to conclude that IIa exist as a keto-hydrazone in the solid state. This conclusion is complemented by IR spectral data, where a change in the intramolecular H-bonding structure of the coupler moieties upon pigment formation, is indicated. Studies of the temperature and substituent effects on the ^{13}C NMR spectra of IIa indicate that the keto-hydrazone structure is stable and is unaffected by electronic and steric effects exerted by substituents in the coupler moieties. The dominance of the keto-hydrazone tautomers is attributable to both intra- and intermolecular H-bonding effects. CP MAS ^{13}C NMR data of bisazo pigments III–VIII clearly reveal that these pigments are keto-hydrazones also. The impact of the realization of the electronic structure on the molecular design and synthesis of near-IR-sensitive azo pigments is discussed.

Introduction

Azo dyes and pigments are the most important class of colorants produced in the dye industry, comprising over 50% of the total world dyestuff production. The common structural characteristic of azo compounds is the azo chromophore (—N=N—) connecting two carbon systems, at least one of which is aromatic. Depending on the number of azo linkages, these compounds can further be classified into subgroups, such as monoazo, bisazo, trisazo, etc. The preparative procedures for azo compounds, by the classic azotization and coupling reactions, are very simple and low cost. These attractive features have offered unlimited possibilities for tailor-making azo compounds for a variety of industrial applications. In addition to their conventional application, as colorants for wools, fabrics, prints, inks, and toners, azo compounds have also found their way into high-technology areas, such as colorants in liquid-crystalline materials[1] and as photoconductors for photoreceptors in copiers and laser printers.[2]

The photoconductivity of azo compounds was recognized as early as 1969 by Rau, who reported the spectral characteristics and the photoconductive properties of 1-phenylazo-2-naphthol in a thin film device.[3] In 1975 Champ and Shattuck showed that chlorodiane blue, [4,4′-bis(1″-azo-2″-hydroxy-3″-naphthanilide)-3,3′-dichlorobiphenyl], could photogenerate electron–hole pairs in bilayer xerographic devices.[4] Subsequent activities on azo pigments have been extensive, and a large variety of azo pigments have been synthesized, xerographically screened and claimed in the patent literature.[2] Among the azo compounds that have been examined for xerographic applications, pigments synthesized from 2-naphthol derivatives were consistently found to exhibit moderate-to-high photoconductivity. These compounds primarily absorb and photorespond in the visible region, 400–650 nm. Current technology thrusts on azo pigments are to improve the photosensitivity in devices and extend the photoresponse of these materials to the near-IR, enabling them to be useful for diode laser printers which operate at 780 nm.

It is important to point out that azo compounds synthesized from 2-naphthol derivatives are known to exist in both azo and hydrazone forms in solution[5] as well as in the solid state.[6] A fundamental understanding of the electronic structure of photoconductive azo pigments is crucial towards the design and synthesis of highly sensitive, near-IR-absorbing azo pigments. Despite the ongoing efforts in the photoreceptor industry, very little attention has been devoted to the structure–photoconductivity relationship of these materials in devices. Photoconductive azo pigments are amorphous (or microcrystalline), pigmentary powders in the solid state. Their electronic structures are neither accessible by solution spectroscopic

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study nor X-ray structure determination. Here the use of cross-polarization magic angle spinning (CP MAS) ^{13}C NMR spectroscopy to determine the electronic structure of the bisazo pigment 1,5-bis(1′-azo-2′-hydroxy-3′-naphthanilide)naphthalene (IIa) and derivatives IIb–IIi is described. Our ^{13}C data, which are complemented by IR spectral results, reveal that IIa–IIi exist exclusively as keto-hydrazones in the solid state. The tautomerism is not sensitive to electronic or steric effects exerted by substituents in the coupler moieties or to temperature. Work has been extended to bisazo pigments III–VIII, synthesized by coupling 2-hydroxy-3-naphthanilide with 2,7-diaminonaphthalene, 2,7-diaminofluorenone, 2,7-diaminodibenzothiophene sulfone, 3,3′-dichloro-4,4′-diaminobiphenyl, 4,4′-diaminoterphenyl, and 4,4′-diaminoazobenzene, respectively. Without exception, all these bisazo pigments were found to be keto-hydrazones in the solid state. The technological implication of these findings on the molecular design and synthesis of near-IR-sensitive azo pigments is discussed.

Experimental Section

Materials. 1,5-Diaminonaphthalene was purchased from Pfaltz & Bauer and was recrystallized from a mixture of ethanol and water before use. 2,7-Diaminonaphthalene was from Tokyo Kasei and was recrystallized from methanol and water. 3,3′-Dichloro-4,4′-diaminobiphenyl was obtained by neutralizing the dihydrogen chloride salt (from Pfaltz & Bauer) in an aqueous NaOH solution, followed by recrystallization from a mixture of ethanol and water. 4,4′-Diaminoterphenyl and 4,4′-diaminoazobenzene were bought from Lanchester and were used as received. 2,7-Diaminofluorenone and 2,7-diaminodibenzothiophene sulfone were prepared by reducing the corresponding dinitro compound with stannous chloride using the method of Barker and Barker.[7] Azoic couplers, such as 2-hydroxy-3-naphthanilide, 2-hydroxy-3-naphtho-*o*-anisidide, 2-hydroxy-3-naphtho-*p*-anisidide, 2-hydroxy-3-naphtho-*o*-toluidide, and 2-hydroxy-3-naphtho-*p*-chloroanilide were purchased from Pfaltz & Bauer and were recrystallized from a mixture of *N,N*-dimethylformamide and methanol before use. Other couplers used in this work were synthesized from the acid chloride of 2-hydroxy-3-naphthoic acid as described by Rochat.[8] Fluoboric acid (purified, 48–50%), concentrated hydrochloric acid (reagent), sodium nitrite (certified), *N,N*-dimethylformamide (+99%), methylene chloride (certified), acetone (certified), methanol (certified), and diethyl ether (anhydrous) were bought from Fisher. Thionyl chloride (Gold Label) and hexafluorophosphoric acid (60 wt %) were obtained from Aldrich.

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. Cross-polarization magic angle spinning (CP MAS) ^{13}C NMR spectra were recorded on a Bruker CXP spectrometer operating at 50.3 MHz in a Cryomagnetic Systems, Inc. superconducting magnet system. Magic angle spinning (3–5 kHz) was performed in a Doty Scientific probe with approximately 100 mg of each sample packed into 6-mm-o.d. sapphire rotors. The TOSS technique for sideband suppression was used for all measurements. Spectral assignment is facilitated by distinguishing the protiated and nonprotiated carbons using a spin temperature reversal pulse sequence. A detailed description of the spectrometer and the procedure have been reported earlier.[9]

Pigment Synthesis. 1,5-Diaminonaphthalene (0.79 g, 5 mmol) was stirred in 20 mL of 18% hydrochloric acid at ~60 °C for about 1 h and then at room temperature overnight. The resulting white dispersion was cooled to 0–5 °C by an ice-water bath. A cold aqueous solution of sodium nitrite (1 g in 2.5 mL of water) was added dropwise (in ~15 min) into the dispersion. After the addition was completed, the mixture was stirred in an ice bath for another 45 min, and a brown solution was resulted. This brown solution was filtered (by 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. This mixture was stirred at 0–5 °C for ~30 min. The yellow precipitate was collected by filtration. After washing with cold water, cold methanol, and ether, the product was air-dried for 1 h, yielding tetrazonium salt, ~1.7 g. The above prepared tetrazonium salt was dissolved in 40 mL of DMF inside a three-neck, 1-L flask surrounded by an ice-water bath. A cold DMF solution containing 2-hydroxy-3-naphthanilide (2.9 g, 11 mmol) in 250 mL of DMF was added slowly into the salt solution in ~25 min. The color of the salt solution changed from orange brown to dark purple. A cold solution of 5 g of sodium acetate in 75 mL of water was then added. The temperature of the DMF solution was kept below 7 °C during the addition, which took ~30 min. After the addition was completed, the ice bath was removed and the product mixture was stirred at room temperature overnight. Crude pigment product was isolated by filtration using a fine sintered glass funnel. It was purified by washing with warm water (2 × 250 mL, at 80 °C), warm DMF (3 × 250 mL at 80 °C), acetone (1 × 250 mL) and ether (1 × 250 mL). After vacuum drying, a dark blue powder, which was identified as 1,5-bis(1′-azo-2′-hydroxy-3′-naphthanilide)naphthalene (IIa) was obtained, yield 2.23 g (63%).

Bisazo pigments IIb–IIi and III–VIII were synthesized and purified in a similar fashion. The physical and IR spectral data of these materials are tabulated in Tables I and II.

Results and Discussion

Synthesis, Properties, and IR Spectra of Bisazo Pigments. All bisazo pigments studied in this work were synthesized by first azotizing an aromatic diamine with a slight excess of sodium nitrite in 18% hydrochloric acid and then by coupling the resulting tetrazonium salt (which is normally isolated and purified as a tetrafluoroborate salt) with an anilide coupler in DMF in the presence of sodium acetate. The synthesis is very general and is illustrated in Scheme I using the synthesis of 1,5-bis(1′-azo-2′-hydroxy-3′-naphthanilide)naphthalene (IIa) as an example. The crude pigment product was isolated by filtration and was purified by repetitive washings with water and DMF to remove inorganic and organic impurities. All bisazo pigments prepared by this fashion were analytically pure. They usually exhibit very high melting points (>300 °C). With the exception of III, which has a red-brown appearance, IIa–IIi and IV–VIII are dark blue solids. The yields, the melting points and the analytical data of these pigments are summarized in Tables I and II.

A characteristic amide C=O stretching, ranging from 1660 to 1690 cm^{-1}, is observed for bisazo pigments II–VIII. The $\nu_{C=O}$ values are sensitive to electronic as well as steric effects exerted by substituents in the coupler moieties. More importantly, the range of $\nu_{C=O}$ for II–VIII is consistently higher than that of the corresponding couplers. The carbonyl stretches for Ia–Ii fall at $\nu_{C=O}$ = 1630 ± 20 cm^{-1}, which is relatively low for aromatic anilides.[10] We attribute these low $\nu_{C=O}$ values to an intramolecular H bonding between the hydroxy group and the amide C=O group. The observed hypsochromic shift for the amide C=O groups in II–VIII thus suggests that these C=O groups are no longer intramolecularly H bonded to the hydroxy group in the pigment structure

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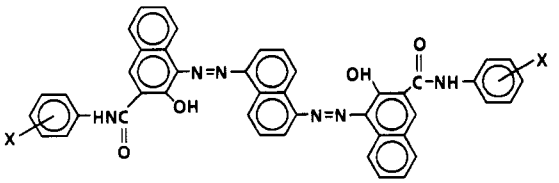
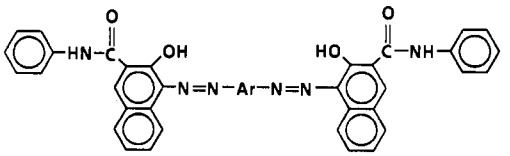
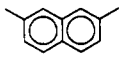
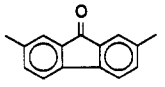
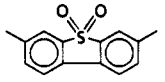
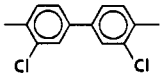
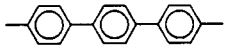
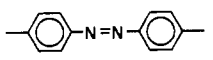
Table I. Synthesis, Physical Properties and IR Data of Bisazo Pigments IIa–IIi



pigment	yield, %	mp (°C)		C	H	N	amide C=O, cm^{-1}
IIa (X = H)	63	>300	calcd	74.78	4.28	11.89	1670
			found	74.75	4.28	11.89	
IIb (X = *p*-OCH_3)	44	>300	calcd	72.05	4.47	10.96	1670
			found	70.62	4.71	10.95	
IIc (X = *o*-OCH_3)	52	251 (dec)	calcd	72.05	4.47	10.96	1670
			found	71.96	4.74	10.78	
IId (X = *p*-CH_3)	63	>300	calcd	75.19	4.66	11.44	1666
			found	74.84	4.84	11.12	
IIe (X = *o*-CH_3)	58	>300	calcd	75.19	4.66	11.44	1670
			found	75.06	4.84	11.35	
IIf (X = *p*-Cl)	65	>300	calcd	68.13	3.64	10.84	1675
			found	67.82	4.06	10.82	
IIg (X = *o*-Cl)	68	>300	calcd	68.13	3.64	10.84	1678
			found	67.75	4.06	10.46	
IIh (X = *p*-NO_2)	39	>300	calcd	66.33	3.54	14.06	1688
			found	66.50	3.72	13.24	
IIi (X = *o*-NO_2)	37	>300	calcd	66.33	3.54	14.06	1690
			found	66.18	3.71	13.31	

Table II. Synthesis, Physical Properties, and IR Data of Bisazo Pigments III–VIII



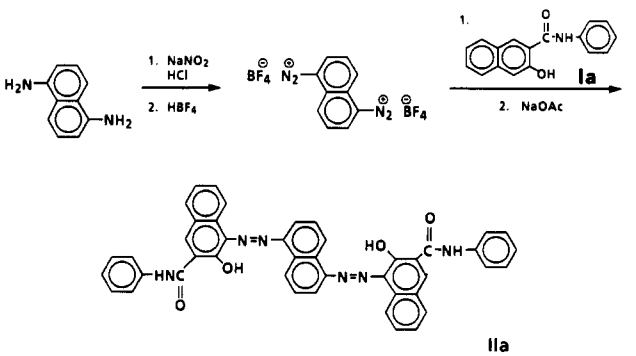
pigment	Ar	yield, %	mp (°C)		C	H	N	amide C=O, cm^{-1}
III		67	>300	calcd	74.78	4.28	11.89	1675
				found	73.70	4.35	11.84	
IV		85	>300	calcd	74.40	3.99	11.08	1676
				found	73.50	4.00	10.88	
V		70	>300	calcd	69.51	3.80	10.57	1674
				found	69.38	4.18	10.47	
VI		56	>300	calcd	72.62	4.24	14.73	1673
				found	72.16	4.13	14.75	
VII		81	>300	calcd	77.21	4.49	10.39	1672
				found	77.12	4.73	10.33	
VIII		83	>300	calcd	72.62	4.24	14.73	1677
				found	72.16	4.13	14.75	

(Scheme II). As will be seen, II–VIII are keto-hydrazones in the solid state. The release of the intramolecular H bonding between the hydroxy and amide C=O groups in the coupler moieties is merely a consequence of stabilization of the keto-hydrazone pigment structure (Scheme II).

Solution and Solid-State CP MAS ^{13}C NMR Spectral Data of 2-Hydroxy-3-naphthanilide (Ia) and Derivatives (Ib–Ii). To facilitate the chemical shift assignments of bisazo pigments, the solution and CP MAS ^{13}C NMR spectra of couplers Ia–Ii were measured.

The CP MAS ^{13}C NMR spectrum of Ia is presented in Figure 1a. Nonprotiated carbons in Ia are distinguished by a spin temperature inversion experiment[9] and the ^{13}C spectrum of these carbons are shown in Figure 1b. The protiated carbons are plotted in Figure 1c as the calculated

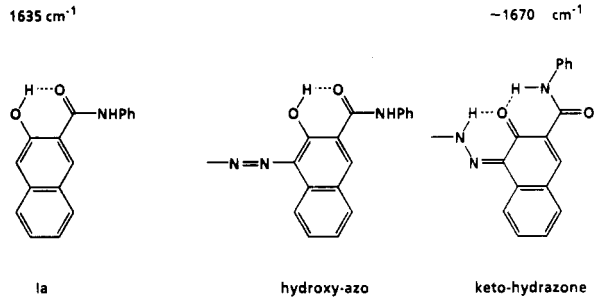
Scheme I



IIa

difference of Figures 1a and 1b. The chemical shift assignments are determined as follows. There are six

Scheme II



nonprotiated carbons in Ia, and signals corresponding to six carbons are observed in Figure 1b. The most downfield signal is a doublet at 164.6/166.0 ppm, assigned to the amide carbonyl carbon (C11). The doublet may be due to the effect of crystal packing or to interactions with the neighboring quadrupolar ^{14}N nuclei.[11] The peak at 153.7 ppm is assigned to C2, due to the strong deshielding effect exerted by a hydroxy group on the bonded aromatic carbon.[12] The shoulder at ~139 ppm shows the characteristic broadening by the quadrupolar ^{14}N nuclei and can be assigned to C12. The remaining signals at 136.2, 128.5/126.8 (doublet), and 120.4 ppm can be assigned to C9, C10, and C3, respectively, by comparison with chemical shifts in the solution spectrum.[13]

There are 11 protiated carbons in Ia. With the exception of C1 and C4, which can be assigned to signals at 110.9/113.1 (doublet) and 132.6 ppm due to the characteristic substituent shifts,[12] detailed chemical shift assignments of the remaining signals are difficult due to spectral overlap. However, by comparison of shifts with the solution data, all protiated carbons can be tentatively assigned. Both solution and solid-state CP MAS ^{13}C NMR data of Ia are summarized in Table III.

The CP MAS ^{13}C NMR spectra of Ib–Ii were recorded using the same conditions as for Ia. Again, spin reversal experiments were applied in each case to differentiate the non-protiated from the protiated carbons. The solution ^{13}C NMR spectra of Ib–Ii were also recorded, and the chemical shifts of individual carbons are assigned using Ia as a reference compound and applying known substituent effects on the chemical shifts.[12] As a result, most of the solid state peaks are assigned. The solution and the CP MAS ^{13}C NMR data of Ib–Ii are also tabulated in Table III.

CP MAS ^{13}C NMR Spectra of Bisazo Pigments IIa–IIi. *Spectral data of IIa.* Figures 2a and 2b depict the full CP MAS ^{13}C and the nonprotiated ^{13}C spectra of IIa, respectively. The protiated ^{13}C spectrum is shown in Figure 2c as the calculated difference between Figures 2a and 2b. There are nine magnetically nonequivalent nonprotiated carbons in IIa. If one assumes (based on relative intensities) that the peaks at 126.3 and 134.9 ppm each represent two carbons, all nine nonprotiated carbons can be accounted for. First, we assign the ^{13}C signal at ~161 ppm to the amide carbonyl carbon (C11), because it is expected to have a shift similar to that of the coupler and because it shows the expected broadening of carbons

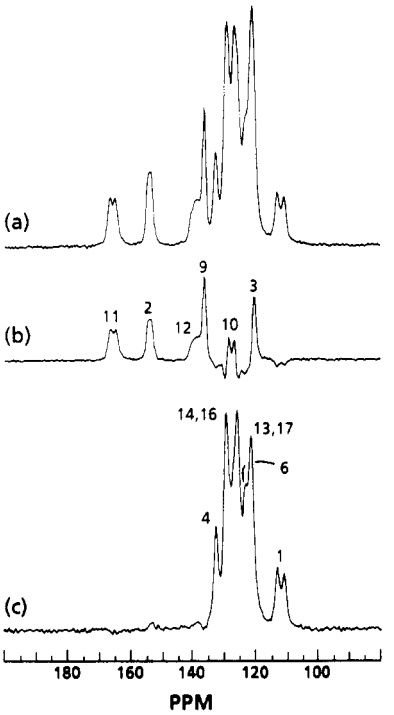
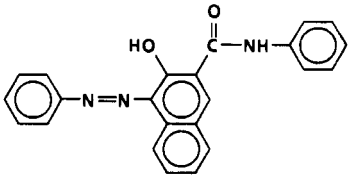


Figure 1. CP MAS ^{13}C NMR spectra of Ia (a) cross polarization time = 5 ms, spinning rate = 4800 Hz, repetition time = 15 s, number of scans = 256; (b) same as (a) except with a 100-μs spin temperature reversal time inserted between the cross polarization and observed periods; (c) Figure 1a – Figure 1b. (see Table III for labeling).

bonded to ^{14}N nuclei.[11] The most downfield signal at 176.8 ppm is attributable to a carbonyl carbon resonance. We conclude from this characteristic carbonyl shift that IIa has a keto-hydrazone structure rather than a hydroxy-azo structure in the solid state and that the 176.8 resonance is due to the keto carbonyl carbons. This interpretation is supported by the following: (1) the chemical shifts of analogous keto-hydrazone carbonyl carbons are reported to be in the range 170–180 ppm in solution,[14-16] (2) the hydroxy carbons in the coupler moieties, which fall at 155 ppm, are absent from IIa, and (3) the infrared spectral data indicate that the intramolecular H bonding between the amide C=O and the hydroxy group is absent in IIa. A more detailed discussion on the electronic structure of IIa will be given in the next section. Here we focus on the chemical shift assignments of the remaining carbons in IIa.

To assist with the chemical shift assignments of the complex bisazo pigment, model compound IX, which is



IX

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(12) Eyring, D. F. *Org. Magn. Reson.* **1979**, *12*, 525.
(13) The solution (DMSO) chemical shifts Ia were assigned based on results obtained from a two dimensional ^{1}H–^{1}H COSY, ^{13}C–^{1}H HETCOR NMR experiment.
(14) Kelemen, J.; Moss, S.; Sauter, H.; Winkler, T. *Dyes Pigm.* **1982**, *3*, 27.
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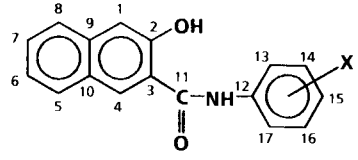
Table III. Solution and CP MAS ^{13}C NMR Spectral Data of 2-Hydroxy-3-naphthanilide Derivatives Ia–i Chemical Shift



		Chemical Shift[a]																	
compd		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	
Ia state (X = H)	DMSO-d_6[a]	110.6	153.9	121.8	130.6	128.7	123.7	128.1	125.8	135.8	126.9	165.7	138.5	120.6	128.8	124.1	128.8	120.6	
	solid[b]	110.9	153.7	120.4	132.6		~123			136.2	126.8	164.6	~139	121.4	129.3		129.3	121.4	
		113.1									128.5	166.0							
Ib (X = *p*-OCH_3)	DMSO-d_6[a]	110.6	154.3	120.8	130.2	128.6	123.6	128.1	125.7	135.8	126.7	165.7	131.3	122.3	113.8	155.9	113.8	122.3	55.1 (OCH_3)
	solid[b]	111.2	152.2	122.2	133.3	130.5	122.8	126.9	126.9	135.5	127.9	164.3	~134	122.8	114.7	156.1	114.7	122.8	55.0
												165.8			117.4		117.4		
Ic (X = *o*-OCH_3)	DMSO-d_6[a]	110.7[c]	152.6	121.3	132.6	128.9	123.7[d]	128.2	125.6[d]	135.8	127.2[e]	162.8	127.9[e]	148.5	110.8[e]	123.8[d]	120.1[f]	120.6[f]	55.9 (OCH_3)
	solid[b]	111.6	151.6	118.5	134.9	130.9	122.4	125.4	125.4	136.0	126.9	162.2	~132	149.1	111.6	122.4	121.0	121.0	58.2
												163.5							
Id (X = *p*-CH_3)	DMSO-d_6[a]	110.6	154.0	121.2	130.4	128.7	123.7	128.1	125.7	135.8	126.8	165.6	135.8	120.6	129.1	133.1	129.1	120.6	20.4 (CH_3)
	solid[b]	111.9	154.1	121.3	~132	127.2		127.2		136.1	128.2	165.1	136.1		129.8	132.7	129.8		22.5
Ie (X = *o*-CH_3)	DMSO-d_6[a]	110.7	153.5	120.6	131.5	128.8	123.8[g]	128.2	125.7[h]	135.8	127.0	164.4	136.4	129.8	130.3	124.8[g]	126.3[h]	123.2[g]	17.7 (CH_3)
	solid[b]	113.8	151.3	122.4	132.3	~128	~123	~128	~128	137.8	127.4	165.2	137.8	127.4	132.3	~123	~128	~123	18.6
If (X = *p*-Cl)	DMSO-d_6[a]	110.5	153.6	121.8	130.5	128.6	123.7	128.1	125.7	135.7	126.8	165.7	137.4	121.9	128.6	127.6	128.6	121.9	
	solid[b]	111.1	153.5	119.7	132.1					135.8	127.3	165.1	~137	121.5	128.1		128.1	121.5	
												166.5							
Ig (X = *o*-Cl)	DMSO-d_6[a]	110.7	152.6	120.5	132.7	128.0[i]	123.8	128.4	125.6	135.3[j]	127.1	163.4	136.0[j]	123.2	129.2[i]	125.0	127.8	122.5	
	solid[b]	112.5	151.0	118.3	134.3					136.4	~127	~163	~138						
Ih (X = *p*-NO_2)	DMSO-d_6[a]	110.6	153.1	122.4	130.8	128.6	123.7	128.1	125.7	135.8	126.8	165.9	144.8	119.8	124.8	142.6	124.8	119.8	
	solid[b]	111.4	152.7	118.2	132.7	129.7	~123	126.7	126.7	135.1	126.5	166.6	141–	119.5	124.9	141–	124.9	119.5	
										136.2	128.3		145			145			
Ii (X = *o*-NO_2)	DMSO-d_6[a]	110.7	152.9	120.8	133.0	129.1	124.1[k]	128.6	125.7	136.2	127.1	164.2	133.2	139.1	124.0[k]	125.4	134.9	123.8	
	solid[b]	112.2	151.2	118.1	135.5	130.7	124.8	128.9	126.6	136.6	126.5	163.1	~136	~136	124.8	126.6	135.5	121.8	
												164.6							

[a] Ppm from TMS. [b] Referenced to the methyl carbons of hexamethylbenzene (17.4 ppm), accuracy ±0.5 ppm, ~ denotes ±1 ppm. [c–k] These carbons cannot be assigned unambiguously and may be interchanged.

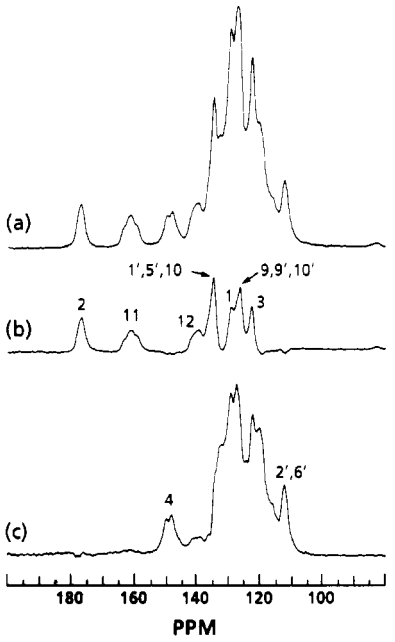


Figure 2. CP MAS ^{13}C NMR spectra of IIa (a) cross polarization time = 1.5 ms, spinning rate = 4700 Hz, repetition time = 4 s, number of scans = 4480; (b) same as (a) except with 100-μs spin temperature reversals; (c) Figure 2a − Figure 2b. (see Table V for labeling).

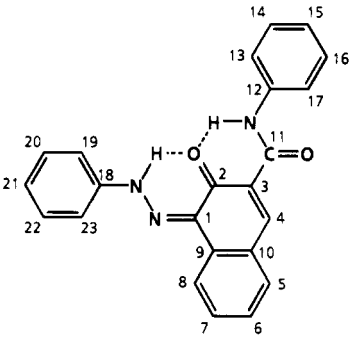
known from X-ray analysis of similar structures,[17,18] to exist as a keto-hydrazone, was synthesized. The ($CDCl_3$) solution ^{13}C and the CP MAS ^{13}C NMR spectra of IX were measured. The solution chemical shifts for each carbon can be unambiguously assigned using two-dimensional ^1H–^1H COSY, ^{13}C–^1H HETCOR NMR spectroscopy. The chemical shifts in the solid state are found to be similar to those in solution and are assigned based on the solution data. The results of this analysis are tabulated in Table IV. The amide and the keto carbon resonances fall at ~161 and ~177 ppm, respectively, and are comparable to those of IIa. Again, no hydroxy carbon at ~155 ppm is observed. By comparing the data in Table IV with the spectral data for IIa (Figure 2b), the chemical shifts of the remaining nonprotiated carbons in IIa can be assigned, and the data are given in Table V.

The protiated ^{13}C NMR spectrum of IIa (Figure 2c) is quite complex due to spectral overlap. It is, however, possible to assign the doublet at 148.0/148.5 ppm and the singlet at 112.2 ppm, both of which are well resolved. By comparison with the shifts of IX (Table IV), we assign the doublet to C4 and the singlet to C2′,6′ of IIa, respectively. The high-field singlet, which is a signature of the strong ortho shielding effect exerted by an –NH group, is supportive of the structure assignment of IIa, which is a keto-hydrazone.

Discussion of the Electronic Structure of IIa. Hydroxy-azo/keto-hydrazone tautomerism of 1-phenylazo-2-naphthol (X) and its derivatives is well documented, both in solution and in the solid state.[5,19–21] It has been calculated theoretically that the keto-hydrazone form is thermodynamically favored[22] and that electron-withdrawing functionality[19,20] and H bonding (both inter- and intramolecular)[22,23] are key driving forces that shift the equilibrium in favor of the keto-hydrazone form. This conclusion is also supported by X-ray analyses of several 1-(phenylazo)-2-naphthols bearing electron-withdrawing groups.[17,18]

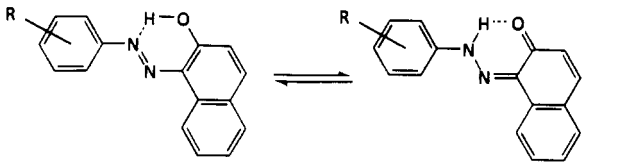
Less attention has been paid to more complex structures, such as IX. Nevertheless, it has been reported that 1-(2′,5′-dichlorophenylazo)-2-hydroxy-3-naphthoic acid 4-chloro-2,5-dimethoxyanilide (XI) has a keto-hydrazone structure

Table IV. Solution and CP MAS ^{13}C Spectral Data of Model Compound IX

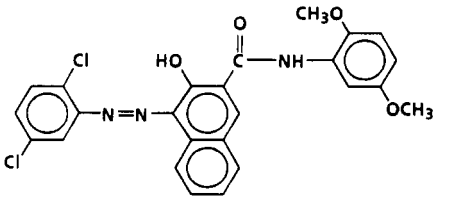


carbon	chemical shift in $CDCl_3$[a]	chemical shift in solid[b]
1	130.5	~129
2	177.1	177.5
3	126.1	126.8
4	148.0	148.1
5	121.6	c
6	131.4	131.6
7	126.7	c
8	131.1	131.6
9	126.6	126.8
10	135.4	137.0
11	162.0	160.6, ~161
12	138.5	~141
13, 17	120.6	c
14, 16	129.0	c
15	124.2	c
18	141.9	~141
19, 23	117.8	c
20, 22	129.9	130.0
21	127.4	c

[a] Ppm from TMS. [b] Same as footnote *b* of Table III. [c] These carbons cannot be assigned unambiguously.



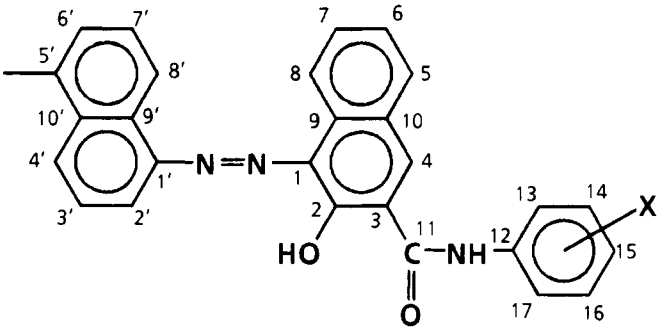
X: R = H



XI

(17) Guggenberger, L. J.; Teuffer, G. *Acta. Crystallogr.* **1975**, *B31*, 785.
(18) Whitaker, A. *J. Soc. Colourists* **1978**, *94*, 431.
(19) Bershtein, I. Ya.; Ginzburg, O. F. *Russ. Chem. Rev.* **1972**, *41*, 97.
(20) Ball, P.; Nicholls, C. H. *Dyes Pigm.* **1982**, *3*, 5.
(21) Matsunaga, Y.; Miyajima, N. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 361.
(22) Kuder, J. E. *Tetrahedron* **1972**, *28*, 1973.
(23) Monahan, A. R.; Flannery, J. B. *Chem. Phys. Lett.* **1972**, *17*, 510.

Table V. CP MAS ^{13}C NMR Chemical Shifts of Bisazo Pigments IIa–IIi



compound	chemical shift[a]														
	1	2	3	4	9	10	11	12	13	14	15	1',5'	2',6'	9',10'	
IIa (X = H)	129.0	176.8	122.6	148.0, 149.5	~126.3	134.9	161	~139.7[b]				~135[b]	112.6	~126.3	
IIb (X = *p*-OCH_3)	130.5	177.6	122.9	150.2	126.4[c]	~136[k]	160.4	~133[k]		115.7	156.8	136.0	~113	126.2[c]	56.7 (OCH_3), 58.6
IIc (X = *o*-OCH_3)	131.3	178.1	124.6	149.8	128.1	~134[d]	160.5		147.1	109.3		~136[d]	115.3	128.1	55.3 (OCH_3)
IId (X = *p*-CH_3)	~132	178.1	~125	149.9	128.3	~134	160.7	~140[e]			~134	~138[e]	110.8	~128.3	22.1 (CH_3)
IIe (X = *o*-CH_3)	~131	178.5	123.3	150.5	127.5[f]	133.4	~160	~139	124[f]			~136.9	111.4	~124[f]	19.2 (CH_3)
IIf (X = *p*-Cl)	130.1	177.1	123.2	149.3	126.8	135.5	160.5	~139[g]				~136[g]	113.5	126.8	
IIg (X = *o*-Cl)	~131	178.0	123.1	149.7	125.9[h]	134.3	160.5	~139				~137	112.0	~127[h]	
IIh (X = *p*-NO_2)	131.0	176.8	123.5	150.2	128.3[i]	135.1	161.2, 162.7	~146[j]			143.2[j]	135.1	115.6	123.5[i]	
IIi (X = *o*-NO_2)	130.7	175.8	123.1	148.9	126.7	~135	162.4	~135	~135			~135	112.3	126.7	

[a] Same as footnote *b* of Table III. [b–k] These assignments cannot be assigned unambiguously and may be interchanged.

in the solid state.[24] The present conclusion, based upon IR and ^{13}C NMR data, that IIa has a keto-hydrazone structure in the solid state is consistent with these earlier studies.

The hydroxy-azo/keto-hydrazone tautomerism of IIa has been characterized by measuring the variable temperature CP MAS ^{13}C NMR spectra of IIa from 25 to 80 °C.[25] Chemical shifts of IIa are found to be insensitive to temperature. This observation is in contrast to the temperature dependence of the hydroxylic/keto aromatic ring carbon resonance (C2) of 1-(phenylazo)-2-naphthol. The upfield shift of this resonance with increasing temperature is attributed to a shift in the tautomeric equilibrium toward the azo form.[25] The lack of a temperature effect for IIa suggests that IIa exists exclusively as a keto-hydrazone tautomer in the solid state. The result is attributable to H-bonding stabilization effects.[22,23]

Electronic and Steric Effects. It has been reported that the hydroxy-azo/keto-hydrazone tautomerism of compounds of general structure X is sensitive to electronic as well as steric effects.[19,20] To examine these effects on bisazo pigments of the general structure II, the CP MAS ^{13}C NMR spectra of IIb–IIi were studied. Typical spectra are highlighted in Figure 3. Chemical shift assignments are made by using IIa as a reference compound and by using known substituent effects on chemical shifts.[12] The results in Table V and Figures 3 show that, without exception, the C2 hydroxy carbons in the coupler moieties are absent in IIb–IIi and that new carbonyl carbons are observed. We conclude that IIb–IIi are keto-hydrazones also in the solid state. The lack of substituent effects on the tautomerism of bisazo pigments II is again attributable to the stabilization of the keto-hydrazone structure by H bondings.[22,23]

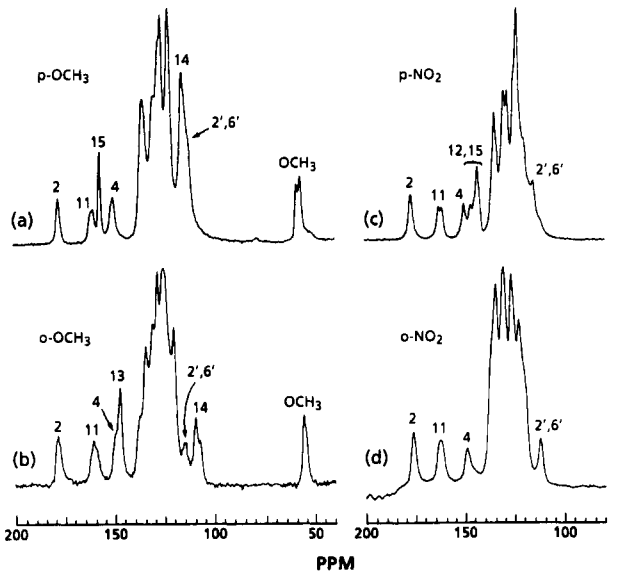
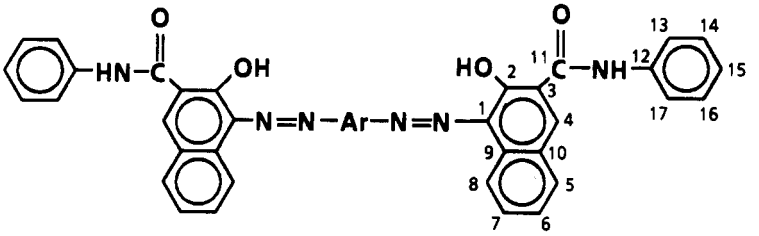


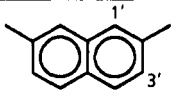
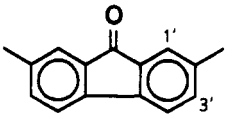
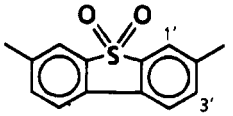
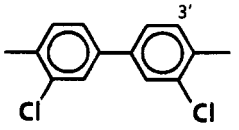
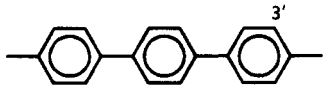
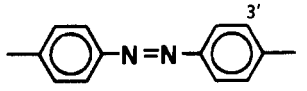
Figure 3. CP MAS ^{13}C NMR spectra of bisazo pigments IIb, IIc, IIh, and IIi (conditions: IIb cross polarization time = 1 ms, spinning rate = 5000 Hz, repetition time = 4 s, number of scans = 5120; IIc cross polarization time = 2 ms, spinning rate = 4060 Hz, repetition time = 1.5 s, numbers of scans = 2560; IIh cross polarization time = 2.5 ms, spinning rate = 5000 Hz, repetition time = 1.5 s, number of scans = 3072; IIi cross polarization time = 2 ms, spinning rate = 3340 Hz, repetition time = 1.5 s, number of scans = 12 288. (see Table V for labeling).

Effects of Structural Changes on the Tautomerism of Bisazo Pigments. Bisazo pigments III–VIII were

(24) Kobelt, Von D.; Paulus, E. F.; Kunstmann, W. *Acta. Crystallogr.* **1972**, *B28*, 1319.
(25) Kaplan, S.; Law, K. Y., unpublished results.

Table VI. Partial CP MAS ^{13}C NMR Spectral Data of Bisazo Compounds III–VIII



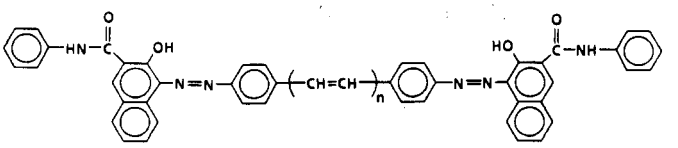
pigment	Ar	chemical shift[a] 2	3	4	11	12	others
III		~177	126.5	148.3 150.8	~161	~140	1′ = 111.2, 3′ = 116
IV		176.9		152.6	159.6	~142	1′ = 109.5, 3′ = 114.3, 190.5[b]
V		178.1 180.8	124.8	149.0 153.7	~160	~141	1′ = 109.9, 3′ = 116.3
VI		177.0	123.1	150.1	160	~138.2	3′ = 116.9
VII		176.1	121.4	140.0 ~150	~160.7		3′ = 115.6
VIII		178.7	~125	~151	~160.5	~142	3′ = 113.8, 115.9

[a] Same as footnote *b* of Table III. [b] Carbonyl carbon of the fluorenone unit.

synthesized by coupling 2-hydroxy-3-naphthanilide with 2,7-diaminonaphthalene, 2,7-diaminofluorenone, 2,7-diaminodibenzothiophene sulfone, 4,4′-diamino-3,3′-dichlorobiphenyl, 4,4′-diaminoterphenyl, and 4,4′-diaminoazobenene, respectively. Their electronic structures were studied by CP MAS ^{13}C NMR spectroscopy. The ^{13}C NMR spectra of III–VIII are found to be very similar to those depicted in Figures 2 and 3. Again, the C2 hydroxylic carbons in the coupler moieties are absent in the pigment structure, and new carbonyl carbons at 178 ± 2 ppm are observed. These spectra data indicate that III–VIII are keto-hydrazones in the solid state. Complementary evidence supporting this conclusion comes from the protiated ^{13}C spectra of these compounds. In each pigment, a low-field resonance at 146–152 ppm, assigned to the C4 carbon of the coupler moiety, and a high-field resonance at 109–117 ppm, assigned to the carbon ortho to the NH group of the hydrazone unit, are observed. The chemical shift data of most of the resolvable carbons in III–VIII are summarized in Table VI. From these results we arrive at the general conclusion that bisazo pigments synthesized 2-hydroxy-3-naphthanilide derivatives are keto-hydrazones in the solid state, irrespective of the structure of the aromatic amine precursor. The dominance of the keto-hydrazone structure is again attributable to the stabilization effect resulted from both intra- and intermolecular H bondings of the keto-hydrazone units in the solid state.

Technological Implications. As noted in the introductory section, bisazo pigments from substituted 2-hydroxy-3-naphthanilides and various aromatic diamines exhibit useful photoconductivity for xerographic applications. Current research efforts aimed at new structures with improved performance characteristics, such as higher photosensitivity, photoresponding at longer wavelengths (e.g., 650–850 nm), etc., are very active. Recognizing that the keto-hydrazone tautomer dominates the electronic structure of bisazo pigments gives us a cutting-edge molecular design principle on the synthesis of improved structures for future photoreceptors.

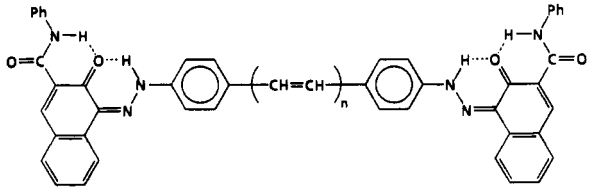
In 1988, Sasaki and co-workers[26] reported the design and synthesis of bisazo pigments with long-wavelength absorptions, e.g., >650 nm, using the approach of extended π-conjugation (structure XII). If XII is a hydroxy-azo, its



XII (hydroxy-azo form)

absorption maximum would shift to longer wavelength as *n* increases. Experimentally, the λ_{max} of XII in tetrahydrofuran solution are 577, 587, 591, 594, 596, and 596 nm

for n = 0, 1, 2, 3, 4, and 5, respectively. Considering the magnitude of the bathochromic shifts induced by π-conjugation on carbocyanine dyes (~100 nm for each additional double bond),[27] the observed bathochromic shift in XII as n increases is insignificant. Sasaki and co-workers' observation is, however, consistent with the result of this work, which predicts that the λ_{max} of XII would not be sensitive to n, because as soon as tautomerization occurs, the π-system in XII loses its extended conjugation. The actual absorbing chromophores in XII are the keto-hydrazone unit and the polyene. Probable approaches to



XII (keto-hydrazone form)

synthesize bisazo pigments with long-wavelength absorptions (>650 nm) are (1) to extend the aromatic conjugation of the keto-hydrazone unit using anilides from 2-hydroxy-11*H*-benzo(*a*)-carbazole-3-carboxylic acid, (2) to use red or near-IR aromatic amines as precursors so that the resulting pigment would be red or near-IR absorbing after losing its conjugation, or (3) a combination of approaches 1 and 2. Synthetic work along these directions is in progress.

Concluding Remarks

This work shows that bisazo pigments synthesized from aromatic diamines and substituted 2-hydroxy-3-naphthanilides are keto-hydrazones rather than hydroxy-azos in the solid state. The tautomerism is sensitive neither to temperature nor substituents effects (electronic and steric) exerted by the coupler moieties. It is also insensitive to the structure of the aromatic amine. The dominance of the keto-hydrazone structure is attributable to the stabilization effect resulted from both inter- and intramolecular H bondings of the keto-hydrazone units in the solid state. Finally, this work demonstrates the use of solid-state ^{13}C NMR technique to study the electronic structure of amorphous and microcrystalline, pigmentary solids, where solution NMR is not applicable and X-ray crystal structural analysis is not possible.

(26) Sasaki, M.; Shimada, T.; Hashimoto, M. *Proc. Japan Hardcopy* 1988, 325.

(27) James, T. H. *The Theory of Photographic Processes*, 4th ed.; MacMillan Company: New York, 1977; p 197.