# Azo or Hydrazone Structure in Some Hydrogen-Bonded Azo Pigments

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Abstract. Azo dyes and pigments are typical of the classical colorants as characterized by the azo group. However, there is still a controversial issue on the azo (-N=N-) or hydrazone (=N-NH-) form in some hydrogen-bonded azo pigments:  $\beta$ -naphthol type [for example, pigment red 3 (PR3)], acetoacetanilide type [for example, pigment yellow 3 (PY3)], and pyrazolone type [for example, pigment yellow 60 (PY60)]. This is essentially a problem which resonance form should be designated as the chemical scheme. The authors have tackled this problem from the standpoint of the x-ray structure analysis and the chromophoric theory together with semiempirical molecular orbital calculations using methyl orange derivative (MOH) as the model substance. Our close examination of the MOH structure confirmed that the protonated-azo structure (-N=N<sup>+</sup>H-) is still the case rather than the hydrazone form. This motivated us to apply this form to PR3, PY3, and PY60. The result suggested that the protonated-azo structure could be more reasonable rather than the hydrazone one as far as the azo colorants are concerned. In other words, the more azolike structure is the case rather than the hydrozonelike form. © 2011 Society for Imaging Science and Technology. [DOI: 10.2352/J.ImagingSci.Technol.2011.55.3.030508]

# INTRODUCTION

## Background

Azo pigments which carry an azo function (-N=N-) are widely used in imaging and printing industries because of their versatile colors as well as their low price.<sup>1,2</sup> Therefore, the azo compounds are by far the largest group of colorants with respect to number and production volume of currently marketed dyes and pigments. As is well known, the color of azo compounds arises from a push-pull system composed of a chromophore (i.e., conjugated  $\pi$ -electron system composed of the alternation of single/double bonds) together with auxochromes.<sup>2</sup> In methyl orange derivative (MOH: Figure 1), for example, the "phenyl/azo/phenyl" moiety serves as the chromophore, and the dimethyl amino group  $[-N(CH_3)_2:$  electron donor] and the sulfo group  $[-SO_3H:$ electron acceptor] are the auxochromes. Then, the lone pair of the N atom of the dimethyl amino group can be transferred through the chromophore to the acceptor  $(-SO_3H)$ , resulting in the formation of  $=N^+(CH_3)_2$  (acceptor) and

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=SO<sub>2</sub><sup>-</sup>OH (donor). Then, back electron transfer also occurs from donor to acceptor, leading to the full delocalization of electrons in the chromophoric system. In this way, the color appears in the visible region.

However, there are several structural reports which support the hydrazone form in the hydrogen-bonded azo pigments.<sup>1,3-8</sup> Among others, Whitaker carried out a series of investigations on the x-ray structure of monoazo pigments based on the three representative types of couplers:  $\beta$ -naphthol [for example, pigment red 3<sup>4</sup> (PR3) (Figure 2)], acetoacetanilide [for example, pigment yellow 3<sup>5</sup> (PY3) (Figure 3)], and pyrazolone [for example, pigment yellow  $60^8$ (PY60) (Figure 4)]. Whitaker showed that the hydroxyl H atom in Fig. 2(a) and 3(a), or 4(a) is transferred to the azo bond to form a hydrazone structure (=N-NH-), and this in turn results in the formation of the keto form (-C=O), as shown in Figs. 2(b), 3(b), and 4(b). As a consequence, these structural reports caused a big confusion for dye and pigment chemists because they design azo molecules on the basis of the azo form, but they later become aware that the real structure is of the hydrazone form. The hydrazone form is unacceptable for the chemists because the N—N single bond of the hydrazone form disturbs the chromophoric system, for example, as shown in Fig. 2(b), where the electron donor is the -OH group while the -NO2 group serves as an acceptor. Nevertheless, the vivid red appears in reality in the solid state.

The hydrazone structure seems to have been proposed presumably because the H atom was found attached to the



Figure 1. Molecular structure of MOH.



**Figure 2.** Molecular structure of PR3: (a) azo form, where the donor is —OH and the acceptor is —NO<sub>2</sub>, and (b) hydrazone form.

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Figure 3. Molecular structure of PY3: (a) azo form, where the donor is —OH and the acceptor is —NO<sub>2</sub>, and (b) hydrazone form.



Figure 4. Molecular structure of PY60: (a) azo form and (b) hydrazone form.

azo group. However, in our view, it would appear rather inadequate to determine the azo or hydrazone structure solely on the basis of the x-ray structure analysis. Instead, we need to rely on the careful analysis in combination with chemical knowledge, especially with the color generation mechanism. For this reason, we have initiated our investigation on the azo or hydrazone structure, using MOH, PR3, PY3, and PY60 as the examples. In the present investigation, we propose a protonated-azo structure ( $-N=N^+H-$ ) as an alternative model that is compatible with the x-ray structure analysis and the chromophoric theory.

# Motivation for the Proposal of the Protonated-Azo Structure

In our previous report,<sup>9</sup> we studied the electronic structure of MOH by polarized reflection spectra measured on single crystals, together with density-functional theory calculations. We isolated two kinds of single crystals: one is vivid red and the other is purple. The structure of the red phase is in good agreement with that reported by Burke et al.,<sup>10</sup> whereas the purple phase is a new crystal modification. Between the red and purple phases, we found a distinct difference in crystal structure as follows. The red phase [reflection maximum: around 590 nm<sup>9</sup>] is characterized by the formation of NH ... O intermolecular hydrogen bonds, showing that the H atom of the sulfo group in one MOH molecule is transferred to the neighboring MOH (Figure 5). Burke et al. attributed this situation simply to the formation of a zwitterionic structure  $[-N^+H=N-$  and  $-SO_3^-$  (Figure 6)].<sup>10</sup> On the other hand, the purple phase [reflection maximum around 420 nm<sup>9</sup>] possesses the typical azo structure as shown in Fig. 1. Then, we carefully examined the formation of the zwitterionic structure on the basis of the S/O bond length of the sulfonate group. The three S/O bond lengths are found to be nearly equal and lie in the range of 1.45-1.47 Å, where







Figure 6. Proposed zwitterionic structure for MOH:  $N=N^+H$  and  $-SO_3^-$ .

the standard single and double S/O bonds are 1.57 and 1.43 Å, respectively.<sup>11</sup> This suggests that the negative charge is delocalized in the sulfonate group in the form of  $SO_3^-$ , while the proton (H<sup>+</sup>) is transferred to the azo group of the neighboring molecule to form a protonated-azo form ( $-N2=N^+H_{1N}$ — in Fig. 5). Furthermore, the N/N bond length is 1.307(3) Å and is fairly consistent with the standard azo bond of 1.24 Å rather than the single N—N bond of 1.44 Å.<sup>11</sup> The above result motivated us to apply the protonated-azo structure to PR3, PY3, and PY60. The situation in these compounds [Figs. 2(b), 3(b), and 4(b)] is slightly different from that of MOH with respect to the fashion of intra- or intermolecular hydrogen bonds.

As the most basic level of understanding, it is important to note that the protonated-azo structure with its zwitter anion and the hydrazone structure are chemically the same species but can be illustrated as different resonance structures. The actual normal state of the molecule is not represented by any of the alternative structures but can be represented by a combination of them, their individual contribution being determined by their nature and stability. The molecule is then described as resonating among the several valence-bond structures. However, it is conventional to designate the molecule with one of the most reasonable resonance structures in consideration of chemical and physical attributes. Then, the question is how to experimentally determine the dominant structure. One way is to rely on the x-ray structure analysis, where the bond length (for example, N/N bond) is the determinant factor. The structure must also be compatible with the color generation mechanism. The use of molecular orbital (MO) calculations is another alternative. However, in all MO calculations, the input information comprises only geometry (i.e., xyz-coordinates) and the total charge of the molecule. Therefore, the same geometry and the total charge ("zero") are used for the protonated-azo or hydrazone structure. Nevertheless, the calculated dipole moment can serve as a measure of the ionicity of the molecule.

# REDETERMINATION OF THE STRUCTURE OF PR3, PY3, AND PY60

### Materials, Crystal Growth, and Structure Analysis

PR3 and PY3 were purchased from Kishi-Kasei Co., Ltd. and Clariant Ltd., respectively. PY60 was synthesized with a procedure described previously.<sup>1</sup> Single crystals of PR3, PY3, and PY60 were grown from the vapor phase, using Ar as the carrier gas.<sup>12</sup> After 24 h, a number of single crystals were obtained in the form of platelets in all samples.

Reflection data were collected at room temperature on an R-axis rapid-F diffractometer from Rigaku, using Cu  $K\alpha$ as the radiation source ( $\lambda$ =1.5418 Å). All structures were solved by direct methods<sup>13</sup> and refined by the full-matrix least-squares method of  $F^{2.14}$  The H atoms attached to the azo group in PR3, PY3, and PY60 were localized in density maps and were refined with isotropic displacement parameters. All the rest of the H atoms were placed in geometrically idealized position and constrained to ride on their parent atoms, with C—H=0.93 and 0.96 Å with  $U_{\rm iso}({\rm H})$ =1.2 and 1.5 $U_{\rm eq}({\rm C})$ , respectively.

#### Crystal Structure of PR3, PY3, and PY60

Table I details the crystallographic parameters for PR3, PY3, and PY60. The unit cell transformation of PR3 from space group of  $P2_1/n$  to  $P2_1/a$  gives the following parameters which are in good agreement with those of Whitaker:<sup>4,5,8</sup> a=16.316, b=12.86, c=6.96 Å,  $\beta=102.00^{\circ}$ , and  $Z=4.^{4}$  All the results of PR3, PY3, and PY60 are basically in good accord with those of Whitaker. Table II shows the selected bond distances: {C1/O1, C10/N1, N1/N2, and N2/C11 in PR3}, {C10/O1, C7/N2, N2/N1, and N1/C6 in PY3}, and {C7/O1, C8/N2, N2/N1, and N1/C6 in PY60}. The H atoms attached to the azo group in PR3, PY3, and PY60 form bifurcated N—H<sup>...</sup>O or N—H<sup>...</sup>Cl intramolecular hydrogen bonds: {N2—H<sub>2N</sub><sup>...</sup>O1 and N2—H<sub>2N</sub><sup>...</sup>O2}, {N1—H<sub>1N</sub><sup>...</sup>O1 and N1—H<sub>1N</sub><sup>...</sup>O3}, and {N1—H<sub>1N</sub><sup>...</sup>O1 and N1—H<sub>1N</sub><sup>...</sup>O1 and N1—H<sub>1N</sub><sup>...</sup>O1

Figures 7(a)-7(c) show the ORTEP plots of PR3, PY3,

lap	le	I.	Crystal	lograpl	nic	parameters	for	PR3,	PY3,	and	PY60.	(See	Fig.	7	)
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C <sub>16</sub> H <sub>12</sub> N <sub>4</sub> O <sub>4</sub> Cl <sub>2</sub> 395.20 Orthorhombic <i>Pbca</i>	C <sub>16</sub> H <sub>13</sub> N <sub>4</sub> OCl 312.75 Triclinic
395.20 Orthorhombic <i>Pbca</i>	312.75 Triclinic
Orthorhombic <i>Pbca</i>	Triclinic
Pbca	0.1
	<i>P</i> -1
8	2
) 8.337,4(5)	7.581,86(14)
13.252,7(9)	9.462,51(17)
30.171,7(16)	11.126,9(2)
	<b>68.426,0</b> (10)
])	84.401,0(10)
	80.767,0(10)
1.575	1.419
0.046,6	0.040,9
	13.232,7(9) 30.171,7(16) 1) 1.575 0.046,6

"CCDC 808758 (CCDC: Cambridge Crystallographic Data Center).

<sup>b</sup>CCDC 808759. <sup>c</sup>CCDC 808760.

and PY60, respectively. We focus first on the N/N bond length in these compounds that lie in the range of 1.30–1.33 Å (Table II). Obviously, the present N/N bond is too short for the standard N-N bond of 1.44 Å and is much nearer to the typical azo bond (N=N:1.25 Å).<sup>11</sup> In addition, the N=N bond on the order of 1.28-1.33 Å is frequently observed in metal-azo complexes.<sup>15-22</sup> Next, we look at the bond distances of C10/N1, C7/N2, and C8/N2. These are assumed to be single bonds for the protonated-azo structure while double bonds for the hydrazone form. As judged from the experimental value of about 1.30-1.32 Å, the bond is clearly characteristic of the double bond of 1.29 Å, supporting the hydrazone structure. Furthermore, the C1/O1, C10/O1, and C7/O1 bonds are assumed to be single bonds (standard: 1.43 Å) for the protonated-azo structure, whereas these are considered to be double bonds (standard: 1.21 Å) for the hydrazone structure. The analytical result gave bond lengths of 1.23–1.25 Å. This favors the double bond for the hydrazone structure.

Table	II.	Selected	bond	distances.

	Bond distances (Å)				
PR3	РҮЗ	РҮ60	Standard bond length $(\text{\AA})^{\mathfrak{a}}$		
C1/01: 1.2500(19)	C10/01: 1.238(3)	C7/01: 1.229(2)	Single: 1.43	Double: 1.21	
C10/N1: 1.3167(19)	C7/N2: 1.304(3)	C8/N2: 1.310(2)	Single: 1.47	Double: 1.29	
N1/N2: 1.3242(18)	N2/N1: 1.321(3)	N2/N1: 1.318(2)	Single: 1.45	Double: 1.25	
N2/C11: 1.3886(19)	N1/C6: 1.404(3)	N1/C6: 1.397(2)	Single: 1.47	Double: 1.29	

<sup>a</sup>Reference 11.



Figure 7. ORTEP plots, showing 30% displacement ellipsoids: (a) PR3, (b) PY3, and (c) PY60.



Figure 8. Proposed zwitterionic structures: (a) PR3, (b) PY3, and (c) PY60.

### MOLECULAR ORBITAL CALCULATIONS FOR MOH, PR3, PY3, AND PY60 OF THE AZO OR PROTONATED-AZO STRUCTURE

Semiempirical MO calculations were carried out using a QUANTUM CACHE version 3.2 program package<sup>23</sup> which includes MOPAC version 94.10 and ZINDO programs. Geometry was optimized for MOH, PR3, PY3, and PY60, using the AM1 Hamiltonian. Optical absorption bands were calculated with ZINDO on the optimized geometry.

Table III shows the calculated results of the N/N bond length and the dipole moment for MOH, PR3, PY3, and PY60. In all compounds, the dipole moment is considerably larger in the protonated-azo structure or hydrazone structure than in the corresponding azo structure. This indicates that the structure is significantly ionic, supporting the protonated-azo structure [Figures 6 and 8(a)-8(c)] rather

Table III.	Molecular	orbital	calculations	for	MOH,	PR3,	PY3,	and	PY60.

		N/N (Å)	Dipole moment (D)
МОН	Azo structure	1.23	8.6
	Protonated azo or hydrazone structure	1.25	33.4
PR3	Azo structure	1.23	5.4
	Protonated azo or hydrazone structure	1.31	6.5
PY3	Azo structure	1.24	2.0
	Protonated azo or hydrazone structure	1.31	5.1
PY60	Azo structure	1.24	0.9
	Protonated azo or hydrazone structure	1.31	3.4

than the hydrazone form [Figs. 2(b), 3(b), and 4(b)]. Furthermore, the N/N bond length becomes slightly longer with the formation of the protonated-azo structure than that of the azo structure.

The electron density of each atom could also be considered as a good measure of the protonated-azo structure. However, no supporting information was available even from MOH.

#### AZO OR HYDRAZONE STRUCTURE

As stated in the Introduction, the protonated-azo structure (i.e., zwitterionic structure) and the hydrazone structure are chemically the same species but expressed in different resonance structures. Therefore, the question is how to designate the prevailing structure on the basis of the x-ray structure analysis and the chromophoric theory. The x-ray structure analysis supports the protonated-azo structure as far as the N/N bond length is concerned. However, the hydrazone structure is more appropriate with regard to the bonds around the azo form. The MO calculations for MOH, PR3, PY3, and PY60 reveal strong ionic character in favor of the protonated-azo structure. As judged from the above results, no clear-cut assignment to the azo or hydrazone form can be made on the basis of both the x-ray and the MO results. The azo or hydrazone structure lies still in the gray zone.

At this point, we are obliged to incorporate the chromophoric aspect that plays the crucial role in dyes and pigments. The colorant molecules (such as MOH, PR3, PY3, and PY60) must absolutely possess a bond alternation (i.e., chromophore) in their structure. This forces us to finally suggest that the protonated-azo structure is a more reasonable form for the hydrogen-bonded azo pigments rather than the hydrazone form. In other words, the more azolike structure is the case rather than the hydrozonelike form. This aspect is surely borne out by dye and pigment chemists because they can design azo molecules as it was before in the framework of the azo structure. However, we are afraid that this aspect may not always be accepted by crystallographers.

The same discussion on the protonated-azo structure can basically be applied to similar hydrogen-bonded azo pigments of the  $\beta$ -naphthol type (PR1, PR2, PR6, and PR208), of the acetoacetanilide type (PY1, PY4, PY5, PY6, PY12, PY65, PY74, and PY98), and of the pyrazolone type (PY10).

The protonated-azo structures for PR3, PY3, and PY60 will then be named as follows: 1-(4-methyl-2-nitrophenyl)-2-(2oxido-1-naphthyl)diazenium, 1-(2-chloroanilino)-2-[2-(4chloro-2-nitrophenyl)diazen-2-IUm-1-yl]-3-oxobut-1-en-1olate, 1-(2-chlorophenyl)-2-(3-methyl-5-oxido-1-phenyl-1*H*-pyrazol-4-yl)diazenium, respectively.

### CONCLUSIONS

We have investigated the dichotomy between azo and hydrazone structures in hydrogen-bonded azo pigments in the context of chromophore theory, with special attention to intra- or intermolecular proton transfer to form hydrogen bonds. The conclusions can be summarized as follows:

- 1. We pointed out two major problems with the hydrazone structure: the hydrazone structure disrupts the electron conjugation in the chromophore that is absolutely necessary for color generation, and the analyzed N—N bond length of 1.31–1.33 Å is too short for the single N—N bond.
- We proposed a novel "protonated-azo structure" (-N=N<sup>+</sup>H--) as an alternative for the previously reported hydrazone form. This is compatible with both the x-ray analysis and the chromophoric theory. However, this inference appears to be not entirely conclusive.
- 3. The proton in protonated-azo pigments can be supplied either intra- or intermolecularly to form intraor intermolecular hydrogen bonds.

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