Azo or hydrazone structure in azo pigments

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Abstract

Azo dyes and pigments are typical of the classical pigments as characterized by the azo group (-N=N-). However, there are still controversial discussions on the azo form whether it exists as the azo form in the solid state or in the form of hydrazone structure (=N-NH-). We have tackled this problem from the aspects of X-ray structure analysis and the chromophoric theory in an attempt to construct a model that satisfies these requirements, using methyl orange derivative (MOH), Pigment Red 3 (PR3), and Pigment Yellow 3 (PY3). Then, we found a protonated azo structure (-$N=N^+H$*-) in these compounds as caused by NH···O "inter"-molecular hydrogen bonds in MOH, as well as by "intra"-molecular hydrogen bonds in PR3 and PY3. The present protonated azo model is borne out by the crystallographic azo bond-length as well as the chromophoric theory. These results lead us to conclude that the protonated azo structure is the right form in the solid state of hydrogen-bonded azo pigments as described above.*

Introduction

Azo pigments which carry an azo function (-N=N-) are widely used in the imaging industry because of their versatile colors as well as their low price. 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. However, there are still controversial discussions on the azo form whether it exists as the azo form in the solid state or in the form of hydrazone structure (=N-NH-). It was Whitaker who pointed out the hydrazone structure in some monoazo pigments (whose coupling components are *β*-naphthol, acetoacetanilide, and pyrazolone) on the basis of the X-ray structure analysis [1-6]. The pigments in question possess NH···O "intra"-molecular hydrogen bonds, for example, in PR3 (*β*-naphthol type; Fig. 1(a)), PY3 (acetoacetanilide type; Fig. 2(a)), and Pigment Yellow 60 (PY60: pyrazolone type; Fig. 3(a)). Whitaker confirmed that the previously-assigned hydroxyl H atom in Figs. 1(a), 2(a), or 3(a) is attached to the previously-assigned azo-bond to form a hydrazone structure (-NH-N=), and this in turn results in the formation of the keto form (-C=O) as shown in Figs. 1(b), 2(b), and 3(b). The present conclusion is uniquely based on the determination of the H position which supports the hydrazone structure. However, in our view, it would appear inadequate to diagnose azo or hydrazone bonding solely on the basis of the X-ray structure analysis, because the structure must also be consistent with the color generation based upon the chromophoric theory. For this reason, we have tackled the "azo or hydrazone" problem, using methyl orange derivative (MOH: Fig. 4), PR3, and PY3, from the standpoints of both X-ray structure analysis and the chromophoric theory in an attempt to construct a better model that meets the above requirements. We see the following two crucial issues on the proposed hydrazone-form. One is the assignment of the N-N single bond to the proposed hydrazone form and the other is the disturbance of the bond alternation (absolutely necessary for the color generation) due to the hydrazone bonding. The reported N-N bond-lengths are in the range of 1.31-1.33 Å (Figs. 1(b), 2(b), and 3(b)). The present bond length is abnormally too short for the standard single N-N bond of 1.44 Å and is much nearer to the standard N=N bond (1.24 Å) [7]. Furthermore, in the hydrazone form, the bond alternation is blocked by the existence of the N-N single bond (Figs. 1(b), 2(b), and 3(b)). This disturbs the π-conjugation system of the chromophore, resulting in discoloration. However, their characteristic vivid red or yellow color appears actually in the solid state.

In the present investigation, we have re-determined the structure of MOH, PR3 and PY3 and, on this basis, propose a protonated azo-structure in the form of $-N=N^+H-$ which is fully consistent with the crystallographic azo bond-length and the chromophoric theory.

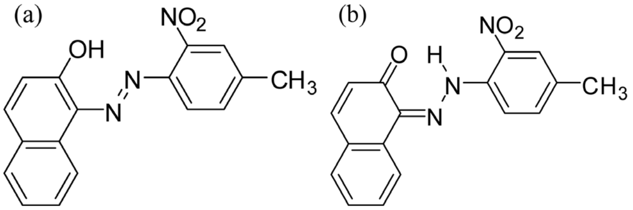

Figure 1. *Molecular structure for PR3: (a) azo form and (b) hydrazone form.*

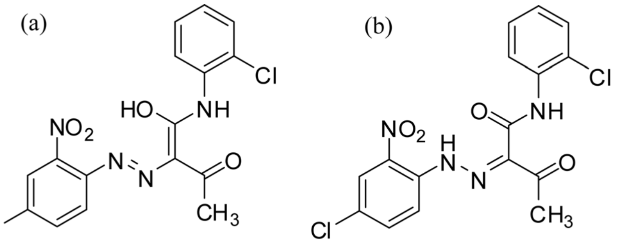

Figure 2. *Molecular structure for PY3: (a) azo form and (b) hydrazone form.*

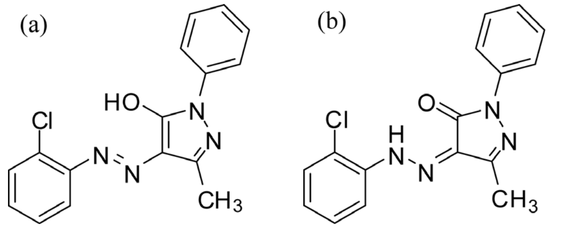

Figure 3. *Molecular structure for PY60: (a) azo form and (b) hydrazone form.*

Motivation for the proposal of the protonated azo-structure (-N=N$^+$H-)

Our motivation for the proposal of the protonated azo-structure (–N=N$^+$H-) originates in the re-investigation of the MOH structure (Fig. 4). As is well known, the color of azo compounds arises from a push-pull system composed of a chromophore (*i.e.* conjugated π-electron system) with auxochromes [8]. In MOH (Fig. 4), for example, the "phenyl/azo/phenyl" moiety serves as the chromophore, and the dimethyl amino group [-N(CH$_3$)$_2$ (donor: push)] and the sulfo group [-SO$_3$H (acceptor: pull)] are the auxochromes. Then, the electron of the N lone pair (donor: push) can be transferred in consistent with the bond alternation through the chromophore to the acceptor (-SO$_3$H: pull), resulting in the formation of =N$^+$(CH$_3$)$_2$ (now acceptor) and =SO$_2^-$OH (now donor). Then, the back electron-transfer also occurs from the new donor to the new acceptor, leading to the full electron delocalization in the chromophoric system. In this way, the color appears in the visible region. Likewise, in PR3, the "naphthol/azo/phenyl" moiety serves as the chromophore, while the hydroxyl group [-OH (donor: push)] and the nitro group [-NO$_2$ (acceptor: pull)] are the auxochromes.

In the course of our study on the structure of methyl orange and its derivative MOH [9], we came across a structure paper of MOH (*i.e.* vivid red) by Burke *et al.* [10], reporting that the H atom of the sulfo group is transferred from one MOH to the neighboring one, forming an "inter"-molecular O3$\cdots$H$_{1N}$-N1 hydrogen bond based on the hydrazone structure (=N2-NH$_{1N}$-C4), as shown in Fig. 5. As stated above, the hydrazone structure disturbs the bond alternation in the chromophore and is thus supposed to quench the red color. However, the crystal exhibits vivid red in reality. This prompted us to believe that the bond alternation is still in operation. In addition, we scrutinized the S/O bond length in the sulfo group. The three S/O bonds are nearly equal in length and lie in the range 1.45-1.47 Å. This shows that the negative charge is delocalized in the sulfo group in the form of SO$_3^-$, while the proton (H$^+$) is transferred to the azo group of the neighboring molecule to form a protonated azo form (*i.e.* -N=N$^+$H-: -N2=N$^+$H$_{1N}$-C4). This forms a zwitterionic structure as shown in Fig. 6: -N=N$^+$H- and -SO$_3^-$. The N/N bond length as obtained by the X-ray structure analysis is 1.307(3) Å and supports the azo bond (standard N=N bond: 1.24 Å) rather than the N-N bond (standard N-N: 1.44 Å). The above protonated azo model is fully compatible with the crystallographic azo bond-length and the chromophoric theory.

Furthermore, our semi-empirical molecular orbital calculations (see below) also support the formation of the above zwitterionic structure. Calculations were carried out for the azo and zwitterionic structures (Table 1). The N=N bond of 1.23 Å for the azo structure is slightly shorter than that of the zwitterionic structure (1.25 Å). On the other hand, some striking differences are found in the dipole moment and absorption maximum (λ). The increase in the dipole moment from 8.4 to 33.2 D bears out clearly the formation of the zwitterionic structure. In addition, the absorption maximum is displaced from 356.3 to 523.7 nm. This is caused by the increased internal electric field due to the enhanced dipole moment of the zwitterionic structure that facilitates the electron transfer from donor to acceptor. The present longer-wavelength-band (523.7 nm) of the zwitterionic structure reflects well the vivid red color of MOH.

As described above, the protonated azo structure (*i.e.* formation of the zwitterionic structure) is attributed to the proton transfer through NH$\cdots$O "inter"-molecular hydrogen bonds from the sulfo group of one molecule to the azo bond of the neighboring one. The similar proton-transfer is also expected to take place within a molecule through "intra"-molecular hydrogen bonds in PR3, PY3, and other hydrogen bonded azo pigments [1-6, 11, 12]. On this account, we firmly believed that we can interpret the "azo or hydrazone" problem in PR3, PY3, and other hydrogen bonded azo pigments on the basis of the protonated azo-structure.

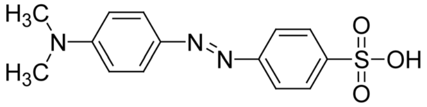

Figure 4. *Molecular structure for MOH.*

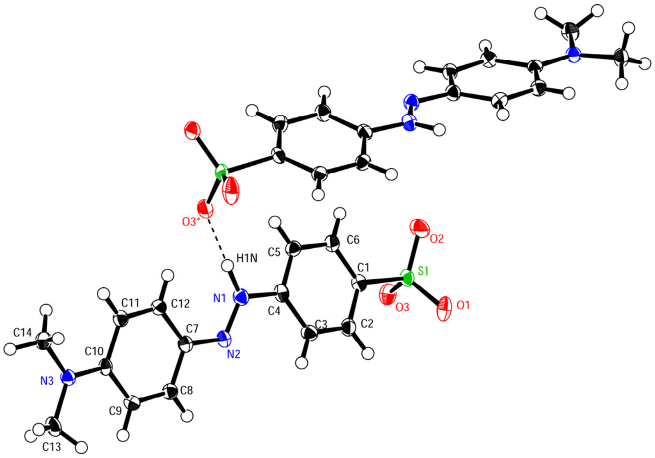

Figure 5. *ORTEP plot of MOH.*

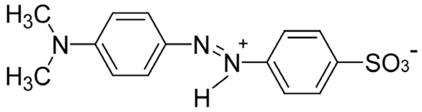

Figure 6. *Proposed zwitterionic-structure for MOH: -N=N$^+$H- and –SO$_3^-$.*

Table 1: MO calculations for MOH

	N/N (Å)	λ (nm)	Dipole moment (D)
Azo structure	1.23	356.3	8.4
Zwitterionic structure	1.25	523.7	33.2

Experimental

Crystal growth of PR3 and PY3

PR3 and PY3 were obtained from Kishi-Kasei Co. Ltd. and Clariant Ltd., respectively. Both single crystals of PR3 and PY3 were grown from the vapor phase, using Ar as the carrier gas. After 24 h, a number of single crystals were obtained in the form of platelets in both samples.

X-ray structure analysis on PR3 and PY3

Reflection data were collected at -180 °C on an R-AXIS RAPID-F diffractometer from Rigaku using Cu$K\alpha$ as the radiation source (λ = 1.5418 Å). The structure was solved by direct methods (SIR2004) and refinement was carried out by the full-matrix least-squares method of F^2 (SHELXL97) [13, 14].

Molecular orbital calculations on MOH and PR3

Semi-empirical molecular orbital (MO) calculations were carried out using a QUANTUM CACHE ver. 3.2 program package which includes MOPAC ver. 94.10 and the ZINDO programs. Geometry was optimized for the vivid-red phase of MOH and PR3, using the AM1 Hamiltonian. Optical absorption bands were calculated with ZINDO program for the optimized geometry.

DFT calculations on PY3

Density-functional theory (DFT) calculations were carried out using the GAUSSIAN 03 suite of programs [15]. Geometry was optimized for PY3, using the density-functional method with the B3LYP hybrid functional together with 6-31+G(d) basis set [16, 17]. Optical absorption bands were calculated with the time-dependent density-functional theory (TD-DFT) using the 6-31+G(d) basis set for the optimized geometry.

Results and Discussion

Protonated azo-structure in PR3 and related β-naphthol-type azo pigments

Fig. 7 shows the *ORTEP* plot of PR3 (β-naphthol type). The structure re-determined is basically in good agreement with that of Whitaker, except for the interpretation of the azo or hydrazone structure. We also found on the Fourier map the H atom of the hydroxyl group (-OH) attached to the azo bond (-N=N-), forming a bifurcated N2-H_{2N}···O1 and N2-H_{2N}···O2 "intra"-molecular hydrogen bond.

The N1-N2 bond-length of 1.326(2) Å is too short for the standard N-N bond of 1.44 Å and is much nearer to the typical azo bond (N=N: 1.24 Å [7]). In addition, the N=N bond of the order of 1.30-1.32 Å is frequently observed in metal-azo complexes [18-23]. As described previously, the hydrazone structure (=N-NH-) obviously interrupts the bond alternation (*i.e.* conjugated system based on the repetition of the "double/single" bond), leading to the discoloration. This contradicts the vivid red color of PR3 in the solid state. Furthermore, the C1-O1 bond length of 1.255(3) Å is longer than the typical C=O double bond of 1.21 Å [7]. Judging from the above results, the protonated azo-structure as shown in Fig. 9(a) can better explain both the crystallographic N/N bond-length as well as the color generation mechanism without contradiction, rather than the hydrazone structure.

Table 2 lists the results of molecular orbital calculations, showing the N=N bond lengths, absorption bands, and dipole moments for the azo structure (Fig. 1(a)) as well as for the zwitterionic structure (Fig. 9(a)). Here again, the zwitterionic structure yields a larger dipole moment than that of the azo structure, supporting that PR3 forms the zwitterionic structure. The spectroscopic calculation is also consistent with experiment.

The same discussion as described above can also be applied to other β-naphthol type azo pigments such as Pigment Red 1 (PR1), PR2, PR6, PR208 etc. where proton transfer occurs from the hydroxyl group (-OH) to the azo group (-N=N-) through "intra"-molecular hydrogen bonds [1, 11].

Protonated azo-structure in PY3 and related acetoacetanilide-type azo pigments

Fig. 8 shows the *ORTEP* plot of PY3 (acetoacetanilide type). Here again, the structure re-determined by us is basically in good agreement with that of Whitaker. We also confirmed that the H atom of the hydroxyl group (-OH) is attached to the azo bond (-N=N-), forming a bifurcated N1-H_{1N}···O1 and N1-H_{1N}···O3 "intra"-molecular hydrogen bonds.

In PY3, the N1-N2 bond length is 1.327(4) Å and the C10-O1 bond length is 1.244(4) Å. The situation is exactly the same as in the case of PR3. DFT calculations also reveal that the N=N bond length is 1.318 Å, the absorption maximum 475.5 nm, and the dipole moment 3.93 D. These are again compatible with the protonated azo-structure (Fig. 9(b)).

The same discussion as described above can also be applied to other acetoacetanilide type azo pigments such as Pigment Yellow 1 (PY1), PY4, PY5, PY6, PY12, PY65, PY74, PY98, etc., where proton transfer occurs from hydroxyl group (-OH) to the azo group (-N=N-) through "intra"-molecular hydrogen bonds [2, 12].

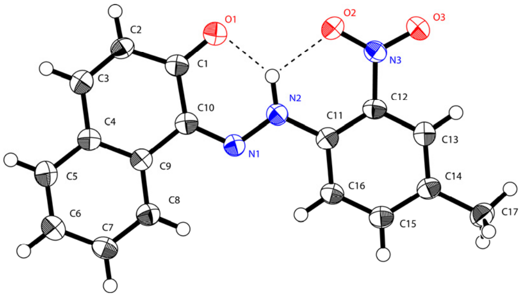

Figure 7. *ORTEP plot of PR3.*

Table 2: MO calculations for PR3

	N/N (Å)	λ (nm)	Dipole moment (D)
Azo structure	**1.23**	**383.1**	**5.4**
Zwitterionic structure	**1.31**	**428.0**	**6.5**

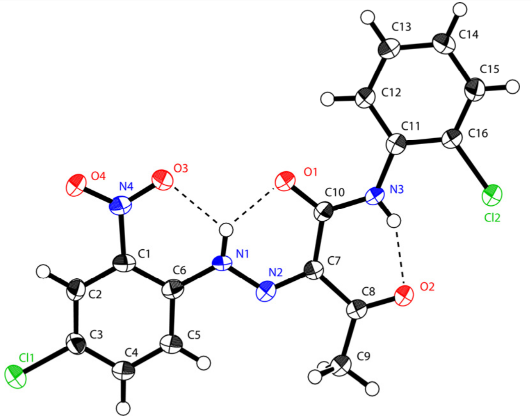

Figure 8. *ORTEP plot of PY3.*

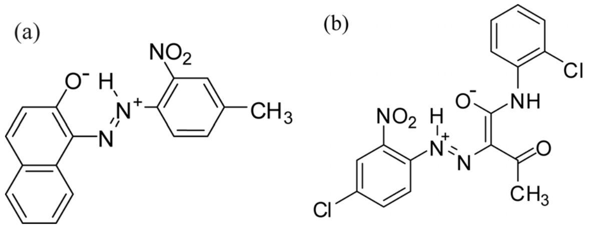

Figure 9. *Proposed zwitterionic-structure for (a) PR3 and (b) PY3: $-N=N^+H^-$ and $-O^-$.*

Pyrazolone-based azo pigments (for example: Pigment Yellow 10 and 60)

As stated in Introduction, Whitaker suggested the hydrazone structure in azo compounds of the three classes: β-naphthol, acetoacetanilide, and pyrazolone types, in which the H atom is transferred from the hydroxyl group (-OH) to the azo group (-N=N-) *via* "intra"-molecular hydrogen bonds. Among these, we could discuss as described above the azo or hydrazone problem in azo pigments of PR3 (β-naphthol type), and PY3 (acetoacetanilide type), since PR3 and PY3 are still commercially available. However, no commercial products of pyrazolone types, for example, PY10 and PY60, are on the market. For this reason, we could not include them in the present investigation. However, we believe that the protonated azo-structure ($-N=N^+H-$) is also operative in azo pigments of pyrazolone types (for example, in PY60, the N-N and C=O bonds reported are 1.318(3) and 1.230(3) Å, respectively). The resulting zwitterionic structure is crucial for the color generation, quite irrespective of the fashion of proton transfer whether it is supplied through "inter"-molecular or "intra"-molecular hydrogen bonds.

Conclusions

We have investigated the azo or hydrazone structure in the solid state of hydrogen bonded azo pigments from the crystallographic and chromophoric points of view, with major focus on the proton transfer. The conclusions can be summarized as follows.

1. We have pointed out two major problems in the hydrazone structure proposed by Whitaker. The first point is that the N-N bond-length of 1.31-1.33 Å is too short to assign them to the N-N bond. The second point is that the hydrazone structure disrupts the electron conjugation in the chromophore that is absolutely necessary for the color generation.
2. We proposed a novel "protonated azo-structure" scheme ($-N=N^+H-$) that is fully compatible with both the crystallographic parameters and the chromophoric theory.
3. The proton in the protonated azo-structure can be transferred through "inter"-molecular or "intra"-molecular hydrogen bonds.

References

[1] A. Whitaker, "Crystal structure analysis fo azo pigments involving β-naphthol: A review", J. Soc. Dyers Colour. **94**, 431-435 (1978).

[2] A. Whitaker, "Crystal structure of azo pigments derived from acetoacetanilide", J. Soc. Dyers Colour. **104**, 294-300 (1988).

[3] A. Whitaker, "Crystal structure of azo colorants derived from pyrazolone: A review", J. Soc. Dyers Colour. **111**, 66-72 (1995).

[4] A. Whitaker, "The crystal structure of C.I. Pigment Red 3, 4-methyl-2-nitrophenylazo-2-naphthol", Zeitschrift fur Kristallographie, **147**, 99-112 (1978).

[5] A. Whitaker, "The crystal structure of C.I. Pigment Yellow 3, α-(1-hydroxyethylidene)-2-chloro-acetanilide-α-azo- (4'-chloro-2'-nitrobenzene)", Zeitschrift fur Kristallographie, **163**, 19-30 (1983).

[6] A. Whitaker, "CI Pigment Yellow 60, 4-(2-Chloroohenylhydrazono)-3-methyl-1-phenyl-5-pyrozolone", *Acta Cryst.***C44**,1587-1590(1988).

[7] P. Mueller, *et al.*, "Crystal Structure Refinement", Oxford University Press (New York, 2006).

[8] H. Zollinger, "Color Chemistry", Verlag Helvetica Chemica Acta (Zurich, Switzerland, 2003).

[9] H. Shibata, K. Sato, and J. Mizuguchi, "Crystal structure of Methyl Orange Derivatives and Their Electronic Spectra", J. Imaging Sci. Technol. **53**, 050302-050302-7 (2009).

[10] N. J. Burke, *et al.*, "Incorporation of sulfonate dyes into hydrogen-bonded networks", Cryst. Eng. Comm. **6**, 429-436 (2004).

[11] E. F. Paulus, "Molecular and crystal structure of C. I. Pigment Red 208, 12514, n-butyl-2-{2-oxo3-[N-(2-oxo-2, 3-dihydro-5-benzimadazolyl)-carbamoyl]-naphthylidenhydrazino}-benzoate (PV-Red HF2B)", Zeitschrift fur Kristallographie, **160**, 235-243 (1982).

[12] M. J. Barrow, *et al.*, "The crystal structure of C. I. Pigment Yellow 12", Dyes and Pigments, **45**,153-160 (2000).

[13] M.C. Burla, *et al.*, "SIR2004: An improved tool for crystal structure determination and refinement", J. Appl. Crystallogr. **38**, 381-388 (2005).

[14] G. M. Sheldrick, "A short history of SHELX", Acta Crystallogr., Sect A: Found. Crystallogr. **64**, 112-122 (2008).

[15] GAUSSIAN 03, revision D. 01., Gaussian Inc. (2004).

[16] A. D. Becke, "Density-functional thermochemistry. III. The role of exact exchange", J. Chem. Phys. **98**, 5648-5652 (1993).

[17] C. Lee, *et al.*, "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density", Phys. Rev. B **37**, 785-789 (1998).

[18] J. Mizuguchi, *et al.*, "Poly[bis(acetone)bis[μ-4-[(5-chloro-2-oxidophenyl)diazenyl]-3-oxido-N-phenylnaphthalene-2-carboxamidato]sodium(I)ferrate(III)]", *Acta Cryst.* **E63**, 1377-1378 (2007).

[19] J. Mizuguchi, *et al.*, "Ammonium bis{3-anilinocarbonyl-1-[(5-chloro-2-oxidophenyl)diazenyl]-2-naphtholato}ferrate(III) acetone solvate", *Acta Cryst.* **E63**, 1329-1330 (2007).

[20] J. Mizuguchi, *et al.*, "Ammonium bis{3-anilinocarbonyl-1-[(5-chloro-2-oxidophenyl)diazenyl]-2-naphtholato}ferrate(III) methanol solvate", *Acta Cryst.* **E63**, 1327-1328 (2007).

[21] S. Ito, *et al.*, "Poly[bis(acetone-κO)bis{μ_3-1-[(5-chloro-2-oxidophenyl)diazenyl]-2-naphtholato-$\kappa^4 O$: *O*, *O'*: *O'*}sodium(I)chromium(III)]", *Acta Cryst.* **E64**, 333-334 (2008).

[22] Y. Sato, *et al.*, "Diacetonitriletetrakis{μ_2-3-anilinocarbonyl-1-[(5-chloro-2-oxidophenyl)diazenyl]-2-naphtholato}tetraaqua-diiron(III)disodium(I)dehydrate", *Acta Cryst.* **E64**, 240-241 (2008).

[23] H. Shibata, *et al.*, "(2,6-Bis{5-amino-3-tert-butyl-4-[(3-methyl-1,2,4-thiadiazol-5-yl)diazenyl]-1H-pyrazol-1-yl}-4-oxo-1,4-dihydro-1,3,5-triazin-1-ido)methanol(phenol)sodiumphenol tetrasolvate", *Acta Cryst.* **E66**, 463–464 (2010).

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