# Crystal and electronic structure of methyl orange

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## Abstract

*Azo pigments are typical of the classical pigments as characterized by the azo group (–N=N–) and used widely in painting and imaging industries. In azo pigments, however, there is still a pending problem associated with the azo or hydrazone structure in the solid state. As a step to clarify this, structure analysis of methyl orange (MO: the simplest azo compound) has been carried out together with its electronic structure. MO is found to crystallize in the space group of $P2_12_12_1$ which includes three molecules in the asymmetric unit. The three N/N bonds are typical of the azo structure and the three Na atoms form two kinds of complexes: two seven-coordinate and one five-coordinate complexes. These are connected through the sulfonic anions and form one dimensional polymer along the a-axis. Furthermore, solvated MO is found to give an additional band around 580 nm on going from solution to the solid state. This makes the color orange.*

## Introduction

The title compound (methyl orange abbreviated to MO: Na(I)-4'-dimethylaminoazobenzene-4-sulfonate: Fig. 1) is one of the classical azo pigments used in painting and imaging industries. We are involved in the color generation mechanism of azo pigments characterized typically by the azo chromophore (–N=N–). However, some types of azo pigments are also known to possess the hydrazone or hydrozone-like structure (=N–NH–), often leading to the formation of intramolecular hydrogen bonds [1]. The present basic problem remains still unsettled in the field of azo pigments. As a step to clarify this, we focused in the present investigation on the simplest azo compound, *i.e.* methyl orange. Our motivation is that the MO's chromophore (phenyl-azo-phenyl) and auxochromes (dimethyl amine and sodium sulfonate) are quite definite and easy to discuss the correlation between color and constitution.

Hanson [2] and Kennedy *et al*. [3] investigated independently the structure of hydrated MOs and clarified that the N/N are typical of the azo bond (1.24 Å). On the other hand, Burke *et al*. studied the structure of a methyl orange derivative ($HO_3SC_6H_4N{=}NC_6H_4NMe_2$: 4'-dimethylaminoazo-benzene-4-sulfonic acid: the Na atom is replaced by H atom). Interestingly, they found a zwitterionic structure in the solid state: $^{-}O_3SC_6H_4NH^{+}{=}NC_6H_4NMe_2$ as characterized by a NH···O intermolecular hydrogen bond between the NH group of one molecule and one of the sulfate oxygen atoms [4]. This structure reveals a lengthening of the N=N bond to 1.307(3) Å, indicating a hydrozone-like structure. In addition, the color of the crystal is no more orange but red violet. This motivated us to study the correlation between the crystal structure and the color in the solid state in these compounds. During this study, we found a new MO complex. This paper deals with the crystal and electronic structure of the present MO complex.

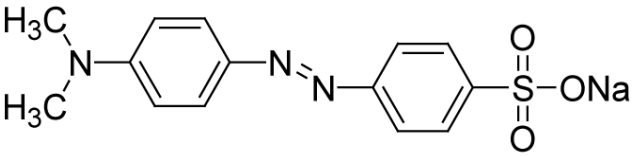


***Figure 1.*** *Methyl orange*

## Experiment

### *Crystal growth of MO*

MO was purchased from Junsei Chemical Co., Ltd. Single crystals of MO were grown by recrystallization from a dimethylacetamide solution by slow diffusion of 1,4-dioxane. After a week, a number of orange needle-like single crystals (size: $0.45\times0.08\times0.07$ mm$^3$) were obtained.

### *X-ray structure analysis*

Reflection data were collected on a R-AXIS RAPID diffractometer from Rigaku using Cu$K\alpha$ radiation ($\lambda$ = 1.5418 Å) at 93 K, since the single crystal was found to include solvent molecules. The crystal structure was solved by direct method (SIR2004) [5] and refinement was carried out by the full-matrix least-squares method on $F^2$ (SHELXL-97) [6].

### *Measurements of absorption and reflection spectra*

UV-visible absorption spectra were recorded on a UV-2400PC spectrophotometer (Shimazu). Diffuse reflectance spectra for powders were measured on the same spectrophotometer together with an integrating sphere attachment (ISR-240 from Shimazu).

## Results and discussion

### *Crystallographic parameters*

Table 1 details the crystallographic parameters of solvated MO. The crystal system is orthorhombic and the space group is $P2_12_12_1$ [7].

**Table 1 Crystal parameters**

| | Methyl orange |
|---|---|
| Molecular formula | $C_{42}H_{42}N_9O_9S_3Na_3 \cdot C_{12}H_{24}O_6$ |
| Molecular weight | 1246.34 |
| Crystal system | Orthorhombic |
| Space group | $P2_12_12_1$ |
| $Z$ | 4 |
| $a$ (Å) | 8.4471(6) |
| $b$ (Å) | 15.5153(10) |
| $c$ (Å) | 44.488(3) |
| $V$ (Å$^3$) | 5830.6(7) |
| Density (g/cm$^3$) | 1.491 |
| $R_1$ | 0.0448 |

### *Molecular conformation and molecular arrangement*

Fig. 2 shows the ORTEP III plot of the monomeric unit of solvated MO. The asymmetric unit includes three MO molecules together with three dioxane ones. These constitute three kinds of Na(I)-complexes, two of which are seven-coordinate and the other is five-coordinate. As shown in Fig. 3, there are two kinds of seven-coordinate complexes, one of which is chelated by six O atoms from the sulfonic group of four different MOs and also by one O atom from dioxane. The other is coordinated to seven O atoms from the sulfonic group of five different MOs. The five-coordinate complex includes three O atoms from the sulfonic group of three different MOs as well as two O atoms from the two different dioxanes. It is also important to note that the N/N bond lengths are typical of the azo group (–N=N–) but these are significantly different: 1.259(4) Å for N1/N2, 1.196(5) Å for N4/N5, and 1.253(4) Å for N7/N8. The monomeric unit is extended alternately to form a one dimensional polymer along the *a* axis as shown in Fig. 4. The present polymer formation ensures the thermal stability of solvated MO.

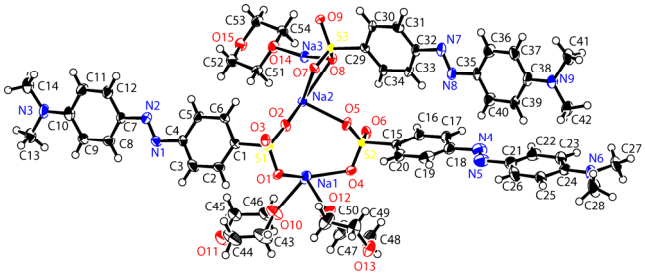


***Figure 2.*** *A view of the monomeric structure of solvated MO, showing 50% displacement ellipsoids*

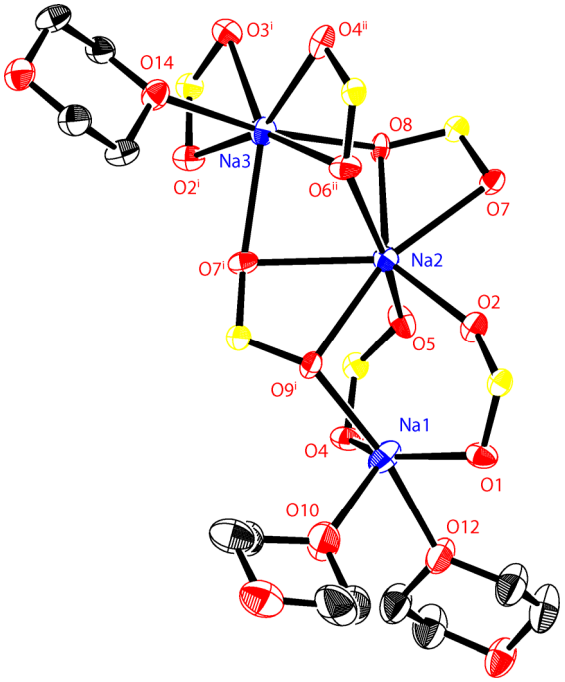


***Figure 3.*** *The three kinds of Na-complexes: five-coordinate Na1, seven-coordinate Na2 and Na3 [symmetry code(i): 1/2+x, 1/2-y, 1-z) and (ii): -1/2+x, 1/2-y, 1-z)]*

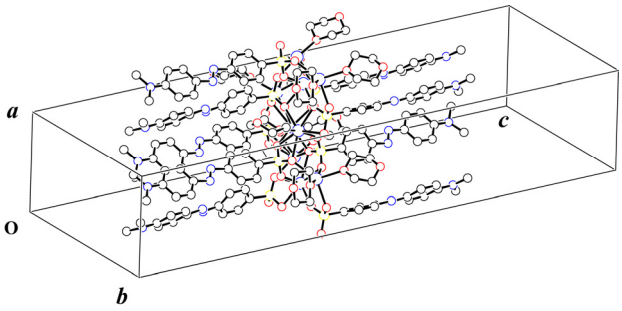


***Figure 4.*** *The crystal packing of solvated MO*

### *Absorption and diffuse reflection spectra*

Fig. 5 shows the absorption spectrum of MO in solution and diffuse reflection spectrum in powders. The absorption band in solution exhibits a broad band in the wavelength region between 350 and 500 nm. However, the vibronic bands such as 0-0, 0-1, and 0-2 transition can still be assigned as denoted by arrows, where the 0-1 transition gives the most intensive band.

The diffuse reflectance spectrum is similar in shape to the solution spectrum, although the most intensive band is characterized by the 0-2 vibronic transition. Furthermore, it is important to note that there is a small shoulder around 580 nm which was absent in solution spectrum this is clearly a new band which appears on going from solution to the solid state. This is due to intermolecular interactions as caused by excitonic interactions. This small shoulder is effective to make the MO color orange.

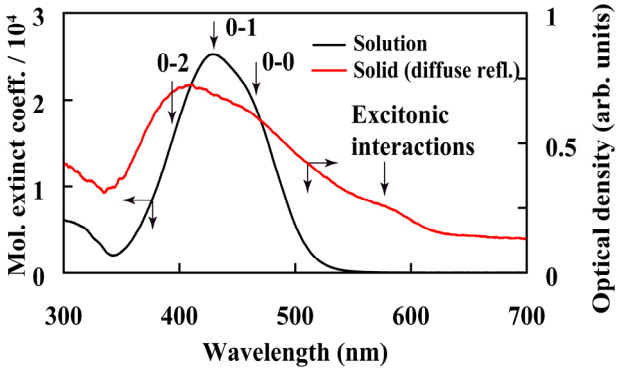


***Figure 5.*** *Absorption spectrum in solution and diffuse reflection spectrum in powders*

## Conclusions

Structure analysis of methyl orange (MO) has been carried out in order to clarify the correlation between constitution and color in the solid state. MO is found to crystallize in the space group of $P2_12_12_1$ with three molecules in the asymmetric unit. The three N/N bonds are typical of the azo structure and the three Na atoms form two kinds of complexes: two seven-coordinate and one five-coordinate complexes. These are connected through the sulfonic anions and form one dimensional polymer along the *a*-axis. Furthermore, solvated MO is found to give an additional band around 580 nm on going from solution to the solid state. This band makes the color orange.

## References

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## Author Biography

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