Polymorph and electronic structure of methyl orange derivative

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Abstract

Azo pigments are typical of the classical pigments 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, we initiated our investigation on the crystal structure of methyl orange and its derivaqtives that are typical of simple azo compounds. Then, we found a different phase of 4-(dimethylamino)azobenzene-4'-sulfonic acid (MOH) from that reported by Burke et al. Because of this, electronic structure of both phases has been studied in the present investigation on the basis of the crystal structure as well as DFT calculations. A striking difference is observed between two crystal structures, showing that the previous phase is red as characterized by a zwitterionic structure; whereas purple in the new phase. Interesting to say, DFT calculation revealed that the zwitterionic structure (that exists only in the solid state) gives an absorption band at a far longer wavelength of about 660 nm as compared with that of the ordinary MOH structure (about 420 nm). It is this longer wavelength band that gives a red color in the zwitterionic phase; whereas the absorption band lies in the shorter wavelength of the visible region in the purple phase.

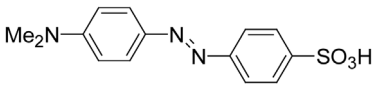
Introduction

Azo pigments are typical of the classical pigments 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. That is, on the one hand, the azo compounds are characterized by the azo group (–N=N–) in open literature. On the other hand, some types of azo pigments are also known to possess the hydrazone structure (=N–NH–), often leading to the formation of intramolecular hydrogen bonds [1]. Even today, the present basic problem remains still unsettled. To clarify this, we believed that the simple azo compounds such as 4-(dimethylamino)azobenzene-4'-sulfonic acid (MOH: Fig. 1(a)) or its sodium salt (methyl orange (MO): Fig. 1(b)) are ideal, as the first step, for the fundamental elucidation on the correlation between the crystal and electronic structures, because the chromophore (phenyl-azo-phenyl) and auxochromes (dimethyl amine and sulfonic group, or sodium sulfonate) in MOH and MO are quite definite. For this reason, we focused in the present investigation on MOH and MO.

Hanson [2] and Kennedy *et al.* [3] investigated independently the structure of hydrated MOs and reported that the N/N bond is typical of the azo structure (1.24 Å). On the other hand, Burke *et al.* studied the structure of MOH and found a zwitterionic structure in the solid state: $^{-}O_3SC_6H_4NH^{+}{=}NC_6H_4NMe_2$. Furthermore, the present zwitterionic form is caused by NH···O intermolecular hydrogen bonds between the NH group of one molecule and the O atom of the neighboring sulfonic group [4]. In addition, this structure reveals a lengthening of the N=N bond to 1.307(3) Å, indicating a hydrozone-like structure. The color of MOH is red violet which is strikingly different from the color of MO (orange). This motivated us to study in details the electronic structure of MOH and MO. In the course of this study, we found a new phase of MOH whose color is purple.

The present paper deals with the crystal and electronic structure of both polymorphs of MOH. The first part describes the solution spectra in the initial, deprotonated and protonated states of MOH together with DFT calculations; whereas the latter part presents the reflection spectra measured on singles of MOH by means of a microscope spectrophotometer.

(a)



(b)

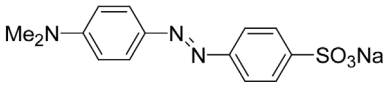


Figure 1. *Molecular structure: (a) MOH and (b) MO*

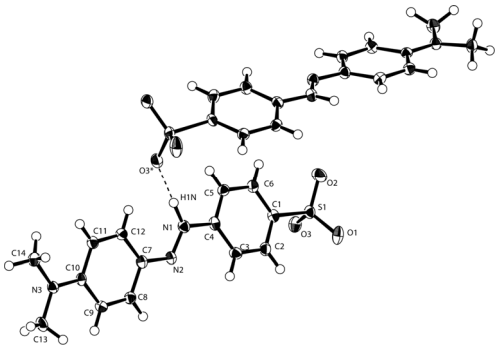


Figure 2*. Hydrogen-bonded two molecules reported by Burke et al. (zwitterionic phase)*

Experimental

Density-functional theory (DFT) calculations

DFT calculations were carried out on the following conformations as shown in Fig. 3: (a) initial state, (b) deprotonated state, (c) protonated state, and (d) zwitterionic state. Geometry optimization was carried out using the density-functional method with B3LYP hybrid functional [5, 6] together with 6-31+G(d) basis set using the Gaussian 03 suite of programs [7]. Spectroscopic calculations were then carried out on the optimized

geometries based on the time-dependent density-functional theory (TD-DFT) using the 6-31+G(d) basis set.

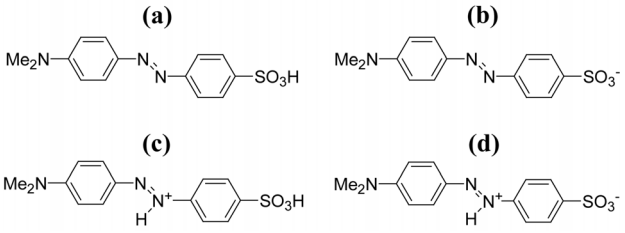


Figure 3. *Initial structures for DFT calculations*

Protonation and deprotonation in solution

Protonation and deprotonation experiments were carried out by successively adding a small amount of 0.002 M hydrochloric acid (HCl) and of 0.002 M sodium hydroxide to an aqueous solution of MOH under N_2 (degassed). The absorption spectra as well as electrical conductivity of the solution ("conductometric titration") were monitored in every titration during the experiments.

Crystal growth and structure analysis

Single crystals of MOH were grown from an aqueous solution. After 72 hours, a number of red platelet single crystals and purple needle-like single crystals were obtained at the same time.

Reflection data were collected on R-AXIS RAPID-F diffractometer from Rigaku using Cu$K\alpha$ radiation (λ = 1.5418 Å) at −180 °C. The structure was solved by direct methods (SIR2004 [8]) and refinement was carried out by the full matrix least squares method of F^2 (SHELXL-97 [9]).

Equipment and measurements

Both diffuse reflectance spectra and solution spectra were recorded on a UV-2400PC spectrophotometer (Shimadzu), the former measurements were recorded using an ISR-240A integrating sphere attachment. Reflection spectra on single crystals were measured by means of a UMSP80 microscope-spectrophotometer (Carl Zeiss). An Ultrafluar (×10) objective was used together with a Nicol-type polarizer. Reflectivities were corrected relative to the reflection standard of silicon carbide.

Results and Discussion

Solution state

DFT caluculations of several molecular configurations

Table 1 shows the N=N bond length obtained from the optimized geometry together with spectroscopic calculations for the initial, deprotonated, protonated, ands zwitterionic states. The N=N bond around 1.26-1.29 Å is near to the double bond length of 1.24 Å rather than 1.44 Å for the N–N single bond, suggesting that the molecule is the azo type. Deprotonation brings about little spetral shift (λ = 421.6 nm); whereas a larger bathochromic displacement is observed by protonation (λ = 453.7 nm). On the other hand, a drastic bathochromic shift occurs with the zwiterionic structure (λ = 658.5 nm). It is also to be noted that the zwiterionic structure exists only in the solid state, not in solution.

Table 1: Calculated N=N bond lengths and optical absorption

MOH	N=N (Å)	λ (nm)	Oscillator strength
(a) Initial state	1.266	419.1	1.044
(b) Deprotonated state	1.264	421.6	0.859
(c) Protonated state	1.289	453.7	1.165
(d) Zwitterionic state	1.282	658.5	0.643

Deprotonation of MOH in solution

Fig. 4(a) shows the conductometric titration of MOH with NaOH for deprotonation experiment of MOH. The conductivity of the solution increases linearly from the commencement of the titration. This represents the neutralization of the acid (MOH). From point A, the conductivity increases with higher gradient. Point A corresponds exactly to equivalence point. This indicates that deprotonation is completed at point A.

The absorption spectra from the initial point to point A are shown in Fig. 4(b). The spectral change during the deprotonation is very little. This is in good agreement with the DFT calculations (Table 1). whereas the deprotonated species give a maximum at 464 nm. This hypsochromic shift is very small and this trend is well reproduced in the results of DFT-calculations.

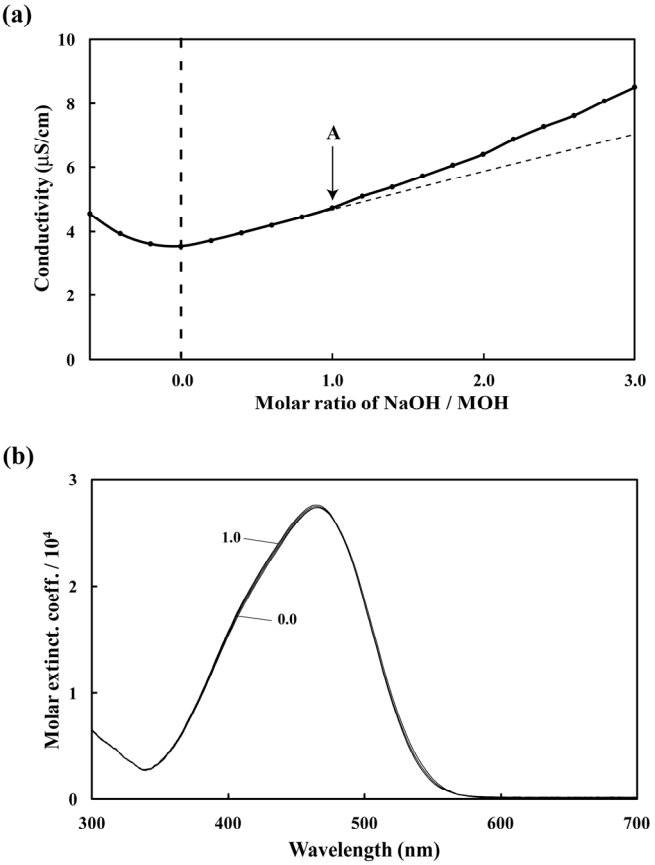


Figure 4. *(a) Conductmetric titration of MOH aqueous solution (2×10^{-5} M; 100 ml) with NaOH and (b) solution spectra of MOH upon deprotonation*

Protonation of MOH in solution

Fig. 5(a) shows the conductometric titration for protonation of MOH. In contrast to the quantitative titration in deprotonation experiment, roughly thirty times more HCl is necessary for the protonation of MOH due to solvation effect with water-molecules.

Fig. 5(b) shows the spectral changes during the protonation, characterized by two isosbestic points at 350 and 470 nm. A relatively large bathochromic shift is observed upon protonation. This agrees fairly well with the calculated absorption bands.

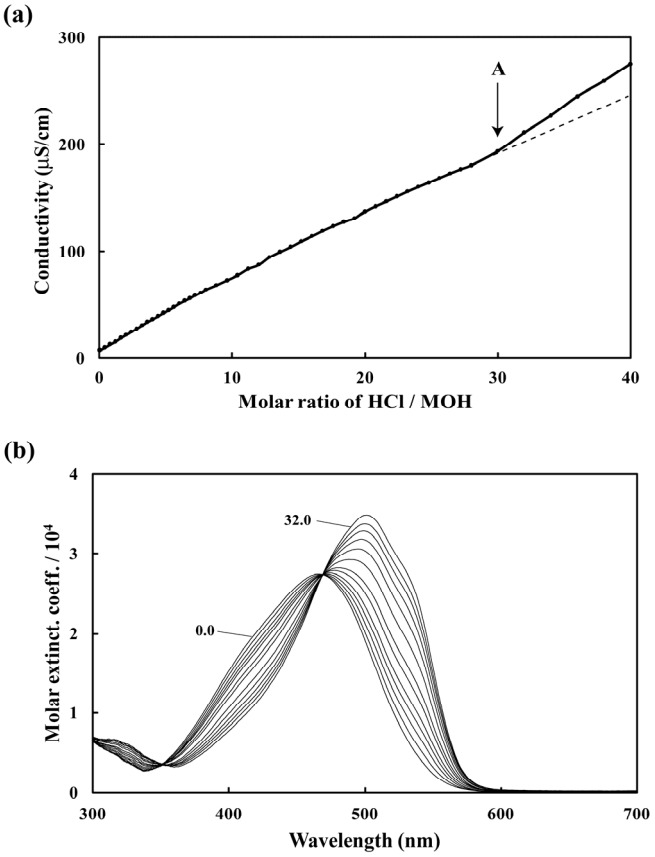


Figure 5. *(a) Conductmetric titration of MOH aqueous solution (2×10^{-5} M; 100 ml) with HCl and (b) solution spectra of MOH upon protonation*

Solid state

Crystal structure of purple phase of MOH

Table 2 details the crystallographic parameters of the purple phase (*i.e.* the new phase) together with those of the red phase (*i.e.* zwitterionic phase [4]). The structure analysis of the purple phase is yet not entirely refined at the moment. Further refinement is necessary.

In the unit cell of the purple phase, there are two independent molecules. The ORTEP plot of the purple phase is shown in Fig. 6(a). The present structure reveals that the N=N bond lengths are 1.218(19) and 1.236(17) Å, which are typical of the azo group (–N=N–). Furthermore, it is to be noted that one of the S/O bonds is apparently longer (1.449(15) Å) than the other two bonds (1.353(18) and 1.363(18) Å), suggesting the sulfonic group ($-SO_3H$).

Fig. 6(b) shows the molecular arrangement of the molecules projected onto the (100) plane. Two molecules are nearly directly overlapped, showing that the slip angle of the two molecules is below 54.7°, displacing the absorption band toward shorter wavelengths due to excitonic interactions.

Table 2: Crystallographic parameters for the purple phase and red phase

	Purple phase	Red phase[4]
Formula	$C_{14}H_{15}N_3O_3S_1$	
Crystal system	Triclinic	Monoclinic
Space group	P-1	$P2_1$
a (Å)	6.8749(3)	7.3080(8)
b (Å)	18.4984(8)	7.5479(8)
c (Å)	18.4984(8)	12.7571(13)
α (°)	88.016(2)	–
β (°)	79.293(2)	104.404(7)
γ (°)	79.290(2)	–
V (Å^3)	2271.30(17)	681.56(12)

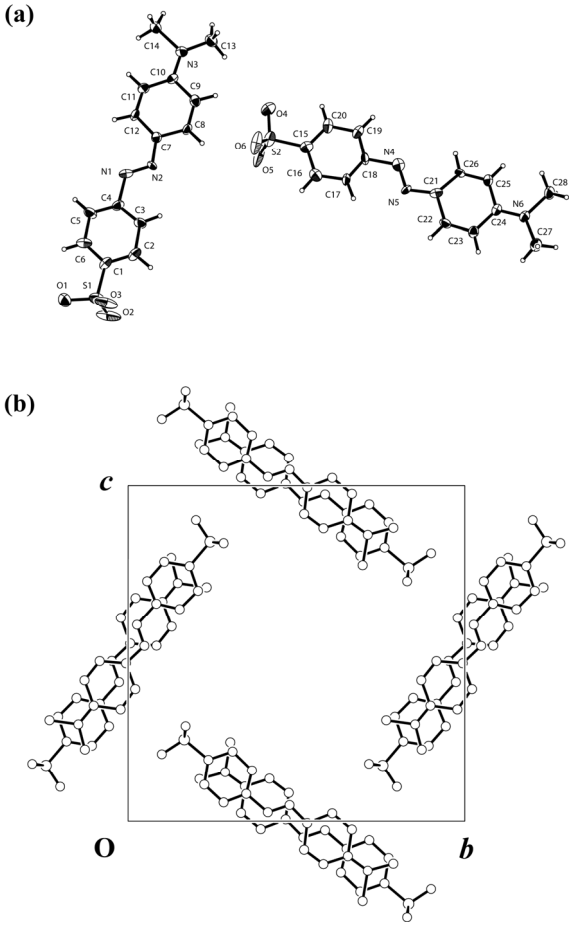


Figure 6. *(a) Molecular conformation and (b) molecular arrangement of the purple phase*

Solid state spectra

Fig. 7 shows the polarized reflection spectra measured on the (001) plane of single crystals of the red phase (*i.e.* zwiterionic phase). A prominent reflection band appears around 590 nm for polarization parallel to the *a*-axis, that is, the direction of the long-molecular axis. On the other hand, the reflection band is completely quenched for polarization perpendicular to the *a*-axis. These results clearly indicate that the direction of the transition dipole points along the long-molecular axis in accord with direction deduced from DFT calculations. It is also important to note that the reflection band at the longest-wavelength is due to the zwitterionic structure which exists only in the solid state. Because of this band, the crystals look red in the zwitterionic phase.

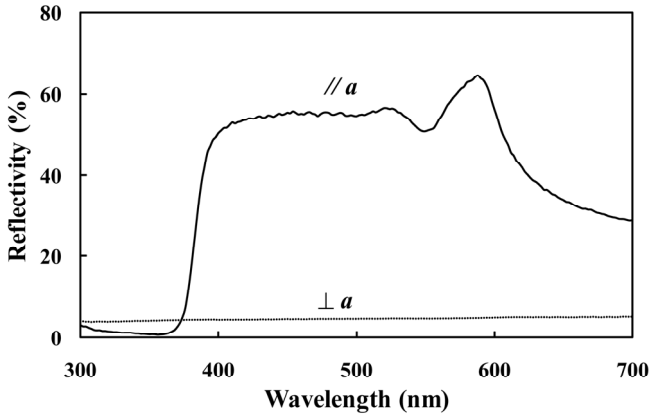


Figure 7. *Polarized reflection spectra measured on the (001) plane of single crystals of the red phase*

Fig. 8 shows the non-polarized reflection spectra measured on single crystals of the purple phase (*i.e.* the new phase). A prominent reflection band appears around 420 nm which yield a color of purple. The present band is apparently displaced shorter wavelength as compared with the absorption band in solution (Fig. 4(b)). This is presumably attributed to the molecular arrangement Fig. 6(b), in which the slip angle of the two overlapped molecules is below 54.7°.

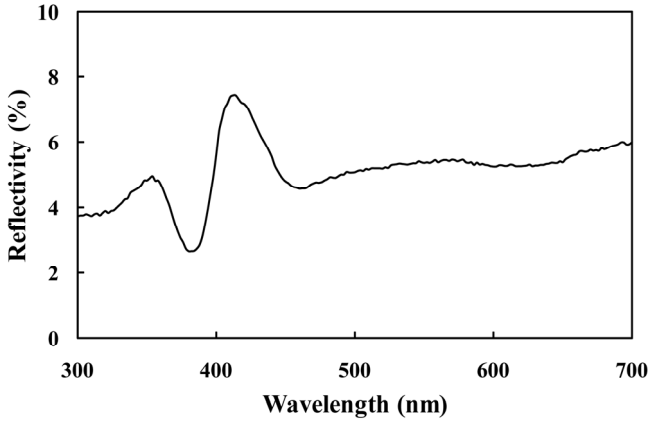


Figure 8. *Reflection spectrum on single crystals of the purple phase*

Conclusions

Electronic characterization has been made on the polymorph of MOH. The red phase is characterized by the zwitterionic structure in the crystal lattice; whereas the typical azo form exists in the purple phase, in which two molecules are nearly directly overlapped with a slip angle below 54.7°. The zwitterionic structure is responsible for the red color in the red phase. On the other hand, the hypsochromically shifted absorption band as compared with that in solution gives rise to a purple color.

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Author Biography

Kazuyuki Sato received his Bachelor of Engineering in 2005 and his Master of Engineering in 2007, both from Yokohama National University. He is currently in the PhD course for applied physics at the same university. His research interest includes structure analysis of organic pigments and their electronic application.