



## Methyl orange: A brief note on its structural changes

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### ABSTRACT

Methyl orange ( $p\text{-Me}_2\text{NC}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_4\text{SO}_3\text{Na}$ ; MO) is one of commonly used azo dyes known as an acid-base indicator, along with phenolphthalein. The chemical structural changes of MO with respect to its acid-base equilibrium in aqueous solutions have been learnt in chemical education. The reaction equations vary among analytical chemistry textbooks. Thus, details on the structures of MO are overviewed from historical perspectives for teaching materials in chemistry. Since protonation of MO potentially occurs not only at the azo group ( $-\text{N}=\text{N}-$ ) but also at the dimethylamino group ( $\text{Me}_2\text{N}-$ ), two different chemical species can be considered; i.e., azonium ( $-\text{N}=\text{NH}^+-$ ) and ammonium ( $\text{Me}_2\text{NH}^+-$ ). In fact, these tautomers of the two protonated MO species exist, and their equilibrium constants have been reported previously. However, ammonium species has not been presented as protonated MO in most textbooks. Misunderstandingly, another confusion concerning the 'resonance' between ammonium and quinonediiminium ( $p\text{-Me}_2\text{N}^+=\text{C}_6\text{H}_4=\text{N}-\text{NHC}_6\text{H}_4\text{SO}_3^-$ ) of MO is also presented; exactly, there should be among azonium and quinonediiminium. In order to avoid misconceptions about the chemical structures of MO, these cases should be introduced to chemical educators and learners.

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## INTRODUCTION

Methyl orange (MO), as shown in Fig. 1, is an azo compound commonly used as an indicator of the neutralization, along with phenolphthalein. Since the proposal of the name of methyl orange and its use as an indicator by Lunge (1881), MO has been used not only as an acid-base indicator in analytical chemistry (Baker, 1964), but also as a learning material in chemical education (Shimada et al., 1992). MO undergoes a structural change from red in strongly acidic aqueous solutions to yellow at a pH 4 or higher (Barbosa, 2005).

How and when was the knowledge of the chemical structures of MO found and demonstrated in chemical education? This brief note aims therefore to provide teachers and students of chemical education with a more precise understanding of the structural changes in MO accompanied by color change.

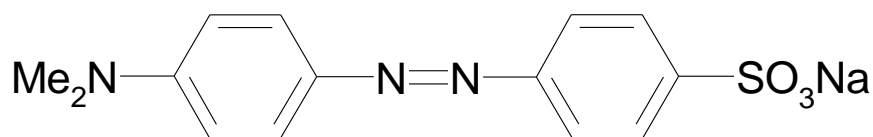


Fig. 1. Chemical structure of methyl orange (MO).

## ORIGIN OF METHYL ORANGE (MO)

Griess, a German organic chemist, prepared MO by coupling the diazo compound of sulphanilic acid with dimethylaniline, which means that the utilization of sulphonated compounds in the synthesis of azo products was known (Reinhardt & Travis, 2000). However, since Griess himself supposed that most nitrogen-substituted azo compounds offer absolutely no new chemical interest, and it was unnecessary to mention them even if only by name (Griess, 1875), MO was not characteristic at that time. Indeed, there are few references to the discovery of MO in the biographies of Griess (Ivanov, 2004; Yates & Yates, 2016). Subsequently, to titrate alkaline carbonates with an important practical advance, the name of “Methyl-orange” was introduced, instead of other names such as Poirrier’s Orange No. III, helianthine, and Tropæoline D (Baker, 1964; Lunge, 1881).

## AMMONIUM AND AZONIUM FORMS OF METHYL ORANGE (MO)

The journal of chemical education contains an article titled ‘PHENOL-PHTHALEIN and METHYL ORANGE’, which provided insight into the understanding of MO in the early 20th century:

*“Various authors do not agree with the action of common indicators. In discussing methyl orange, Willard and Furman pitted the hydrogen on the dimethyl nitrogen, while Kolthoff and Sandell placed it in the red form on the azo group”* (Peters & Redmon, 1940).

When MO is protonated, there are two presumed red chemical species; the ammonium form (am-), in which the dimethylamino group ( $\text{Me}_2\text{N}-\text{Ar}$ ) is protonated, and the azonium form (az-), where the azo group ( $-\text{N}=\text{N}-$ ) is protonated (Fig. 2).

From a modern qualitative viewpoint, the tertiary amino group ( $\text{Me}_2\text{N}-\text{Ar}$ ) in MO is not easily protonated because of steric hindrance by the two methyl groups in addition to the aryl moiety. Since the atom of nitrogen (N) in the dimethylamino group is directly bonded to the aromatic ring, and the lone electron pair on that delocalizes by the interaction with the  $\pi$  electrons in the bonded aromatic ring, further weakening of its basicity is considered to occur. In other words, red MO species are less likely to exist as the am-tautomer. This means that the chemical equilibrium of the tautomerism shifts toward the az-tautomer rather than the am-tautomer. Simultaneously, it is necessary to add that the az-species resonates with the quinonediiminium (q-) species demonstrated in Fig. 2 (Fifield & Kealey, 2000; Bolotov et al., 2011).

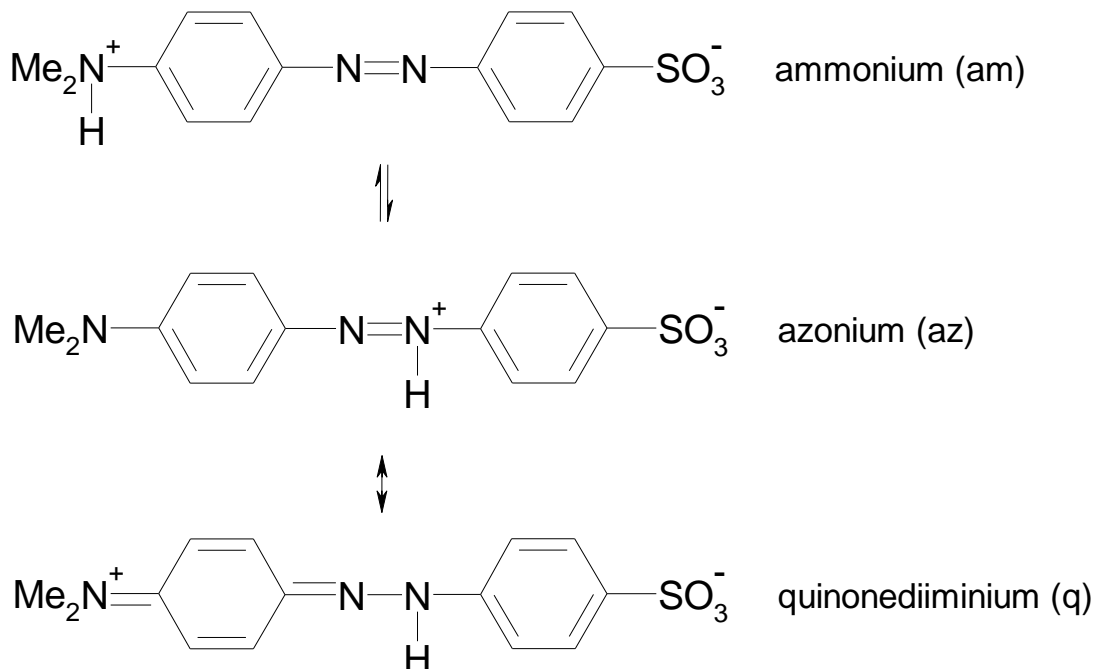


Fig. 2. The tautomerism between the ammonium (am-) tautomer and the azonium (az-) tautomer of MO (above), and the resonance between the az-form and the quinonediiminium (q-) form (below).

As an azo group contains two N atoms, it can be protonated on either N atom. In the case of MO, the two N atoms of the azo group are asymmetric, that is, on the one hand, protonation occurs on the  $\alpha$ -N atom at the side having a dimethylamino group; on the other hand, it potentially occurs on the opposite  $\beta$ -N atom at the side with the sulpho-nate group. In fact, both az-tautomer and q-species are described as having a chemical structure with  $\text{H}^+$  bonded to the  $\beta$ -N atom rather than the other  $\alpha$ -N atom. This is explained by the theory of resonance hybrids. The basicity of azobenzene with different substituents (X, Y) on the two benzene rings has been investigated (Yeh & Jaffé, 1959). When X is an electron-releasing group, the resonance structural formula is expressed as in Fig. 3, and the electron pair is shifted toward the substituted Y on the opposite side of the two nitrogen atoms in the azo group compared to the case without X. The structural contribution is attributed to the electron pairs being biased toward the one substituted by Y, opposite to X, among the two N atoms within the azo group.

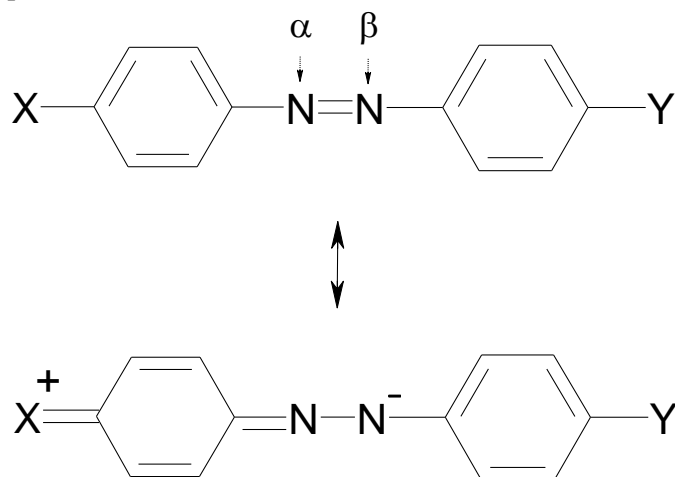


Fig. 3. The resonance hybrid structure of a disubstituted azobenzene, X is an electron-releasing group and Y is an electron-withdrawing group.

In subsequent research, the following conclusions were drawn:

“Existing evidence does not allow an unequivocal assignment of the sites of protonation of these and related molecules\*” (Bolton et al., 1973). \*MO and its analogues.

According to the above, it is obvious that it has been impossible to determine the exact protonation site by acidifying MO in aqueous solutions for decades. However, consequently, Del Nero et al. (2005) stated that interested readers can find an extensive discussion of the microscopic equilibria between different MO structures in an article (Tawarah & Abu-Shamleh, 1991). Viz., rather than only one species exists, both forms exist as tautomers. Afterwards, the existing microscopic equilibria among species derived from MO are outlined below.

#### MICROSCOPIC EQUILIBRIA OF MO FROM ITS ABSORPTION SPECTRA

According to the previous study (Tawarah & Abu-Shamleh, 1991), the UV-Vis spectra of MO have been measured in alkaline, acidic, and strongly acidic aqueous solutions at 25°C. The pH was adjusted by adding an appropriate amount of aqueous NaOH or HCl solution. The absorption maximum ( $\lambda_{\max}$ ) at 466 nm was observed in an aqueous solution of MO (pH 11.0). As the pH was lowered, az-tautomer ( $\lambda_{\max} = 508$  nm) and am-tautomer ( $\lambda_{\max} = 316$  nm) were also observed. Two isobestic points at 470 nm, an acid-base equilibrium with an apparent acid dissociation ( $K_{a2}$ ), and 344 nm were considered to represent a tautomeric equilibrium ( $K_t$ ) (Fig. 4). The thermodynamic dissociation constant ( $K_{a2}$ ) and tautomeric equilibrium constant ( $K_t$ ) can be obtained from the equations below:

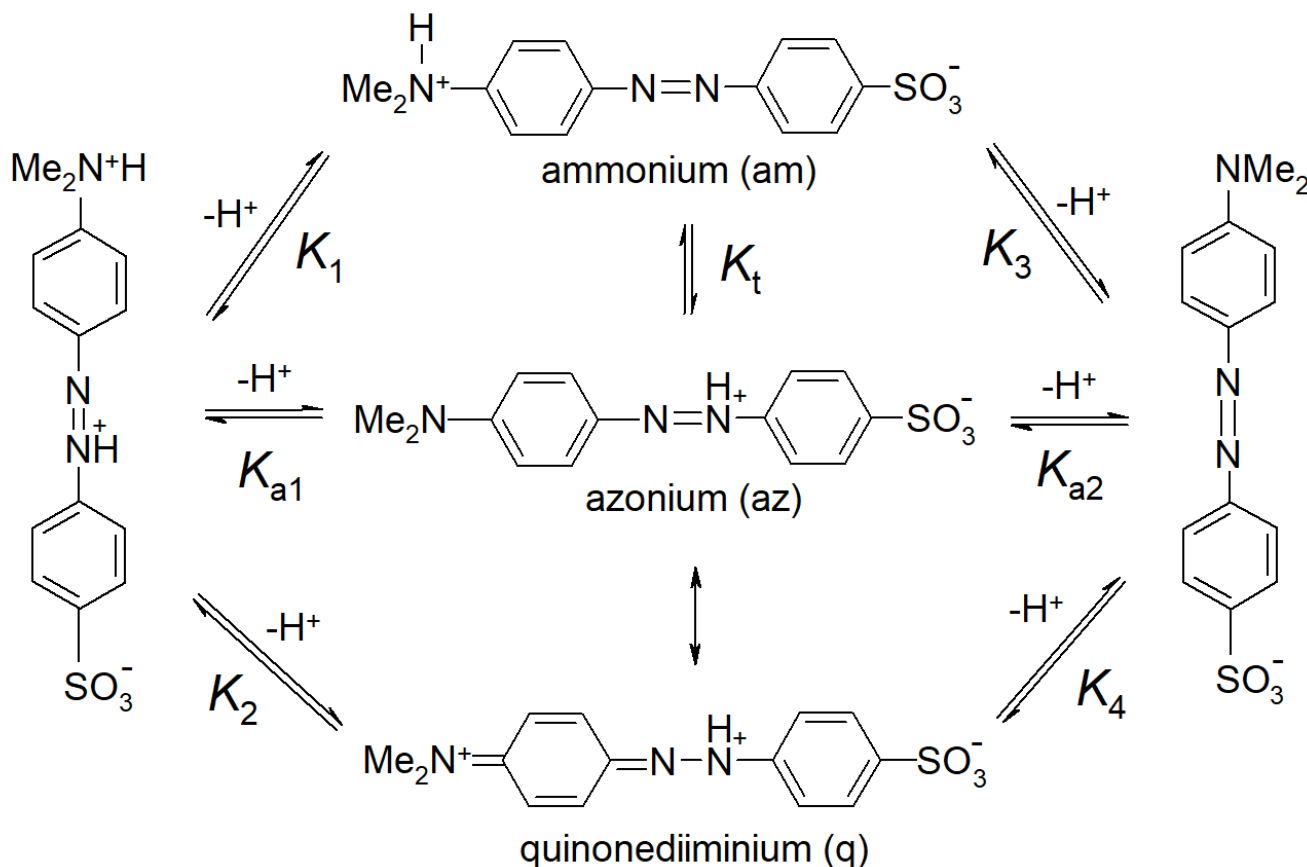
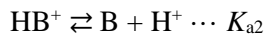
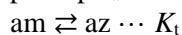


Fig. 4. The tautomeric and acid-base equilibria of methyl orange (MO) in aqueous acidic solution.



$$\text{pH} = \text{p}K_{a2} + \log[(A - A_a)/(A_b - A)] + \log(\gamma\text{B}/\gamma\text{HB}^+)$$



$$K_t = [\text{az}]/[\text{am}] = (E - E_{\text{am}})/(E_{\text{az}} - E).$$

The Equation for  $K_{a2}$  represents a macroscopic acid-base equilibrium of MO, where  $\text{HB}^+$  (red in color) represents the monoprotonated form (a zwitterion for MO), and B (yellow in color) is an anion for MO.  $A$  is the absorbance of a test solution which contains the forms  $\text{HB}^+$  and B;  $A_a$  or  $A_b$  is the absorbance of a solution that contains either  $\text{HB}^+$  or B, which is isomolar with the test solution;  $\gamma$  means the molar activity coefficient of either species B or  $\text{HB}^+$ , calculated by the ionic strength with the Debye-Hückel equation's extension of Guggenheim.  $E$  stands for the apparent molar absorptivity of the tautomeric mixture and  $E_{\text{am}}$  and  $E_{\text{az}}$  are the molar absorptivities of the am- and az-tautomers, respectively. The microscopic acid dissociation constants  $K_1$ ,  $K_2$ ,  $K_3$ , and  $K_4$  are related to the tautomeric constant  $K_t$  and the constants of macroscopic acid dissociation ( $K_{a2}$  and  $K_{a1}$ ):

$$K_1 = K_{a1}/(1 + K_t)$$

$$K_2 = K_{a1} \times K_t/(1 + K_t)$$

$$K_3 = K_{a2}(1 + K_t)$$

$$K_4 = K_{a2}(1 + K_t)/K_t.$$

The values of each constant were shown in Tawarah & Abu-Shamleh (1991); however, only the value of  $K_{a1}$  had been estimated from the data by Reeves (1966).

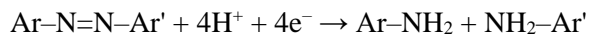
#### TOPICS FOR APPLICATIONS IN CLASSROOMS OF CHEMICAL EDUCATION

Some analytical chemistry textbooks present the chemical structure of the protonated form of MO in a format that is unclear as to its source, and which can only be assumed to be not based on the research described so far. The following two textbooks on analytical chemistry and related literature are cited as examples. The first is the textbook "Principles and Practice of Analytical Chemistry" (Fifield & Kealey, 2000), which depicts a diagram of a protonated dimethylamino group, and a protonated azo group connected by a ' $\leftrightarrow$ ' symbol, indicating resonance. In this instance, the chemical species are tautomers of each other and not resonance mixtures, rendering the notation inappropriate. In the second case, the azonium ion is protonated at the azo group of MO, which is then connected to the orange chemical species. "Analytical Chemistry: Collection of lectures on quantitative analysis: The manual for students of higher schools" (Bolotov et al., 2011) are showing the red quinonediiminium ion is connected to the azonium ion by a ' $\rightleftharpoons$ ' representing the state of chemical equilibrium. It is important to distinguish between resonance and equilibrium in order to avoid confusion. It is postulated that such misunderstandings are likely to occur in the context of chemical education. Therefore, it is imperative that these misconceptions be avoided in the chemistry classroom, where they can impede effective teaching and learning. This can be achieved by incorporating the knowledge and information gained into instructional materials and activities.

Multimedia-based instructional modules have been developed in science (Basilio & Sigua, 2021). Previously, the usage of Information and Communication Technology (ICT) equipment has proposed to enable the comprehensively visual learning of the three-dimensional structures of organic molecules (Noguchi, 2020a, b; 2022). For the useful materials of chemistry teachers and students, the crystal structures of MO, and azonium ions with a proton attached to the azo group in MO are shown in Fig. 5.

It is essential to explore the potential applications or extensions of MO's structural changes, such as in the study of MO and related azo compounds. The synthesis of azo dyes is a fundamental topic in the field of education of organic chemistry (Simão & Cerdeira, 2016). In contrast, experiments to decolorize synthesized azo dyes have also been introduced. When MO was added to the reaction between a metal and an acid, the color of MO was coincidentally observed to disappear (Yoshimoto et al., 1995). However, while the chemical reaction equations for the synthesis of azo dyes are well documented in the literature, the chemical changes occurring during the decolorization

reaction are not shown in chemical educational textbooks and are therefore unclear. A survey of the literature revealed that the metal  $M$  ( $Fe^0$ ) and the azo compound  $Ar-N=N-Ar'$  undergo the following redox reactions (Cao et al., 1999; Nam & Tratnyek, 2000):



( $M = Fe^0$ ,  $Ar$  &  $Ar' =$  Aryl groups).

Given that the decolorization of azo dyes is a reduction reaction, it is of interest to ascertain whether it is possible to establish a simple experimental system for decolorizing azo dyes by electrochemical methods. Such a system could prove invaluable in the development of effective teaching materials for electrochemical demonstrational experiments. Also, it will be useful inquiry material for the students in junior high school engaging research activities (Real, 2022).

Other research conducted to support the teaching of analytical chemistry has resulted in computer calculation of the UV-Vis absorption spectra of MO before and after acid dissociation. This research proposed the possibility of computer calculations for chemistry classrooms (Hanai, 2018). Nevertheless, microscopic equilibrium has not yet been considered. Conversely, Boily & Seward (2005) reported that the spectra did not provide evidence of tautomeric equilibria between protonated azo ( $-N=NH^{+}$ ) and ammonium ( $Me_2NH^{+}$ ) species of MO within the experimental range studied. Consequently, when simulating the chemical structures of MO and its protonated adducts as learning materials for analytical chemistry, it may be necessary to consider the potential existence or absence of the microscopic equilibrium states, including ammonium-azonium tautomers, in future studies.

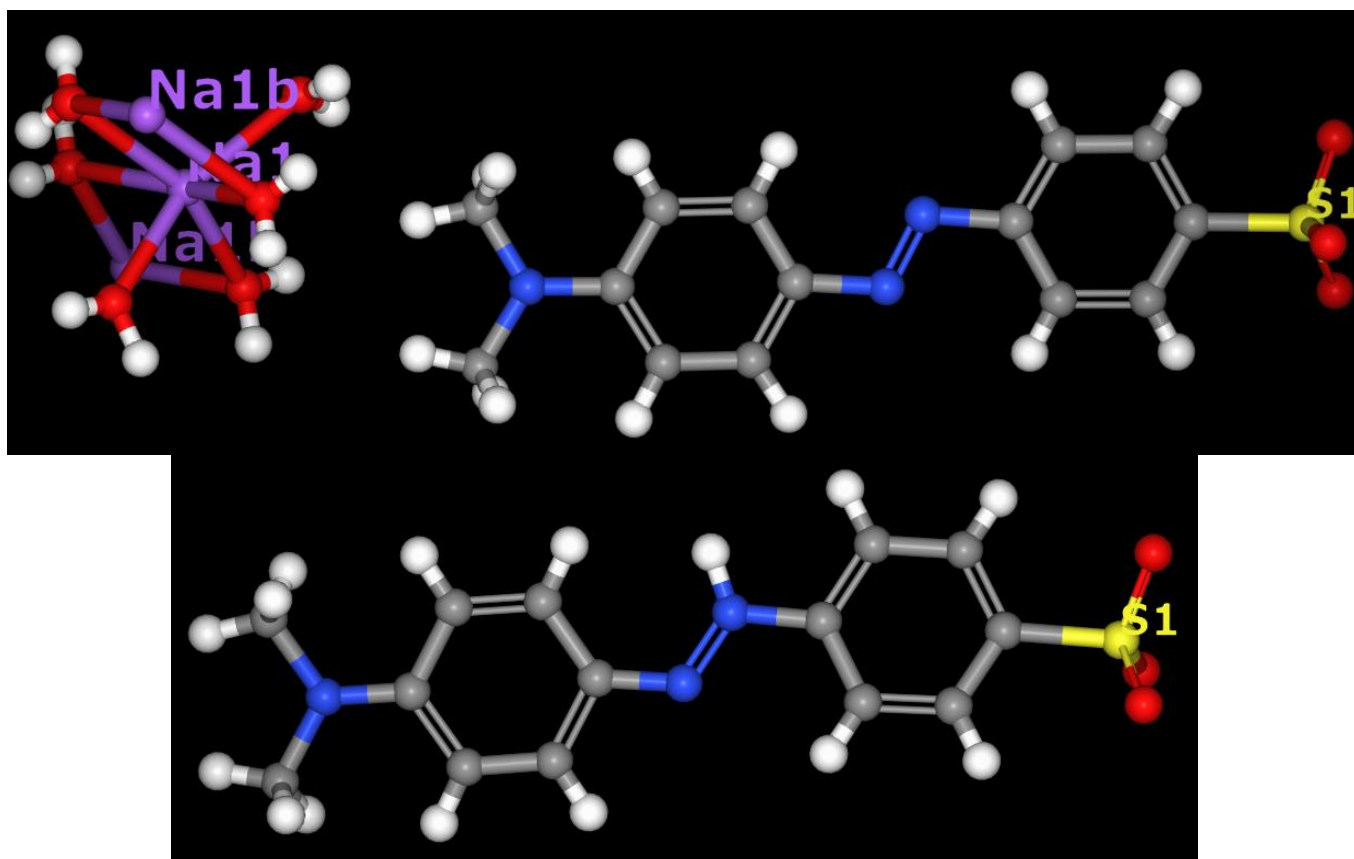


Fig. 5. Crystal structures are displayed by the web browser at the Cambridge Crystallographic Data Centre (CCDC); above:  $MO \cdot 4H_2O$  by Kennedy et al. (2004); below:  $H^+MO$  by Burke et al. (2004).



## CONCLUSION

The name of the azo compound methyl orange (MO) was first introduced as an indicator of neutralization titrations by Lunge in 1881. For the chemical structures of MO, when it shows a red color in strongly acidic aqueous solutions, only azonium (az-) with a protonated azo group is shown in standard analytical chemistry textbooks. However, studies based on UV-Vis absorption spectroscopy have shown that in strongly acidic aqueous solutions, a microscopic equilibrium state, 'ammonium-azonium tautomerism,' is established between az- and ammonium (am-) having a protonated dimethylamino group ( $\text{Me}_2\text{NH}^+$ ) in MO that exists as an equilibrium mixture.

Additionally, az-tautomer is one of the contributing structures in the resonance mixture and is thought to exist as a resonance hybrid with quinonediiminium (q-), in which resonance (rather than equilibrium) is established. This would be confusing if they were not properly learned by novice students. However, some analytical chemistry textbooks contain misleading demonstrations. Chemistry instructors should therefore thoroughly understand these backgrounds, if necessary, when teaching the acid-base equilibria of MO.

For the chemistry classroom, the crystal structural data of both normal MO and azonium form of MO are available via the Cambridge Crystallographic Data Centre (CCDC) for visual learning. Given the established phenomenon of decolorization of azo compounds by metals and acidic solutions, there is expected to have potentials for the development of further teaching materials for electrochemical education on redox reactions. It is anticipated that computer calculations will have the potential to facilitate the teaching and learning of chemistry in relation to MO, particularly in regard to its microscopic equilibrium with its structural changes.

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