Thermally Reversible Photochromism of Pyrazole Derivatives

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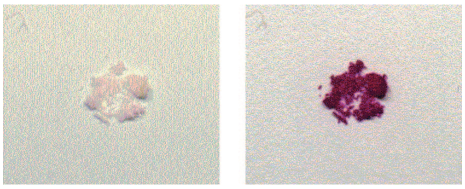
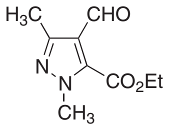
Ethyl 4-formyl-1,3-dimethylpyrazole-5-carboxylate showed coloration upon 366-nm light irradiation in the solid state at room temperature. The red color disappeared either by melting or dissolving into solvents. The initiation of coloration is most likely based on a photochemical intramolecular hydrogen abstraction by the formyl oxygen from the methyl group on C-3. It also exhibited coloration in 2-methyltetrahydrofuran matrix at low temperature.

Photochromism,[1] the light-induced reversible change of structure and properties including absorption spectra, has been regarded as one of the most fascinating phenomena to study and to apply to realize photoresponsive functional materials. The properties of photochromic organic compounds have mostly been examined either in solution or in polymer matrices, but not so often in solids.[2] Particularly, the organic compounds that exhibit photochromism only as their pure solid state at ambient environment are rare.[3] We here report a new class of photochromic pyrazole derivative **1A**,[4] exhibiting color by photoirradiation only in the solid state, most likely based on the photochemical intramolecular hydrogen abstraction termed as Norrish Type II reactions.[5]

The pyrazole derivative **1A** was synthesized by the condensation of ethyl 2,4-dioxopentanoate and *N*-methylhydrazine followed by hydroxymethylation on C-4 and oxidation.[6,7] Transesterification with an excess of alcohol and sodium hydride afforded the corresponding different esters.[4]



Before 366-nm irradiation. After 366-nm irradiation for 30 s.



1A

Figure 1. Color change of **1A** (powder) by UV irradiation.

Upon 366-nm light irradiation, the colorless powder of **1A** exhibited red color immediately. The color is highly stable. When it was stored under the room light, the color lasted for a few days. When the colored solid was irradiated with 500-nm light (2.04 mW cm^{-2}) for 45 min, no change was observed. However, when the colored solid was heated to its melting point, the resulting liquid was colorless, and the solid obtained after cooling was **1A**. Therefore the cycle of photochemical coloration and thermal decoloration was repeatable. The red color also disappeared immediately when it was dissolved in an organic solvent. Evaporation of the solvent gave **1A**. However, when the colored powder was dispersed in water, the red color of the solid remained unchanged. The pictures before and after the 366-nm light irradiation to the powder of **1A** at room temperature are shown in Figure 1.

When **1A** was irradiated with 366-nm light at 86 K in 2-methyltetrahydrofuran (MTHF), the absorption maximum was 495 nm. It shifted to 504 nm irreversibly during warming up to 101 K. It disappeared gradually when warmed up to 140 K. The ease of restoration of **1A** from the colored form in an MTHF matrix than in crystalline solid indicates the restriction of molecular movement. It also rules out a possible explanation for the coloration attributed to an intermolecular phenomenon, because isolated molecules in an MTHF glass gave the same colored species as in a solid.

The absorption spectra of a thin film of **1**, prepared from the melt of **1A** between two Pyrex glass plates (therefore the solid film maybe amorphous rather than crystals), after 366-nm light irradiation were measured. Before UV irradiation, it has no absorption in the visible region. After 366-nm light irradiation, a broad absorption band around 540 nm appeared (Figure 2). The predicted absorption calculated by ZINDO MO[8] for **1Q** (Scheme 1) was 502 nm.

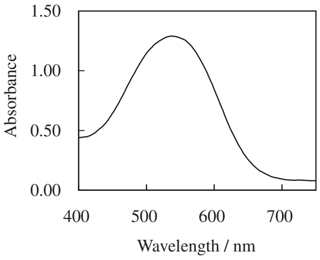
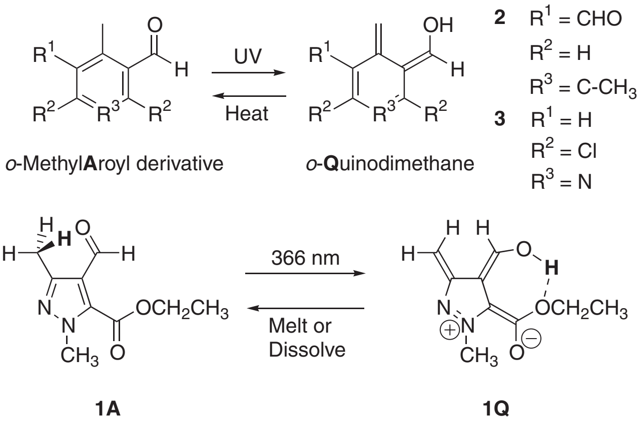


Figure 2. Absorption spectrum of amorphous **1Q** film.

There are several reports that the aromatic carbonyl compounds exhibit the intramolecular hydrogen abstraction by the carbonyl oxygen from the adjacent alkyl substituent such as methyl group on the aromatic core.[3,9] The essential reaction course exemplified by **2**[3a] and **3**[3b] is depicted in Scheme 1. When this kind of photoreaction mechanism is applied to **1**, the colored species is forced to take either the zwitter-ionic or biradical structure.

Because the π-system of **1Q** is similar to that of hydrocarbon diradical tetramethyleneethane (TME), we tried an EPR measurement of **1**. After UV irradiation in an MTHF glass at cryogenic temperature (17–25 K), several peaks were observed within 6 mT of spectral width (no peak due to $|m| = 2$ transition was observed), and they disappeared at 102 K while the color was still remaining. The observed spectral width is far smaller than that of TMEs ($|D/hc| \approx 0.025\,\mathrm{cm}^{-1}$). Although we could not assign the EPR-active species, TME-like biradical structure may be ruled out for the colored species. Thus we considered the colored species as zwitterionic **1Q**.[10]



Scheme 1. Photoreaction of *o*-methylaroyl compounds and **1**.

The distances between the abstracted hydrogen and the abstracting oxygen atoms are reported to be 0.258 nm for **2A** and 0.260 nm for **3A**, respectively. The distance of the corresponding hydrogen and oxygen atoms in **1A**, obtained from X-ray crystallographic analysis, is 0.280 nm. The crystal structure of **1A** is shown in Figure 3.[11]

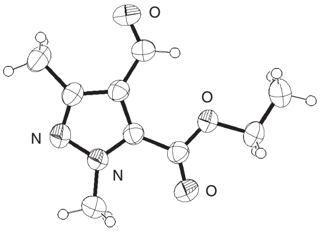


Figure 3. X-ray structure of **1A**.

Although the change in IR spectra of **1** before and after UV irradiation was very subtle, a small peak at 3271 cm^{-1} appeared after UV irradiation. The peak is assigned to an enol O–H bond, and is slightly shifted from that observed in **2Q**[3a] (3350 cm^{-1}). The reason is attributable to an intramolecular hydrogen bonding as shown in Scheme 1 (cf. β-diketones, 2900–3500 cm^{-1}; methyl salicylate, 3210 cm^{-1}).[12] Concomitant diminishing of two carbonyl peaks (1725 and 1682 cm^{-1}) of **1A** and appearance of a peak at 1700 cm^{-1} during the UV irradiation also indicates the mechanism of hydrogen abstraction with the Norrish type II.

From these experimental results and the precedents of similar compounds, we concluded that the initial photochemical process might be the abstraction of a hydrogen atom on the C-3 methyl group by the carbonyl oxygen atom of the formyl group. Because of the stability of the colored species and the IR data, a hydrogen bond might be formed as the result of *E-Z* isomerization of the enol moiety of the "hot" ground state. As the resulting species cannot be depicted as a neutral, fully valence-bonded formula, and with the EPR data, we assigned the structure of **1Q** as shown in Scheme 1.

In conclusion, we found a new solid-state photochromic compound which turns red by UV irradiation and returns colorless by melting or dissolving in solvents, but highly stable to visible light. The colored form was deduced to be zwitterionic. It also exhibits red color in matrix at low temperature.

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References and Notes

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4 The ester cognates of **1** (methyl and propyl) showed coloration. However, 2-propyl and butyl esters did not.

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7 **1A**: mp 72.5–75 °C. IR (KBr): 1721, 1678, 1525, 1477, 1456, 1411, 1390, 1373, 1283, 1200, 1110, 1039, 1012, 896, 818, 774 cm^{-1}. ^{1}H NMR (270 MHz, CDCl$_3$, TMS): 1.44 (3H, t, J/Hz = 7.09), 2.49 (3H, s), 4.14 (3H, s), 4.47 (2H, q, J/Hz = 7.25), 10.39 (1H, s).

8 ZINDO (INDO/S) calculations were done for AM1-optimized conformation of **1Q**.

9 B. A. Johnson, A. Gamarnik, and M. A. Garcia-Garibay, *J. Am. Chem. Soc.*, **100**, 4697 (1996).

10 Although the colored species can be a singlet biradical, we also ruled it out from the energetic consideration. Details including other possible isomers of **1Q** will be reported in due course.

11 Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-221042. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk). Instruction for depositing the crystallographic data is available on the Web at http://www.ccdc.cam.ac.uk/conts/depositing.html.

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