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Photochromism and mechanism of pyrazolones in crystals: structural variations directly observed by X-ray diffraction[†]

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Structural changes of photochromic pyrazolones were first verified by an X-ray crystallographic method directly. A tautomeric transformation between enol and keto form isomers occurs, accompanied by proton transfer during the photochromic processes.

The reversible change of color as the result of structural, environmental, and/or molecular orientation changes of materials, which have distinguishably different absorption properties by electromagnetic stimulation, is well-known as photochromism,¹ and it has been investigated extensively for its diverse potential uses such as optical data storage² and switches.³ Although a variety of organic photochromic compounds in solutions⁴ or in dispersed systems⁵ have been investigated, it is rare to find photochromic organic compounds in the crystalline state in literature. Therefore, it is of technical as well as fundamental interest to seek photochromic materials in the crystalline state.⁶

Toward this end, we have devoted our effort to develop a photochromic system derived from pyrazolones, which exhibit reversible photochromism in the crystalline state.⁷ It is found that the materials can change their color from white to yellow upon irradiation with UV light, and then return to white upon storage in visible light or heating. The photochromic system shows advantages including high sensitivity, excellent fatigue resistance and reversible fluorescent switching properties with high contrast signals.^{7h,c} Based on spectroscopic measurements together with theoretical calculations, our studies indicate that the photochromism of pyrazolones could originate from the tautomerism between the enol form (*E*-form) and keto form (*K*-form) by photo-chemically triggered proton transfer.⁸ However,

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the mechanism of photochromic reactions in crystals is still open. In the case of organic photochromic crystals, however, it is usually hard to obtain sufficient colored species detectable with the X-ray crystallographic method,⁹ because the photo-reaction takes place on the surfaces of macroscopic single crystals.¹⁰ It is still a challenge to directly probe the structure changes brought about by photochromism of pyrazolones, while it is critical for understanding the photochromic mechanism and designing new photochromic systems.

In this work, the crystal structural changes related to the photochromism of pyrazolones were first observed by using X-ray crystallographic analysis and their photochromic mechanism was demonstrated. A new photochromic compound: 1-phenyl-3-(4fluorophenyl)-4-(2-chlorobenzal)-5-hydroxypyrazole 4-methylthiosemicarbazone (1), which performs a reversible photoisomerization reaction under alternating UV light irradiation/heating and visible light in the solid state (Scheme 1), was successfully synthesized by condensing 4-acylpyrazolone with methylthiosemicarbazone. The same yellow colored materials can be yielded by UV light irradiation or heating the white sample of 1a. In order to increase the populations of colored species in single crystals suitable for X-ray crystallographic analysis, we found that it was effective to treat the materials by heating at 180 °C. The yellow crystals of 1b, which were very similar to those irradiated by UV light (Fig. S1, ESI[†]), were obtained by heating the single crystal of 1a for X-ray diffraction. The crystal structure analysis of the materials reveals the photochromic mechanism of the



Scheme 1 Photochromic reactions of 1.

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pyrazolone family for the first time. It was found that the photochemically or thermally triggered intra- and intermolecular proton transfers have resulted in tautomerism in single crystals.

Compound 1 has an absorption band at 443 nm after irradiation with light of 365 nm (Fig. 1A). Subsequently, the white materials changed to yellow, and the yellowed 1b can keep their color for more than one year when stored in the dark at room temperature. The colored reactions can take place not only under UV light irradiation. but also by heating. The chromic behaviors occurred after heating, and the spectra of the yielded products were exactly the same as those obtained under UV light irradiation (Fig. S2, ESI[†]). In other words, the structure of the materials could convert from the E-form of 1a into the K-form of 1b both photo-chemically and thermally. The yellow colored materials can be bleached back to white under visible light irradiation (\geq 420 nm). A characteristic fluorescence band of 1 was observed at 443 nm after excitation at 320 nm as shown in Fig. 1B. Upon irradiation with 365 nm light, the intensity of the fluorescence band decreased gradually with increasing the irradiation time, and the emission reached a photostationary state after irradiation for 160 min. The switchable fluorescent property of 1 may also arise from converting the E-form of 1a to the K-form of 1b. The fluorescent contrast between the E-form and K-form isomers of 1 was 32: 1. Compared to other pyrazolones reported previously, this is the highest photo-induced fluorescent modulation observed, which is essential for designing optical devices. Fluorescent switches could be realized by alternating light irradiation based on the photochromic reaction of 1 in the crystalline state.

To obtain direct evidence for verifying the photoisomerization mechanism of pyrazolones, crystal structures of 1a¹¹ and 1b¹² were identified using single-crystal X-ray crystallography (Fig. 2A and 2B). In order to increase the population of the K-form in the single crystal, 1a was treated at 180 °C to obtain the thermal products of 1b. The IR and XPS spectra of the sample heated at 180 °C showed that the thermal products obtained by heating were identical with the photoproducts obtained by irradiation with 365 nm light (Fig. S3, ESI[†]). Selected bond lengths obtained from the X-ray crystallographic analysis of 1 are listed in Table 1. After comparing the data displayed in Table 1, we can find that the length of the O-C bond varies significantly between 1a and 1b. The O-C7 bond of 1b is shorter than that of 1a by 0.14 Å. Thus, the C7-C8 bond of 1b is

700

600

500

300

200

100

350 400 450 500 550 600

Wavelength / nm

missior 400 B



A

Absorbance

0.0

350

400 450

500 550



Fig. 2 Molecular structures of (A) 1a and (B) 1b with atom numbering. The disordered part in 1a are omitted for clarity and the ellipsoid represents 10% and 30% displacement of atoms, respectively. Difference Fourier maps of (C) 1a and (D) 1b. The contour lines are at 0.02 e $Å^{-3}$ intervals. The peak corresponding to the changes is indicated by an arrow.

longer than that of 1a, N2-C9 is shorter than that of 1a and the C8-C9 bond of 1b is also shorter than that of 1a. The length of the O-C7 bond of 1a is considerably shorter than the standard length of the O-C bond [1.350 Å] and longer than the length of the O=C bond [1.222 Å].¹³ These results suggest that the two isomers (*E*-form and K-form) might coexist in the crystal of 1a. The length of the O-C7 bond of 1b becoming shorter than that of 1a after heating indicates that the amount of the K-form isomer increases in the crystal produced by heating. It is safe to conclude that there is equilibrium between the E-form and K-form isomers in the crystals.

The H atoms on O and N2 atoms were treated as disordered in the refinement of structure 1a, and the population of the E-form was determined to be ca. 34.6% based on the occupancy of hydrogen atom connected to oxygen. The structure 1b was refined as the pure K-form due to no significant residual peak located around the oxygen atom. The conclusion becomes much clearer based on the difference of Fourier synthesis using the refined structure from which only the tautomeric hydrogen atom is removed. The difference synthesis for structure 1a locates two peaks assigned to two hydrogen atoms, one connected to O and the other to N2 (Fig. 2C). In contrast, the difference synthesis for the structure 1b locates no distinguished residual peak that can be assigned to the hydrogen atom connected to O (Fig. 2D). Hence, the X-ray diffraction can unambiguously and directly display the occurrence of tautomeric transformation of 1 between E-form and K-form isomers in the crystal. This is the first and direct observation of molecule structural changes accompanying

Table 1 Selected bond lengths of 1 (Å)

Compd	O–C7	C7–C8	C8–C9	C9–N2
1a	1.249(5)	1.436(5)	1.381(5)	1.360(5)
1b	1.235(4)	1.440(5)	1.382(5)	1.357(4)

the photochromism of pyrazolones. The X-ray diffraction data have proved that the *E*-form of **1a** coverts into the *K*-form of **1b** after photochromic reaction.

Based on the existence of intramolecular [N4-H···O] (2.695(4) Å, $156(3)^{\circ}$) and intermolecular [S···H–N2'] (3.240(3) Å, 172(4)^{\circ}) hydrogen bonds (Fig. S4B, ESI[†]), we can find convenient channels for transferring protons exist in the crystalline state of pyrazolones. Firstly, an intermediate state thiol form 1a' is established under UV light irradiation (as shown in Scheme 1). The H on N4 atom transfers to S atom by means of intramolecular rearrangement, forming intermolecular [S-H···N2']. One proton subsequently transfers from O atom to N4 atom by the channel of intramolecular [N4···H–O], forming another intramolecular hydrogen bond [N4-H···O]. Another proton transfers from S atom to N2' atom by the channel of intermolecular [S-H···N2'] at the same time, and forms another intermolecular hydrogen bond [S···H-N2']. The processes of intraand intermolecular proton transfer lead to enol-keto photoisomerization.

Photochromic reactions of pyrazolones have been further investigated with IR and XPS spectra, which strongly support the mechanism suggested: transformation from the E-form to the K-form occurs in the materials after UV irradiation. The structure differences between the E-form and the K-form of 1 result in IR and XPS spectra changing clearly (Fig. 3). Under irradiation of 365 nm light, a new sharp band attributed to C=O stretching vibration appears at 1671 cm^{-1} in the IR spectrum of 1 for the formation of the K-form of 1b along with a relative intensity increase of the band at 3220 cm⁻¹ (Fig. 3A). The band of 3220 cm⁻¹ can be ascribed to N2-H vibration in the solid state. Ultraviolet irradiation can activate the transformation of 1 from the E-form to the K-form. While IR spectroscopy is a useful method to study the hydrogen bonded structure,¹⁴ it cannot give definite structure change corresponding to the O-H stretching band of 1. Because the binding energies in the XPS spectra of materials are sensitive to the chemical environment perturbation, the materials were also characterized with XPS for distinguishing the tautormers.15 We have focused our efforts on examining the O1s spectra changes for verifying the photochromic mechanism. The O1s XPS spectra of 1 are shown in Fig. 3B, which can be decomposed into two peaks by curve fitting. The O1s peaks at 531.8 and 532.3 eV can be assigned to oxygen atoms of C-O groups, and the peaks corresponding to binding energies of 529.6 and 530.3 eV to oxygen atoms

B Absorbance 1a 1a ntensity 1b 1b 3320 3500 3000 2500 2000 1500 1000 540 538 536 534 532 530 528 526 Wavenumber / cm Binding Energy / eV

Fig. 3 (A) FT-IR spectra and (B) O1s spectra (XPS) of **1** before and after UV irradiation. The colored lines in (B) show the results of curve fitting.

of C=O groups. The relative amounts of the tautomers can be estimated from the *E*-form/*K*-form isomer ratio of 62:38 for **1a** before irradiation. The *E*-form/*K*-form isomer ratio changed to 40:60 for **1b** after UV irradiation. These results are consistent with X-ray crystallographic analysis. The population of C=O increases along with a decreasing of the C-O population after illumination with UV light. The data indicate that the white *E*-form of **1a** transforms to the yellow *K*-form of **1b** during the photochromic process. The *K*-form exists appreciably in the crystalline state and increases in population after UV light irradiation/heating.

In conclusion, direct observation of structure changes has strongly proved the mechanism of photochromic reaction of pyrazolones in single crystals. The length of the O–C7 bond of white products becomes shorter than that of the yellow products by 0.014 Å. Hence, the X-ray diffraction can unambiguously and directly display the occurrence of the tautomeric transformation between the *E*-form and *K*-form isomers in single crystals of **1**. The IR and XPS results of **1** before and after photo-irradiation are well consistent with those from X-ray crystallographic analyses and further verify the mechanism of photochromic pyrazolones. The photochromic reactions of pyrazolones are due to tautomerization between their *E*-form and *K*-forms accompanied by proton transfer.

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References

- E. Hadjoudis and I. M. Mavridis, *Chem. Soc. Rev.*, 2004, 33, 579–588;
 K. Amimoto and T. Kawato, *J. Photochem. Photobiol.*, *C*, 2005, 6, 207–226.
- H. Dürr, H. Bouas-Laurent, *Photochromism: Molecules and Systems*; Elsevier: Amsterdam, The Netherlands, 1990; S. Kawata and Y. Kawata, *Chem. Rev.*, 2000, **100**, 1777–1788; C. C. Corredor, Z. L. Huang and K. D. Belfield, *Adv. Mater.*, 2006, **18**, 2910–2914; G. Y. Jiang, S. Wang, W. F. Yuan, L. Jiang, Y. L. Song, H. Tian and D. B. Zhu, *Chem. Mater.*, 2006, **18**(2), 235–237.
- Y. Yokoyama, Chem. Rev., 2000, 100, 1717–1739; G. Berkovic, Chem. Rev., 2000, 100, 1741–1753; C. Weber, F. Rustemeyer and H. Dürr, Adv. Mater., 1998, 10, 1348–1351; J. Areephong, T. Kudernac, J. J. D. D. Jong, G. T. Carroll, D. Pantorott, J. Hjelm, W. R. Browne and B. L. Feringa, J. Am. Chem. Soc., 2008, 130, 12850–12851; L. Y. Zhu, W. Wu, M. Q. Zhu, J. J. Han and J. K. Hurst, J. Am. Chem. Soc., 2007, 129, 3524–3526.
- 4 Y. Kishimoto and J. Abe, J. Am. Chem. Soc., 2009, 131, 4227–4229;
 Y. Chen and D. X. Zeng, J. Org. Chem., 2004, 69, 5037–5040;
 R. Siewertsen, H. Neumann, B. Buchheim-Stehn, R. Herges,
 C. Nather, F. Renth and F. Temps, J. Am. Chem. Soc., 2009, 131, 15594–15595.
- K. Uchida, M. Saito, A. Murakami, S. Nakamura and M. Irie, Adv. Mater., 2003, 15, 121–125; T. Tsujioka, M. Kume and M. Irie, J. Photochem. Photobiol., A, 1997, 104, 203–206; R. Pardo, M. Zayat and D. Levy, J. Mater. Chem., 2009, 19, 6756–6760; R. Métivier, S. Badré, R. Méallet-Renault, P. Yu, R. B. Pansu and K. Nakatani, J. Phys. Chem. C, 2009, 113, 11916–11926; S. Z. Xiao, Y. Zou, M. X. Yu, T. Yi, Y. F. Zhou, F. Y. Li and C. H. Huang, Chem. Commun., 2007, 4758–4760; D. Levy, Chem. Mater., 1997, 9, 2666– 2670; J. Whelan, J. T. C. Wojtyk and E. Buncel, Chem. Mater., 2008, 20, 3797–3799.
- M. Irie, Chem. Rev., 2000, 100, 1685–1716; E. Hadjoudis and I. Mavridis, Chem. Soc. Rev., 2004, 33, 579–588; K. Amimoto and T. Kawato, J. Photochem. Photobiol., C, 2005, 6, 207–226; T. Yamada, S. Kobatake, K. Muto and M. Irie, J. Am. Chem. Soc., 2000, 122, 1589–1592; J. Harada, R. Nakajima and K. Ogawa, J. Am. Chem. Soc., 2008, 130, 7085–7091; I. Yildiz, E. Deniz and F. M. Raymo, Chem. Soc. Rev., 2009, 38, 1859–1867.

- 7 J. X. Guo, D. Z. Jia, L. Liu, H. Yuan and F. Li, J. Mater. Chem., 2011, 21, 3210–3215; J. X. Guo, L. Liu, G. F. Liu, D. Z. Jia and X. L. Xie, Org. Lett., 2007, 9, 3989–3992; L. Liu, X. Y. Xie, D. Z. Jia, J. X. Guo and X. L. Xie, J. Org. Chem., 2010, 75, 4742– 4747; J. X. Guo, L. Liu, D. Z. Jia, J. H. Wang and X. L. Xie, J. Phys. Chem. A, 2009, 113(7), 1255–1258.
- 8 H. Lin, D. L. Wu, L. Liu and D. Z. Jia, *THEOCHEM*, 2008, **850**, 32– 37; Y. T. Zhong, L. Liu, G. F. Liu, D. L. Wu, J. X. Guo and D. Z. Jia, *J. Mol. Struct.*, 2008, **889**, 259–264.
- 9 T. Yamada, S. Kobatake, K. Muto and M. Irie, J. Am. Chem. Soc., 2000, **122**, 1589–1592; T. Yamada, K. Muto, S. Kobatake and M. Irie, J. Org. Chem., 2001, **66**, 6164–6168.
- 10 P. Naumov, A. Sekine, H. Uekusa and Y. Ohashi, J. Am. Chem. Soc., 2002, **124**, 8540–8541; J. Harada, H. Uekusa and Y. Ohashi, J. Am. Chem. Soc., 1999, **121**, 5809–5810.
- 11 Crystal data for **1a**: colorless, $C_{24}H_{19}N_5OFSCl$, M = 479.95, monoclinic, $P2_1/c$, a = 12.4255(8), b = 14.4075(8), c = 13.4165(7)Å, $\beta = 107.9890(10)^\circ$, V = 2284.4(2)Å³, Z = 4, $D_c = 1.396$ g cm⁻³, $\mu = 0.294$ mm⁻¹, and T = 293(2) K. Reflections collected/unique

17794/4207 [R(int) = 0.0436]. The refinement converged to R_1 (observed reflections with $I > 2\sigma(I) = 0.0706$, w $R_2 = 0.1866$ and S = 1.097. CCDC 797540.

- 12 Crystal data for **1b**: yellow, $C_{24}H_{19}N_5OFSCl$, M = 479.95, monoclinic, $P2_1/c$, a = 12.4127(16), b = 14.3970(18), c = 13.3934(14) Å, $\beta = 108.020(2)^\circ$, V = 2276.1(5) Å³, Z = 4, $D_c = 1.401$ g cm⁻³, $\mu = 0.295$ mm⁻¹, and T = 293(2) K. Reflections collected/ unique 17943/4200 [*R*(int) = 0.0477]. The refinement converged to R_1 (observed reflections with $I > 2\sigma(I)$) = 0.0666, w $R_2 = 0.1951$ and S = 1.076. CCDC 797541.
- 13 K. Ogawa, Y. Kasahara, Y. Ohtani and J. Harada, J. Am. Chem. Soc., 1998, 120, 7107–7108.
- 14 J. N. Moorthy, P. Mal, R. Natarajan and P. Venugopalan, Org. Lett., 2001, 3, 1579–1582; E. Hadjoudis, A. Rontoyianni, K. Ambroziak, T. Dziembowska and I. M. Mavridis, J. Photochem. Photobiol., A, 2004, 162, 521–530.
- 15 E. Ito, H. Oji, T. Araki, K. Oichi, H. Ishii, Y. Ouchi, T. Ohta, N. Kosugi, Y. Maruyama, Y. Naito, T. Inable and K. Seki, J. Am. Chem. Soc., 1997, 119, 6336–6344.