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Synthesis and Solid-State Photochromism of 1,3-Diphenyl-4-(2-chlorobenzal)-5-hydroxypyrazole 4-Methylthiosemicarbazone

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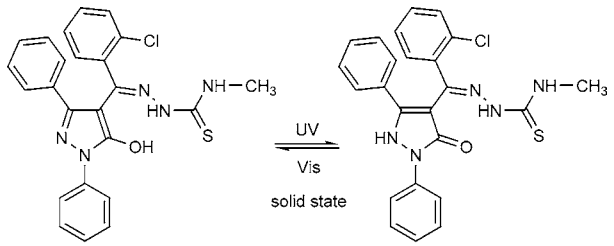
ABSTRACT



A new photochromic compound containing a pyrazole-ring unit, 1,3-diphenyl-4-(2-chlorobenzal)-5-hydroxypyrazole 4-methylthiosemicarbazone, was synthesized. Its structure, photochromic properties, and photochemical kinetics were characterized. The results show that the title compound exhibits reversible enol–keto photoisomerization, excellent photostability, and high fatigue resistance. An intra- and intermolecular proton-transfer mechanism is proposed.

The development of photochromic materials has been an area of intense research in recent years because of their potential applications, such as high-density optical storage media, molecular switching devices, holographic processes, light-controlled enzyme activation, nonlinear-optical materials, etc.[1] A large number of photochromic compounds based on spiropyrans, spiroxazine, dithienylethenes, fulgides, and Schiff bases have been extensively investigated.[2] However, most of them show the reversible photoisomerization only in the solution state. To develop new compounds with photochromic behavor in the solid state is very important for their applications. Pyrazolones and their derivatives are widely used in biological applications,[3] but little information is available on their photochromic properties. In previous studies, we have reported the photochromic properties of a series of 4-acyl pyrazolone thiosemicabazone derivatives in the solid state, and proposed a photochromic mechanism of intermolecular proton transfer through hydrogen bonds based on analyses of their crystal structures.[4] Unfortunately, the reversibility of their photoisomerization reactions is not satisfied and most of them show irreversible behaviors. So the molecular design and synthesis of novel pyrazolone

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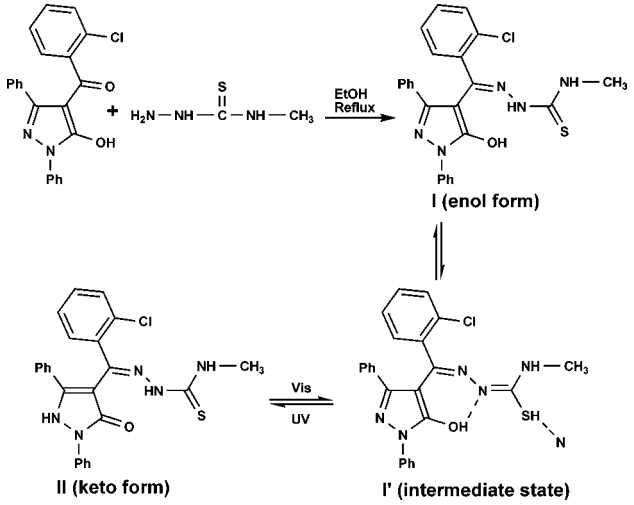
derivatives with excellent photochromic properties has become an active area of extensive research.

In this letter, we synthesized a novel photochromic compound of 1,3-diphenyl-4-(2-chlorobenzal)-5-hydroxy-pyrazole 4-methylthiosemicarbazone (**I**), which undergoes reversible photoisomerization reactions with UV/vis light irradiation in the solid state, and propose a new intra- and intermolecular proton-transfer mechanism.

Scheme 1. Synthesis and Photoisomerization of the Title Compound



Scheme 1 illustrates the synthetic route of the title compound and its photoisomerization from white enol form (**I**) to yellow keto form (**II**) named 1,3-diphenyl-4-(2-chlorobenzal)-5-pyrazolone 4-methylthiosemicarbazone via the intermediate state (**I′**). The chemical composition and structure were confirmed by elemental analysis, ^{1}H NMR, and X-ray single-crystal diffraction analysis. The experimental details and data are available in the Supporting Information.

Figure 1a is the UV absorption spectra of **I** (enol-form) irradiated by 365 nm UV light in the solid state at 298 K

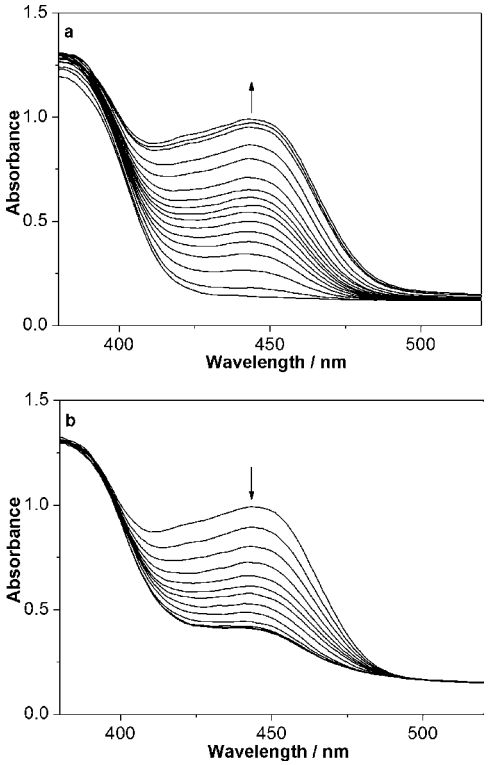


Figure 1. Time-resolved spectra of **I** irradiated by 365 nm UV with interval time of 60 min (a) and **II** iradiated by visible light with interval time of 3 min (b) in the solid state.

for different times. It can be seen that a new band appears between 400 and 500 nm, corresponding to the UV absorption of **II** (keto-form), and its intensity increases with irradiation time. Subsequently, the white **I** gradually changes to the yellow **II**. And it can remain yellow for more than half a year when it is stored in the dark at room temperature, which indicates that the keto form (**II**) is stable in air and retains its coloration memory. Under visible light irradiation (>420 nm), the yellow **II** (keto-form) is bleached back to the white **I** (enol-form); the related time-dependent absorption spectra are shown in Figure 1b. Obviously, the intensity of the band around 400−500 nm gradually decreases, but the original intensity is not fully recovered (the degree of photobleaching is ca. 70% based on their absorption values). However, the bleached powder is irradiated by UV again, it returns to yellow, and its UV absorption intensity approximates that of the first colored state. The reason for this will be studied later.

As shown in Figure 2, the photoisomerization of the title compound can be repeated at least 10 times, which indicates its photoisomerization exhibits excellent photostability and high fatigue resistance. From the viewpoint of application to high-density optical memory media, it is desired to develop photochromic compounds that have light sensitivity in the region between 407 and 532 nm.[5] As mentioned above, the title compound exhibits the maximium absorption of photocolored isomers in the region of 400 to 500 nm, and

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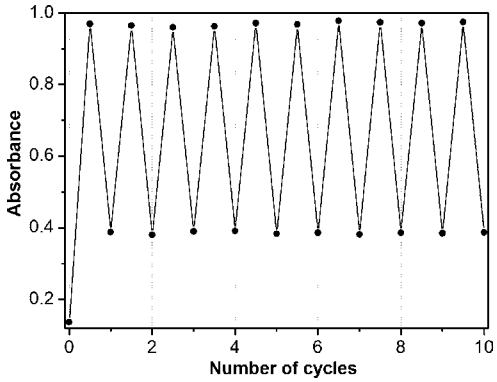

Figure 2. Photoswitching cycles of **I** under the irradiation on and off with alternating 365 nm light and 450 nm visible light.

excellent photostability. It will become a promising candidate for practical applications.

The corresponding first-order rate constants of the reversible photoisomerizations are determined by fitting the experimental data to the following equation,[6]

$$kt = \ln[(A_\infty - A_0)/(A_\infty - A_t)] \quad (1)$$

where A_0, A_∞, A_t are the observed absoption data corresponding to 450 nm wavelength at the time zero, infinite time, and time t of the reaction, respectively. The first-order kinetic curves for enol-to-keto and keto-to-enol isomerizations are shown in Figure 3. The slopes correspond to kinetic rate constants for enol-to-keto ($k_{e-k} = 1.72 \times 10^{-5}$ s^{-1}) and keto-to-enol ($k_{k-e} = 7.31 \times 10^{-4}$ s^{-1}) isomerizations, respectively.

For the analogue compound 1-phenyl-3-methyl-4-(2-chlorobenzal)-5-hydroxypyrazole 4-methylthiosemicarbazone,[7] the kinetic constant of the photoisomerization from the enol-to-keto form is 1.17×10^{-3} s^{-1}, which indicates its photoisomerization reaction is faster than that of the title compound. Furthermore, under the irradiation of 365 nm light, a new aborption band appears at the range of 380−460 nm, which has blue-shift phenomenon in comparison with that of the title compound. The results indicate that the phenyl and methyl groups on the 3-position of pyrazole rings have a significant effect on its photochromic properties. The substitution of the phenyl group instead of the methyl group can not only enhance the molecular electronic conjugation or delocalization, but also increase its steric hindrance obviously, leading to a decrease in the photocoloring rate and the red-shift maxmium absorption band of the title compound.

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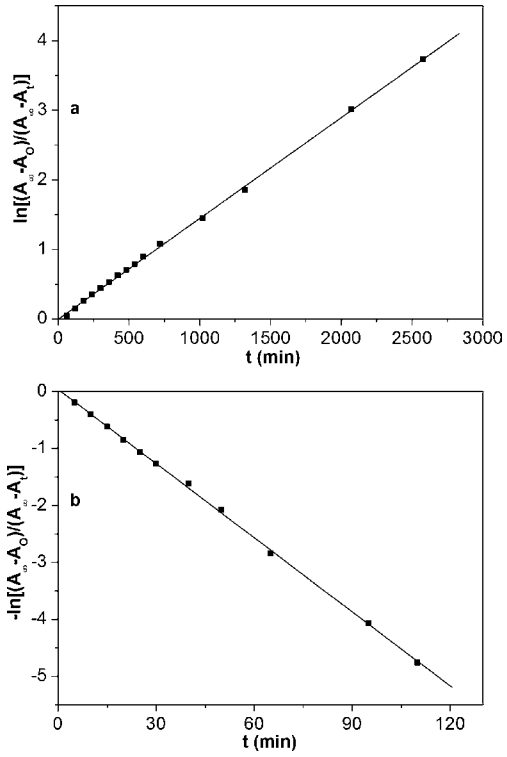

Figure 3. First-order kinetic plots for (a) the photocoloration reaction of **I** under 365 nm light irradiation and (b) the photodecoloration reaction of **II** irradiated by visible light.

To explore the photoisomerization mechanism of the title compound, the crystal structure was identified by using single-crystal X-ray crystallography (see the Supporting Information). Noticeably, the reliable structure data of the white **I** (enol-form**)** are difficult to obtain because its crystal structure (**I)** is inevitably turned into **II** during X-ray measurement. Since the length of the O−C(7) bond is 1.248 Å, which is consistent with the length of the C═O double bond, it can be deduced that the structure of **II** is the keto-form. As shown in Figure 4, molecules stack compactly in an antisymmetric way. There exist intermolecular [N(2)−H···S′] (3.225 Å) and intramolecular [N(4)−H···O] (2.701 Å) hydrogen bonds, which provide a convenient channel to transfer protons. Under UV light irradiation, the intramolecular proton transfers from the O atom to the N(4) atom by the channel of [N(4)···H−O], forming another intramolecular hydrogen bond [N(4)−H···O]. At the same time, the intermolecular proton transfers from the S′ atom to the N(2) atom by the channel of [N(2)···H−S′], forming another intermolecular hydrogen bond [N(2)−H···S′]. Those processes lead to the enol−keto photoisomerization through intra- and intermolecular proton transfer via the intermediate state (**I′**) in Scheme 1.

The photochromic process of the title compound is different from that of Schiff base compounds proposed by Cohen et al.[8] The photocoloration process of Schiff bases such as salicylaldehyde and its derivatives was suggested as the mechanism of intramolecular proton transfer from

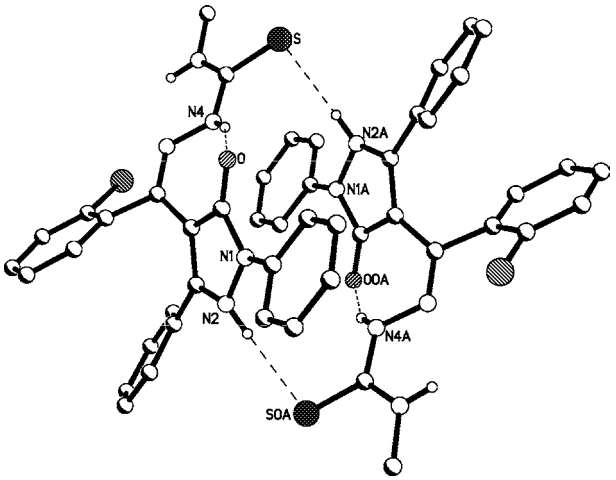

Figure 4. Hydrogen bond connection diagram of **II** (hydrogen atoms of carbon atoms and the disordered part are omitted).

the hydroxylic group to the nitrogen atom in imine (−CH═N−). Since there is no intramolecular hydrogen bond between the O atom and the imine nitrogen atom (N(3)) in the trans-keto form, it is impossible to tansfer a proton between N(3) and O atoms in the title compound. Furthermore, the photochromic process of the title compound is also different from those of other analogous compounds, there is only an intermolecular proton transfer from the O atom of the hydroxyl group to the nitrogen atom of the adjoining molecular pyrazole ring.[4a,b]

To further confirm the above photochromic mechanism, FT-IR spectroscopy is employed to characterize the configurational change during the photochromic transition. As shown in Figure 5, broad absorption bands in the range of 3200−2200 cm^{-1} are observed, which suggests that there exist strong hydrogen bonds in two isomers in the solid state.[9] And a new sharp band appears at 1671 cm^{-1} (curve for **II**), attributed to the C═O stretching vibration. This indicates the formation of the keto-form isomer **II** after irradiation of UV light. Therefore, we can further speculate that the

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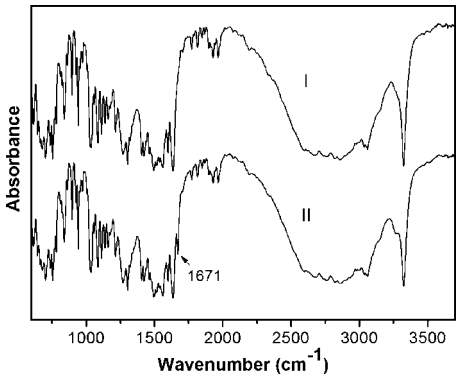

Figure 5. FT-IR spectra of **I** and **II**.

configurational transformation from enol- to keto-form isomers is due to proton transfer via the intra- and intermolecular hydrogen bonds during the photochromic reaction.

In conclusion, a novel photochromic compound containing a pyrazole ring has been synthesized. It exhibits the reversible enol-keto photoisomerization, excellent photostability, and fatigue resistance. The photochomic mechanism is due to the proton transfer via the intra- and intermolecular hydrogen bonds. The results are useful for the design and synthesis of other pyrazolone thiosemicarbazone derivatives with tunable properties.

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Supporting Information Available: Experimental details, elemental analysis, FT-IR, ^{1}H NMR, single-crystal X-ray crystallographic data for the title compound, UV absorption spectra irradiated by 365 nm light in the solid state for different irradiation times, and the first-order kinetic curves for enol to keto photoisomerization of 1-phenyl-3-methyl-4-(2-chlorobenzal)-5-hydroxypyrazole 4-methyl-thiosemicarbazone. This material is available free of charge via the Internet at http://pubs.acs.org.

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