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## Solid-State Photochromic Behavior and Thermal Bleaching Kinetics of Two Novel Pyrazolone Phenylsemicarbazones

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Two novel photochromic compounds, 1,3-diphenyl-4-benzal-5hydroxypyrazole 4-phenylsemicarbazone (**1a**) and 1,3-diphenyl-4-(4-nitrobenzal)-5-hydroxypyrazole 4-phenylsemicarbazone (**2a**), are synthesized and characterized by elemental analysis, mass spectrometry, FTIR spectroscopy, and <sup>1</sup>H NMR spectroscopy. Their properties, including photochromic behavior, fluorescence properties, and thermal bleaching kinetics, are investigated. The results show that the two compounds exhibit improved photochromic performance in coloration and thermal bleaching rates, excellent photostability, high fatigue resist-

## 1. Introduction

Photochromic materials are a well-known class of molecules that change color upon irradiation with light; the photogenerated species can be converted back to the initial species either by heat or by subsequent irradiation with a specific wavelength of light. The main interest in photochromic materials focuses on their applications, including optical waveguides and shutters, optical data storage, and ophthalmic plastic lenses.<sup>[1]</sup> Solid-state photochromism, which is rarely encountered, enables prospective potential applications in information storage,<sup>[2,3]</sup> molecular machines,<sup>[4]</sup> optical switches, displays, sensors,<sup>[5]</sup> and nonlinear optics.<sup>[6]</sup> Appropriate switching rates, particularly the thermal bleaching rate, are indispensable for certain applications, such as optical data processing and light modulators.<sup>[7]</sup> High fatigue resistivity and fast fading kinetics are currently attracting much interest for use in vehicles.<sup>[8]</sup> Due to the wide diversity of the technical applications of photochromic compounds, requirements with respect to their spectral, thermodynamic, and kinetic characteristics are manifold and the synthesis of compounds with desirable properties must be based on the results of investigations into the general relationship between their molecular structures and spectral and kinetic properties. Extensive investigations have been carried on spiropyrans, spiroxazine, dithienylethenes, fulgides, and Schiff bases.<sup>[9]</sup> However, most of them show reversible photochromic behavior only in solution. It is so far rather rare to find single-component solid-state photochromism, whereas solidstate photochromic materials for constructing optical switches are indispensable for practical applications of optical switches. Thus, the development of new compounds with photochromic behavior in the solid state is very important for their applications.

ance, and reversible fluorescence switching properties in the solid state in comparison to reported pyrazolone thiosemicarbazones. The thermal bleaching process obeys first-order kinetics. Bleaching of powders at 130 °C is completed within 90 s for **1b** (the colored isomer of **1a**) and 150 s for **2b** (the colored isomer of **2a**). The activation energy for the thermal bleaching process is determined to be 69 and 95 kJ mol<sup>-1</sup>, with frequency factors of  $9.5 \times 10^7$  and  $9.4 \times 10^{10}$  s<sup>-1</sup> for **1b** and **2b**, respectively.

We have investigated a series of photochromic compounds derived from pyrazolones condensed with thiosemicarbazide derivatives,<sup>[10]</sup> but the majority show irreversible photoisomerization behavior. Thus, many efforts have been dedicated to designing the structures by changing the substituent groups at the 3- or 4-position on the pyrazolone ring and using other thiosemicarbazone derivatives; for example, 1-phenyl-3methyl-4-(2-fluorobenzal)-5-hydroxypyrazole 4-methylthiosemicarbazone/4-ethylthiosemicarbazone<sup>[10a]</sup> and 1,3-diphenyl-4-(2-4-methylthiosemicarbazochlorobenzal)-5-hydroxypyrazole ne,<sup>[10b]</sup> which exhibit reversible photoisomerization in the solid state due to the transformation between an enol form and a keto form through hydrogen bonds upon irradiation with light or by heating. Unfortunately, their performances are unsatisfactory, so their derivatives need to be further developed by structural modification to improve the photochromic properties. Lately, a kind of semicarbazone derivative, 1,3-diphenyl-4-(3-bromobenzal)-5-hydroxypyrazole 4-phenylsemicarbazone,[11] has been synthesized successfully by introducing the phenylsemicarbazide unit, which exhibits excellent photostability, high

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fatigue resistance, and good reversible photochromic and fluorescence properties in the solid state in comparison to those of pyrazolone thiosemicarbazones reported previously.<sup>[10]</sup> All these results gave us encouragement to make novel photochromic compounds. In addition, we previously studied the steady-state photochromic properties of pyrazolone thiosemicarbazones in the solid state, but rarely paid attention to kinetic studies on the thermal bleaching reactions (rate constants and activation energies) and the activation parameters  $(\Delta H^{\neq}, \Delta S^{\neq}, \text{ and } \Delta G^{\neq})$ , which may open a new pathway for the design of compounds with outstanding photochromic properties.

Herein, we describe the synthesis and photochromic behavior of two newly designed pyrazolone 4-phenylsemicarbazone derivatives (Scheme 1). Compared with previously reported pyrazolone thiosemicarbazones, the two compounds exhibit an improved photochromic performance in coloration and decoloration rates as well as high fatigue resistivity, in particular rapid thermal bleaching kinetics in the solid state. Moreover, the effect of substituents on the phenyl group of the 4-position of the pyrazolone ring on the thermal bleaching kinetics is discussed.

### 2. Results and Discussion

# 2.1. Photochromic and Fluorescence Properties in the Solid State

The absorption spectra of 1a and 2a induced by photoirradiation at room temperature in the solid state are shown in Figure 1. Upon irradiation by 365 nm light, the white powders 1a change to yellow due to photoinduced proton transfer from one moiety to another. At the same time, a new broad band in the range of 370-450 nm appears and its intensity increases with irradiation time (Figure 1A). After 40 min of irradiation, no more evolution in the spectra is observed, which indicates that the keto form  $(\mathbf{1} \mathbf{b})$  is obtained.<sup>[12,13]</sup> The proton transfer and configuration rearrangement of the  $\pi$  electrons lead to significant absorption spectral changes in the solid state.<sup>[14]</sup> However, the yellow keto form (1 b) can revert slowly to the white enol form (1 a) in the dark at room temperature. Upon heating at 120°C, the yellow powders rapidly turn to white, which is accompanied by the disappearance of the absorption band in the range of 370-450 nm. Obviously, the





Figure 1. Absorption spectra of 1a and 2a under irradiation by 365 nm light, and thermal bleaching spectra of 1b and 2b by heating at  $120 \,^{\circ}$ C in the solid state. A) Absorption spectra of 1a (0, 10, 20, 40 min). B) Absorption spectra of 2a (0, 10, 36, 55, 113, 158, 208, 223 min). Insets: first-order kinetic plots for the photocoloration reaction of 1a and 2a under 365 nm light.

sample undergoes a complete reverse transformation from the keto form (1 b) to the enol form (1 a). When the bleached powders are re-exposed to UV light, they turn yellow again; the absorption intensity is approximately that of the first colored state. The photochemical process exhibits good reversibility.

Similarly, upon irradiation with 365 nm light, pale yellow powders **2a** turned yellow and the maximum absorption ap-

peared at 460 nm as the keto form (**2b**) was generated (Figure 1 B). Additionally, when the sample was put in the dark or even exposed to light for more than half a year at room temperature, no changes in its UV spectra were observed, which indicates that the keto form is very stable and retains its coloration memory for a rather long time. However, the yellow material (keto form, **2b**) reverts to pale



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yellow (enol form, **2a**) by heating. Compared with that of **1b**, the absorption maximum of **2b** has a red-shift phenomenon due to the introduction of the nitro substituent on the phenyl group of the 4-position of the pyrazolone ring, which indicates that substituents on this phenyl group have a significant effect on the photochromic properties.

The corresponding first-order rate constant of the photoisomerization was determined by fitting the experimental data to Equation (1):<sup>[15]</sup>

$$kt = \ln[(A_{\infty} - A_0)/(A_{\infty} - A_t)]$$
<sup>(1)</sup>

where  $A_0$ ,  $A_v$  and  $A_\infty$  are the observed data corresponding to 400 and 460 nm at time zero, time *t*, and infinite time of the reaction, respectively; *k* represents the photocoloration rate constant. The photocoloring process is fitted to a first-order reaction, and the kinetic constant *k* is  $7.15 \times 10^{-4} \text{ s}^{-1}$  for **1a** and  $1.45 \times 10^{-4} \text{ s}^{-1}$  for **2a** from the kinetic plot in the inset of Figure 1A and B, respectively. Obviously, the photocoloring rate of **1a** is five times faster than that of **2a**.

For the previously reported compound 1,3-diphenyl-4-(2chlorobenzal)-5-hydroxypyrazole 4-methylthiosemicarbazone,<sup>[10b]</sup> the kinetic constant of the enol-to-keto photoisomerization is  $1.72 \times 10^{-5}$  s<sup>-1</sup>, which indicates that its photoisomerization reaction is slower than that of 1 a. Furthermore, under irradiation by 365 nm light, a new absorption band appears in the range of 400-500 nm, which has a red-shift phenomenon in comparison with that of 1b. The results indicate that the oxygen atom on the side chain and the phenyl group at the terminal have a significant effect on the photochromic properties. The incorporation of the phenylsemicarbazide leads to the formation of a novel system of pyrazolone phenylsemicarbazone, which enhances the molecular electronic conjugation, thereby resulting in an increase of the photocoloring rate. However, for 1,3-diphenyl-4-(3-bromobenzal)-5-hydroxypyrazole 4-phenylsemicarbazone (DP3BrBP-PSC),<sup>[11]</sup> the kinetic constant of the enol-to-keto photoisomerization is  $1.13 \times 10^{-3} \text{ s}^{-1}$ , which indicates that its photoisomerization reaction is faster than that of 1a and 2a. These results further confirm that the substituents on the phenyl group of the 4-position of the pyrazolone ring have a significant effect on the photochromic properties. The substituent Br increases the rate of photoisomerization, but the NO2 group decreases the rate in comparison to 1a.

For practical applications as photochromic materials, it is interesting to investigate the reversible photochromic behavior in the solid state. As shown in Figure 2, photoisomerization reversible cycle experiments of **1** and **2** were performed. There was no significant degradation after 15 or 10 cycles for **1** and **2**, respectively. However, the fatigue resistance of **1** is better than that of **2**, which may be attributed to the substituent effect. These results indicate that the photochromism of pyrazolones **1** and **2** exhibits good reversibility, excellent photostability, and high fatigue resistance. Thus, they may be promising candidates for optoelectronic applications, such as high-destiny three-dimensional optical recording media, optical switches, and color displays.<sup>[16]</sup>



Figure 2. Photochromic cycles under irradiation by 365 nm light and heating at 120  $^{\circ}$ C of 1 and 2 in the solid state.

We further investigated the fluorescence properties of the two compounds during their photochromic reaction in the solid state, as shown in Figure 3. A characteristic fluorescence band for the enol form 1 a was observed at 360 nm by 250 nm excitation. The intensity decreased gradually with continuous irradiation by 365 nm light, and after about 30 min it stayed constant, which indicates that the white enol form (1 a) had changed to the yellow keto form (1 b). The fluorescence intensity could be returned fully to the initial state after heating at 120°C. A reversible fluorescence switch was realized along with the photochromic reaction. Compound 2a showed a similar emission spectrum under the irradiation by 365 nm light when excited at 320 nm; a fluorescence band was observed at 460 nm, its intensity decreased gradually with irradiation time, and the keto form 2b was obtained after irradiation for 66 min. Furthermore, it was found that the fluorescence peak of 1a exhibits an obvious blue shift by as much as 100 nm in comparison to 2a, which shows clearly that the substituent on the phenyl group of the 4-position of the pyrazolone ring has a significant effect on the position of the emission peak.





Figure 3. Fluorescence changes of 1a (excited at 250 nm) and 2a (excited at 320 nm) under irradiation by 365 nm light.

#### 2.2. Thermal Bleaching Reactivity

Before performing the measurements, the powders 1a/2a were irradiated with 365 nm light for a sufficient amount of time so that they changed to 1b/2b. Then we investigated the thermal bleaching of 1b and 2b at various temperatures. Figure 4 shows the decay curves of the absorbance at 400 (1b) and 460 nm (2b) in the temperature range from 90 to 130 °C. It takes nearly 600 and 1500 s to completely decolor 1b and 2b at 90 °C, respectively, whereas the decoloring was accelerated with an increase of temperature. Complete decay took nearly 90 and 150 s at 130 °C for 1b and 2b, respectively. Thus the temperature has a direct effect on the bleaching process.

To gain more insight into the corresponding photochromism,<sup>[15]</sup> thermal bleaching kinetic rate constants can be determined from the plot of  $\ln[(A_{\infty}-A_0)/(A_{\infty}-A_t)]$  against time (t). The first-order kinetic curves are shown in Figure 5. The firstorder rate constants (k) of  $1\mathbf{b} \rightarrow 1\mathbf{a}$  and  $2\mathbf{b} \rightarrow 2\mathbf{a}$  are summarized in Table 1. The rate constant k was evaluated to be  $1.02 \times$  $10^{-1}$  and  $4.24 \times 10^{-2} \text{ s}^{-1}$  at  $130 \,^{\circ}\text{C}$  for  $1\mathbf{b}$  and  $2\mathbf{b}$ , respectively. The results indicate that the photochromic compound with a nitro substituent ( $2\mathbf{b}$ ) shows a slower bleaching rate than that of the unsubstituted one ( $1\mathbf{b}$ ). Thus, rate constants are strongly dependent on the structure of the compounds. It can be



Figure 4. Decay profiles of  $1\,b$  and  $2\,b,$  monitored at 400 and 460 nm in the solid state at 90, 100, 110, and 130  $^\circ\text{C}.$ 

<b>Table 1.</b> First-order rate constants for $1b \rightarrow 1a$ (k) and $2b \rightarrow 2a$ (k) estimated from the decay curves.					
7 [K]	<b>1 b</b> → <b>1 a</b> k [s <sup>-1</sup> ]	$2b \rightarrow 2a$ k [s <sup>-1</sup> ]			
363	1.03×10 <sup>-2</sup>	1.94×10 <sup>-3</sup>			
373	$2.39 \times 10^{-2}$	$3.83 \times 10^{-3}$			
383	4.78×10 <sup>-2</sup>	$1.01 \times 10^{-2}$			
403	1.02×10 <sup>-1</sup>	4.24×10 <sup>-2</sup>			

seen that the substituent may play an important role in determining the thermal bleaching rates.

We then determined the activation energy of the bleaching process by applying the Arrhenius equation in the 363–403 K temperature intervals [Eq. (2)]:

$$\ln k = \ln A \frac{E_{\rm a}}{RT} \tag{2}$$

Figure 6 shows the temperature dependence of the rate constant for the thermal bleaching reaction of 1b and 2b. Taking *k* as the rate constant for the reverse reaction, an Arrhenius plot of  $\ln k$  as a function of 1/T reveals a straight line. Con-

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Figure 5. First-order kinetic plots for the thermal bleaching reaction of  $1\,b\!\rightarrow\!1\,a$  and  $2\,b\!\rightarrow\!2\,a$  at various temperatures in the solid state.

sequently, the activation energy ( $E_a$ ) and frequency factor (A) were determined:  $E_a = 69 \text{ kJ mol}^{-1}$  and  $A = 9.5 \times 10^7 \text{ s}^{-1}$  for **1 b**;  $E_a = 95 \text{ kJ mol}^{-1}$  and  $A = 9.4 \times 10^{10} \text{ s}^{-1}$  for **2 b**. Note that the frequency factor of **1 b** is smaller than that of **2 b** by more than three orders of magnitude. The relatively small frequency factor implies that the reverse reaction involves specific reorientation and a large reduction of the entropy factor.<sup>[17]</sup> The decrease in  $E_a$  values enhanced the thermal back reaction, in other words, the slower bleaching rate is due to the slightly higher activation energy.

To further analyze the reactions, by using the Eyring equation the activation parameters of the thermal back reactions and the enthalpies and entropies of activation ( $\Delta H^{\neq}$  and  $\Delta S^{\neq}$ , respectively) were evaluated in the temperature range from 90 to 130 °C [Eq. (3)]:

$$\ln\frac{k}{T} = -\frac{\Delta H^{\neq}}{R}\frac{1}{T} + \ln\frac{k_{\rm B}}{h} + \frac{\Delta S^{\neq}}{R}$$
(3)

As shown in Figure 7, both Eyring plots show an excellent straight line; the  $\Delta H^{\neq}$  and  $\Delta S^{\neq}$  values from standard least-squares analysis of the Eyring plots are summarized in Table 2. The activation free energy barrier is calculated from  $\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$ . From Table 2, it can be seen that  $\Delta H^{\neq}$  for





Figure 6. Arrhenius plot of the thermal bleaching rate constant of  $1\,b\!\rightarrow\!1\,a$  and  $2\,b\!\rightarrow\!2\,a.$ 

Table 2. Thermodynamic parameters for the thermal bleaching process in the solid state.						
Compound	$\Delta H^{\neq}$ [kJ mol <sup>-1</sup> ]	$\Delta S^{\neq}_{\rm 403K} \ [\rm JK^{-1}mol^{-1}]$	$\Delta G^{\neq}_{ m 403K}$ [kJ mol <sup>-1</sup> ]			
1 b→1 a 2 b→2 a	66 92	102 45	107 110			

**1 b** is lower than that for **2 b**, whereas there is a very significant decrease of  $\Delta S^{\neq}$  for **1 b** relative to **2 b**.

The kinetic parameters of the thermal bleaching, determined in the appropriate temperature range for each compound, were satisfactorily fitted to Arrhenius and Eyring relationships, which allowed kinetic (rate constants and activation energies) and activation parameters ( $\Delta H^{\neq}$ ,  $\Delta S^{\neq}$ , and  $\Delta G^{\neq}$ ) of the thermal reactions to be determined. These parameters are significantly different for the two compounds. The nitro substituent on the phenyl group of the 4-position of the pyrazolone ring increases both the activation energy and the frequency factors of the thermal bleaching reaction due to its strong electron-withdrawing properties.



Figure 7. Eyring plots for the thermal bleaching reaction over a temperature ranging from 363 to 403 K.

### 3. Conclusions

Two novel pyrazolones (1 and 2) have been synthesized successfully by introducing a phenylsemicarbazide unit. They show reversible photoisomerization upon irradiation by UV light and heating, excellent photostability, high fatigue resistance, and reversible fluorescence properties in the solid state. Additionally, based on the kinetics of the thermal bleaching reactions, the rate constants, activation energies, and activation parameters ( $\Delta H^{\neq}$ ,  $\Delta S^{\neq}$ , and  $\Delta G^{\neq}$ ) are obtained. The results indicate that the nitro substituent on the phenyl group of the 4position of the pyrazolone ring increases both the activation energy and the frequency factors of the thermal bleaching reaction, thereby leading to a decrease in the photocoloring rate, especially in the thermal bleaching rates, and the red-shift maximum absorption band due to a strong electron-withdrawing effect. The findings may open a new pathway for the design of compounds with outstanding photochromic properties.

#### **Experimental Section**

Experimental Measurements: UV/Vis spectra were recorded on a Hitachi UV-3010 spectrometer equipped with an integrating sphere accessory and a homemade heating accessory. Excitation light (365 nm, 1579 mW cm<sup>-2</sup> on the sample) was applied with a ZF-8 ultraviolet analysis instrument; the reflective filter size was 200 × 80 mm<sup>2</sup> and the distance between sample and light source was 15 cm. Fluorescence spectra were obtained using a Hitachi F-4500 fluorescence spectrophotometer. FTIR spectra were obtained on a Bruker VERTEX-70 spectrometer with the samples as KBr pellets. <sup>1</sup>H NMR spectra were recorded on an Inova-400 NMR spectrometer with [D<sub>6</sub>]DMSO as the solvent and TMS as internal standard. The mass spectra were determined with an HP 1100 liquid chromatograph-mass spectrometer. Elemental analysis was performed with a FlashEA 1112 elemental analyzer. Melting points (uncorrected) were determined with a TECH X-6 melting point apparatus. Powders for testing photochromic properties were directly obtained from the synthesis without any further processing.

Materials: 4-Phenylsemicarbazide (PSC), 4-nitrobenzoyl chloride, and benzoyl chloride were purchased from Aldrich Company, USA. All other chemicals and solvents were purchased from commercial suppliers and used as received without additional purification. 1,3-Diphenyl-5-pyrazolone (DPP),<sup>[18]</sup> 1,3-diphenyl-4-benzoyl-5-hydroxy-pyrazole (DPBP), and 1,3-diphenyl-4-(4-nitrobenzoyl)-5- hydroxypyr-azole (DP4NO<sub>2</sub>BP)<sup>[19]</sup> were synthesized according to the literature.

Synthesis of 1,3-Diphenyl-4-benzal-5-hydroxypyrazole 4-Phenylsemicarbazone (1): A mixture of DPBP (3 mmol) and PSC (3 mmol) in EtOH (20 mL) solution, containing a few drops of glacial acetic acid, was stirred for 6 h at 80 °C in an oil bath. After cooling to room temperature, white powders were obtained. The crude product was filtered and purified by recrystallization using EtOH. Yield: 84%; m.p. 196.7–198.5 °C; <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 11.900 (1H, Pz-OH), 9.737 (1H, N-H), 9.102 (1H, N-H), 7.950–6.977 ppm (20H, phenyl ring); IR (KBr):  $\tilde{\nu}$  = 3343, 3331 (N–H), 1655 (C=O), 1599 (C= N), 1556, 1450 (phenyl ring), 1509, 1394 cm<sup>-1</sup> (pyrazole ring); MS: [M + H]<sup>+</sup>: calcd: 474.19; found: 474.2; elemental analysis calcd (%) for C<sub>29</sub>H<sub>23</sub>N<sub>5</sub>O<sub>2</sub>: C 73.37, H 4.79, N 14.81; found C 73.59, H 4.90, N 14.79.

Synthesis of 1,3-Diphenyl-4-(4-nitrobenzal)-5-hydroxypyrazole 4-Phenylsemicarbazone (**2**): Compound **2** was synthesized by the same method as **1**. Yield: 78%; m.p. 215.4–217.0°C; <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 12.134 (1 H, Pz-OH), 10.119 (1 H, N-H), 9.217 (1 H, N-H), 8.203–7.004 ppm (19 H, phenyl ring); IR (KBr):  $\tilde{\nu}$  = 3364, 3342 (N–H), 1649 (C=O), 1600 (C=N), 1556, 1454 (phenyl ring), 1523, 1348 cm<sup>-1</sup> (pyrazole ring); MS: [*M*+H]<sup>+</sup>: calcd: 519.17; found: 519.0; elemental analysis calcd (%) for C<sub>29</sub>H<sub>22</sub>N<sub>6</sub>O<sub>4</sub>: C 67.17, H 4.28, N 16.21; found: C 67.28, H 4.34, N 16.16.

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