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Synthesis and Properties of a Novel Photochromic Compound with Modulated Fluorescence in the Solid State

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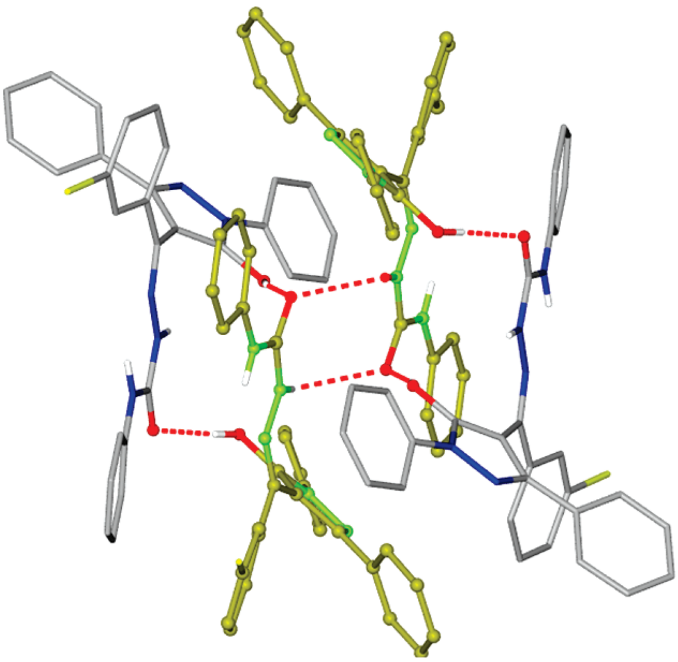

A new photochromic compound, 1,3-diphenyl-4-(3-bromobenzal)-5-hydroxypyrazole 4-phenylsemicarbazone (DP3BrBP-PSC), has been prepared. Its photochromic and thermobleaching behavior, crystal structure, and fluorescent property have been investigated in detail. The results show that the compound exhibits reversible enol−keto photoisomerization due to the intermolecular double-proton transfer, excellent photostability, high fatigue resistance, and remarkable fluorescence.

Introduction

On the basis of reversible changes in color and other properties such as fluorescence, refractive index, oxidation/reduction potential, magnetic properties, and electron transfer, or structural features during irradiation, various types of photochromic compounds have been so far developed[1] that have numerous applications in optical data storage materials, molecular switches, photochromic plastic lenses, self-developing photography, displays, biosensors, nonlinear optical materials,

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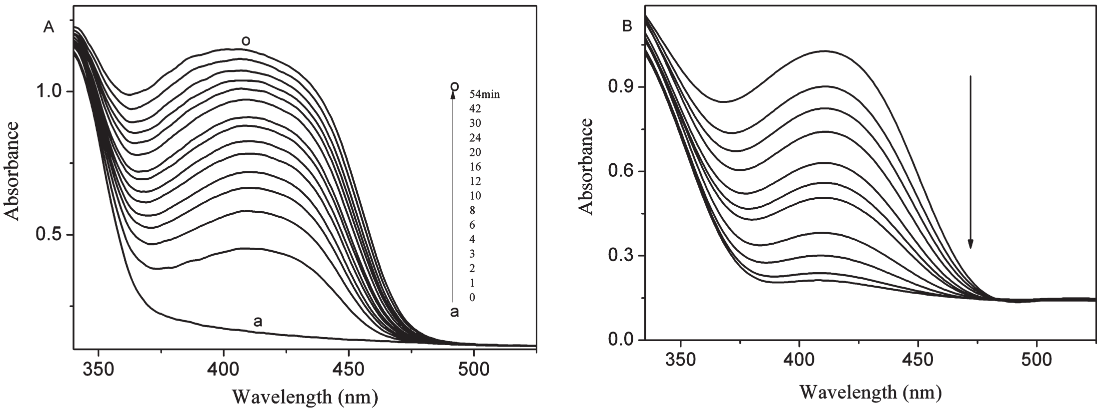

FIGURE 1. (A) UV−vis spectra of white DP3BrBP-PSC powders and (B) thermobleaching spectra of yellow DP3BrBP-PSC powders by heating at 110 °C; heating time interval 8 min in a constant temperature oven.

holography, etc.[2] In particular, reversible photochromic compounds with modulated fluorescence are of potential interest for molecular electronics, fluorescent switches, and optical memory device industries because of their fast response and high sensitivity.[3] Generally, complex systems with photochromic and fluorescent molecules and single molecules incorporating the photochromic and fluorescent functional groups have been reported,[4] and most of them have the two behaviors only in the solution. However, simple molecules integrating both photochromic and fluorescent functions have rarely been reported in the solid state. Therefore, exploiting some novel photochromic compounds with fluorescence in the solid state is desirable.

Many thiosemicarbazones derived from 4-acyl pyrazolones with photoisomerization properties have been systemically studied in our laboratory.[5] Although they can offer an enormous structural diversity and tunable photoisomerization properties, most of the pyrazolone thiosemicarbazones display irreversible photochromic behavior in the solid state. To overcome the disadvantage, many efforts have been dedicated to design the structure by changing the substituted groups at the 3- or 4-position on the pyrazolone ring and using other thiosemicarbazone derivatives. The results indicate that 1,3-diphenyl-4-(2-chlorobenzal)-5-hydroxypyrazole 4-methylthiosemicarbazone (DP2ClBP-MTSC) has reversible photochromism,[5d] but this compound displays slow response to UV and visible light. So its derivatives need to be further developed by structural modification in order to improve the photochromic properties. Now, a novel photochromic compound, 1,3-diphenyl-4-(3-bromobenzal)-5-hydroxypyrazole 4-phenylsemicarbazone (DP3BrBP-PSC), was prepared by the incorporation of oxygen atom in the side chain, which is different from the pyrazolone thiosemicarbazones reported previously.[5] It belongs to the semicarbazone derivative, which exhibits quick response speed to UV light and heating, excellent photostability, high fatigue resistance, and good reversible photochromic and fluorescent properties in the solid state. Interestingly, 1-phenyl-3-methyl-4-(3-bromobenzal)-5-hydroxypyrazole 4-phenylsemicarbazone (PM3BrBP-PSC) was obtained by the methyl group instead of the phenyl group at the 3-position on the pyrazolone-ring of DP3BrBP-PSC, which does not show the photochromic property in the solid state. Compared with the structures of the two compounds, a reasonable photochromic mechanism of DP3BrBP-PSC is proposed based on the reversible enol−keto photoisomerization by the intermolecular double-proton transfer.

Results and Discussion

Photochromic and Thermal Bleaching Properties in the Solid State. The UV−vis spectra for DP3BrBP-PSC powders upon the irradiation of 365 nm light at room temperature (25 °C) and under heating at 110 °C are recorded and are shown in Figure 1. When they were irradiated by 365 nm UV light, the white powders (I) changed to yellow. From Figure 1A, it can be found that a new peak at around 355−480 nm appears, and its intensity increases with the irradiation continuation. The results indicate that the photoisomerization from enol form (I) to keto form (II) occurs in the solid state during the irradiation (Scheme 1). The striking feature is due to the structural change and the configuration rearrangement of the π-electrons.[6] Moreover, the white powders are rather sensitive to light and even turn yellow upon irradiation of sunlight for several minutes, and the colored form can be kept for over three months in the dark,

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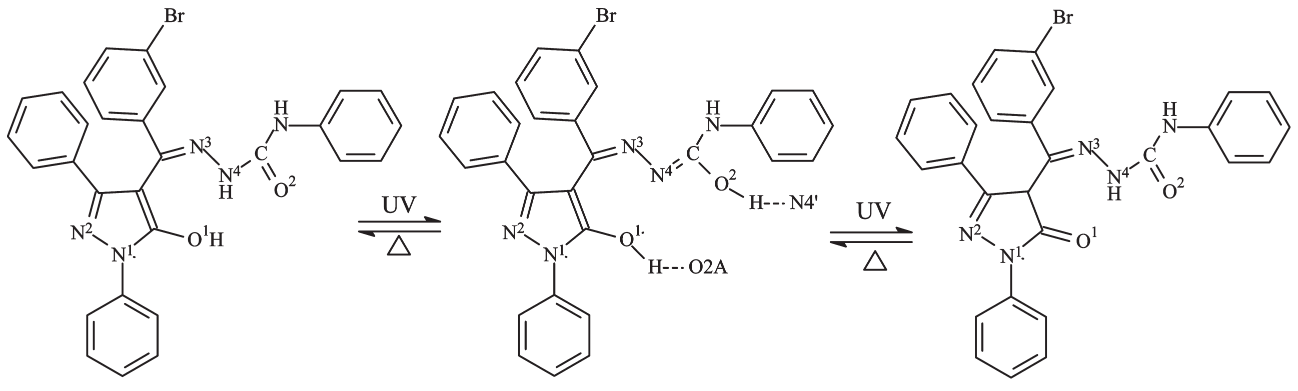
SCHEME 1. Photochromic Reaction of DP3BrBP-PSC



I (enol form)

I' (intermediate state)

II (keto form)

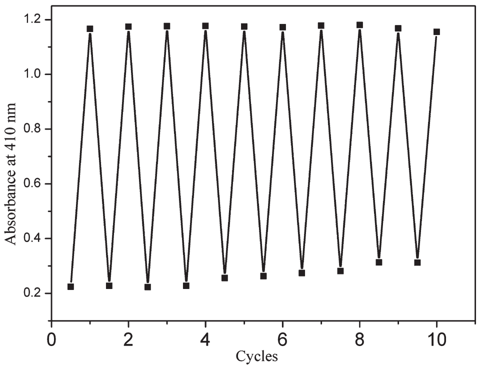


FIGURE 2. Photoswitching cycles of DP3BrBP-PSC powders during alternating irradiation of 365 nm light and heating at 110 °C.

which indicates that the colored DP3BrBP-PSC is very stable in air and retained its coloration memory for a long time.

However, the yellow powders return white when they were heated at 110 °C in a constant temperature oven for several minutes, which was accompanied by the disappearance of the band at around 355−480 nm (Figure 1B). Obviously, it undergoes a complete reverse transformation from keto form (II) to enol form (I). Then, when the bleached powders are irradiated by UV light, they turn yellow again, and the UV−vis absorption intensity approximates that of the first colored state. The photochromic process between the white form and the yellow form can be repeated at least 10 times with a little change of absorbance (Figure 2), which indicates the photochromism of DP3BrBP-PSC exhibits good reversibility and remarkable fatigue resistance. The results show that DP3BrBP-PSC can be regarded as a promising candidate for optoelectronic applications, such as high-density three-dimensional optical recording media, optical switches, color displays, etc.[7]

It is noteworthy that 1-phenyl-3-methyl-4-(3-bromobenzal)-5-hydroxypyrazole 4-phenylsemicarbazone (PM3BrBP-PSC) has no photochromic properties when the phenyl on the 3-position of pyrazolone-ring of DP3BrBP-PSC is replaced with the methyl. Generally, the color and the absorption band changes induced by UV light mainly depend on the π-conjugated length in the molecular structure.[8] The phenyl on the 3-position of the pyrazole-ring is very beneficial to form the extended π-conjugated system, which is one reason why the DP3BrBP-PSC exhibits photochromic properties and PM3BrBP-PSC does not. At the same time, the experimental results also demonstrate that the photochromic performance of pyrazolone phenylsemicarbazones is strongly dependent on the nature of the aryl groups in the side chain because the compound obtained by the phenylsemicarbazide part of DP3BrBP-PSC replaced with semicarbazide (SC) has no photochormic properties.

Kinetics of Photoisomerization. The corresponding first-order rate constant of the reversible photochromic compound is determined by fitting the experimental data to the following equation:[9]

$$k_1 t = \ln[(A_\infty - A_0)/(A_\infty - A_t)] \qquad (1)$$

where k is the first-order rate constant, and A_0, A_∞, and A_t are the observed absorbance measured at the beginning, end, and time t, respectively. All absorbances are collected at the wavelength of 410 nm, where it is the maximum of the optical density. The first-order kinetic curves for the photocoloring and thermal bleaching isomerizations are shown in Figure 3. On the basis of the slopes, kinetic rate constants for the photocoloring and thermal bleaching isomerizations are $k_{\mathrm{e-k}} = 1.127 \times 10^{-3}\ \mathrm{s}^{-1}$ (from the enol to the keto) and $k_{\mathrm{k-e}} = 3.900 \times 10^{-4}\ \mathrm{s}^{-1}$ (from the keto to the enol), respectively.

For the previously reported compound 1,3-diphenyl-4-(2-chlorobenzal)-5-hydroxypyrazole 4-methylthiosemicarbazone,[5d] the kinetic constant of the enol-to-keto photoisomerization is $1.72 \times 10^{-5}\ \mathrm{s}^{-1}$, which indicates its photoisomerization reaction is slower than that of DP3BrBP-PSC. Furthermore, under the irradiation of 365 nm light, a new absorption band appears in the range of 400−500 nm, which has the red-shift phenomenon in comparison with that of DP3BrBP-PSC. The results indicate that the oxygen atom on the side chain and the phenyl at the terminal have a significant effect on its photochromic properties. The substitution of the phenylsemicarbazide instead of thiosemicarbazide leads to the formation

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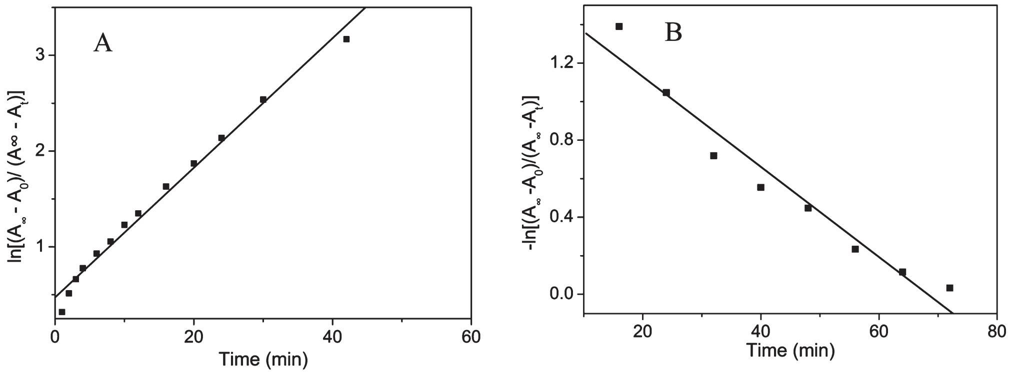

FIGURE 3. First-order kinetic plots for the photocoloration reaction of white DP3BrBP-PSC powders under 365 nm light (A) and the thermobleaching reaction of yellow DP3BrBP-PSC powders by heating at 110 °C (B).

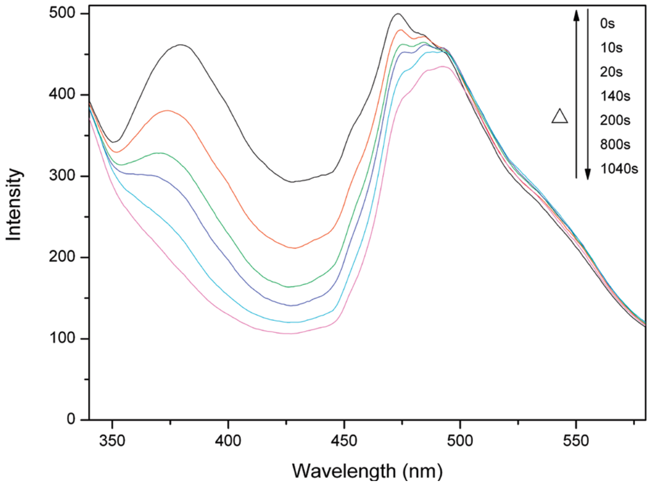

FIGURE 4. Fluorescence emission spectra of DP3BrBP-PSC powders under 365 nm irradiation at room temperature and by heating at 110 °C (excited at 310 nm).

of a novel system of pyrazolone phenylsemicarbazone, which enhances the molecular electronic conjugation, resulting in an increase of the photocoloring rate.

Modulated Fluorescence Properties. Fluorescent properties are useful not only in optoelectronics, but also for digital photoswitching of fluorescence.[10] The proton transfer and the configuration rearrangement of the π-electrons lead to large absorbance or emission spectral changes. In this work, the fluorescent properties of DP3BrBP-PSC powders were studied. As shown in Figure 4, it can be seen that the emission bands of the white powders as enol form (I) appear at 380 and 473 nm after being excited at 310 nm, their intensity gradually decreased with irradiation of 365 nm light. Finally, the emission band at 380 nm is efficiently quenched by the intramolecular energy transfer when the white enol form (I) is changed to the yellow keto form (II) upon UV light irradiation. Subsequently, heating at 110 °C regenerates the white enol form, and restores the original emission spectra, which further indicates that DP3BrBP-PSC can be used in the fluorescent switches.

Crystallographic Explanation and Mechanism of Photochromism. Crystallographic data and selected bond lengths of DP3BrBP-PSC and PM3BrBP-PSC are displayed in Tables 1 and 2 in the Supporting Information, respectively. Figure 5 gives the molecular structures of the two compounds. For DP3BrBP-PSC (Figure 5A), it is observed that there are two crystallographically independent molecules in an asymmetric structure unit, but the corresponding bond lengths in the two molecules are nearly similar (Table 2 in the SI). The bond distances of C7−O1 in the two molecules are 1.354(8) and 1.326(8) Å, respectively, which exhibits the characteristic of the C−O single bond. However, the C23−O2 bond lengths are 1.243(8) and 1.265(7) Å, which belongs to the C=O double bond. These results indicate that the pyrazolone part exists in enol form and the phethylsemicarbazide moiety still exists in keto form. In other words, the compound DP3BrBP-PSC belongs to the enol form isomer (I) as shown in Scheme 1 in the crystal state. When the phenyl at the 3-position on the pyrazolone-ring for DP3BrBP-PSC is exchanged with the methyl, the crystal structure of the formed compound PM3BrBP-PSC (Figure 5B) has a similar phenomenon in comparison with DP3BrBP-PSC. The C7−O1 bond length [1.315(7) Å] is close to that of the C−O single bond, which indicates PM3BrBP-PSC also exists in the enol form in the crystal state. Furthermore, as shown in Table 2 in the SI, all the other bond lengths possess a partial double bond and single bond character, which suggests a delocalized π-electronic system throughout the pyrazolone ring and the phenylsemicarbazide moiety. Interestingly, the structures of the two compounds are different from those of pyrazolone thiosemicarbazides with photochromic properties,[5] all of which are stable as the keto form in the crystal state.

For two crystallographically independent molecules of DP3BrBP-PSC, there are similar bond lengths and bond angles, but the obvious difference is the orientation of the two molecules. From Table 3 in the Supporting Information it can be found that the dihedral angles of the pyrazole-ring (I) and the phenyl rings (III and IV) at the 3- and 4-positions of the pyrazole-ring are 26.2° and 63.7°, respectively. However, the corresponding dihedral angles in another molecule are 147° and 115.2°, respectively. The other dihedral angles are similar. These results show that the two phenyl rings at the 3- and 4-positions of the pyrazole-ring take on a different

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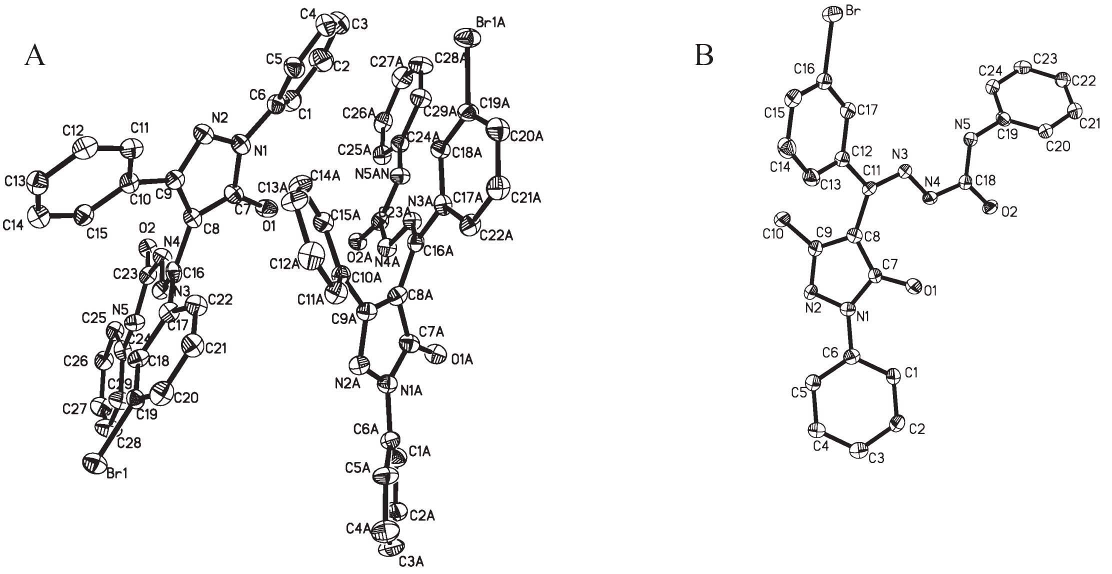


FIGURE 5. Crystal structures of DP3BrBP-PSC (A) and PM3BrBP-PSC (B); H atoms are omitted for clarity. The ellipsoids are drawn at the 30% probability level.

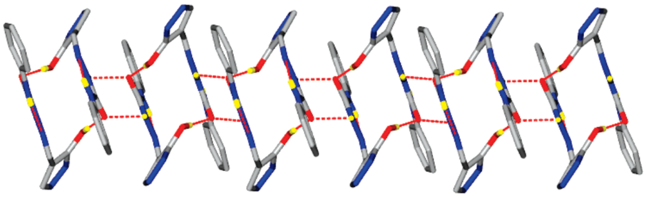


FIGURE 6. Hydrogen bond connection diagram of DP3BrBP-PSC along the *c* axis (a few of the phenyl rings and some H atoms are omitted for clarity).

orientation in the two molecules. In addition, the dihedral angle between the terminal phenyl ring (VI) and the plane (V) defined by N3, N4, N5, and C23 atoms is 9.7° (3.9°), which indicates that the phenylsemicarbazide moiety in the side chain is almost coplanar.

For PM3BrBP-PSC, we have found the dihedral angles among the pyrazole-ring (I) and the phenyl ring (II) at the 1-position and plane (IV) defined by N3, N4, N5, and C18 atoms are 32.2° and 62.9°, respectively. These values are consistent with those of DP3BrBP-PSC. But the dihedral angles between the pyrazole-ring (I) and the phenyl rings (III, V) at the 4-position and the terminal are 99.8° and 46.4°, respectively, which are different from the corresponding values (63.7°/115.2°, 61.1°/52.7°) for DP3BrBP-PSC. In particular, obvious changes exist between the plane defined by N3, N4, N5 atoms and the terminal phenyl ring, which is 53.6° for PM3BrBP-PSC and 9.7° or 3.9° for DP3BrBP-PSC. These results indicate that substituted groups at the 3-position of the pyrazole-ring have an important effect on the structure. Because of the huge steric hindrance of the phenyl group bonded to the C9 atom in DP3BrBP-PSC, the phenylsemicarbazide part in the side chain has a tendency to become coplanar.

In addition, the hydrogen bonds of two compounds are different. Figure 6 is the hydrogen bond connection diagram of DP3BrBP-PSC. It is clear that the dimer can be formed between two crystallographically independent molecules by intermolecular hydrogen bonds O1−H···O2A [2.562(6) Å, 162.3°] or O1A−H···O2 [2.586(7) Å, 165.0°] (where A represents the other molecule). Moreover, these dimers are connected by the intermolecular hydrogens of N4−H···O2 [3.066(7) Å, 130.3°; 2.965(7) Å, 122.8°], leading to an infinite one-dimensional hydrogen-bonded zonal configuration along the *c* axis.

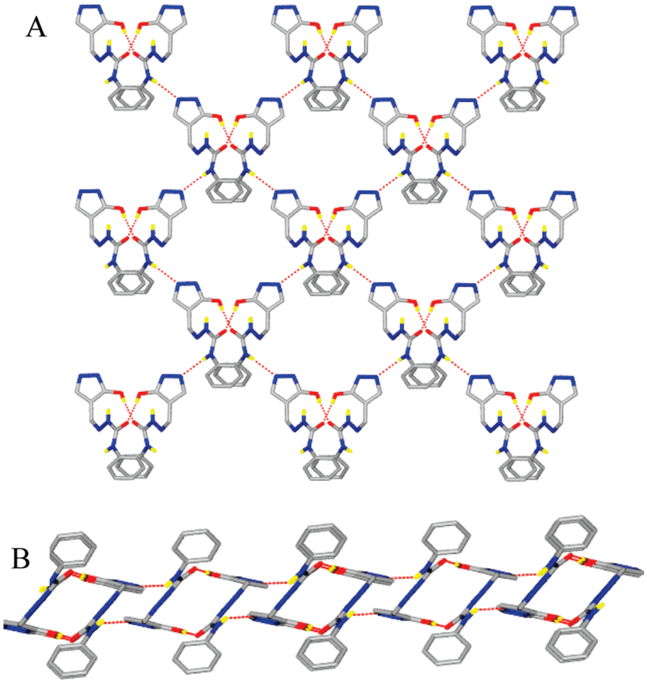


FIGURE 7. Hydrogen bond connection diagram of PM3BrBP-PSC along *c* (A) and *b* (B) axis (a few of the phenyl rings and some H atoms are omitted for clarity).

For PM3BrBP-PSC, there are two kinds of intermolecular hydrogen bonds (O1−H···O2 [2.549(5) Å 174(6)°] and N5−H···N2 [3.069(6) Å, 144.1°]), leading to the 2D grid configuration along the *c* axis (Figure 7A) and the ladderlike configuration along the *b* axis (Figure 7B). Compared with the hydrogen bond connection diagram of DP3BrBP-PSC, there is no N−H···O intermolecular hydrogen bond in PM3BrBP-PSC. On the basis of the analyses above, a reasonable photochromic mechanism is proposed as follows. Under UV light irradiation, the intermolecular proton transfers from the O1 atom to the O2A atom by the channel of O1−H···O2A, forming the O1···H−O2A mode. At the same time, another intermolecular proton transfers from the O2A atom to the N4 atom by the channel of O2A−H···N4′ (where ′ represents the other molecule), forming the intermolecular hydrogen bond N4′−H···O2A mode. Those processes lead to the enol−keto photoisomerization by the intermolecular double-proton transfer via the intermediated (I′) as shown in Scheme 1.

Conclusion

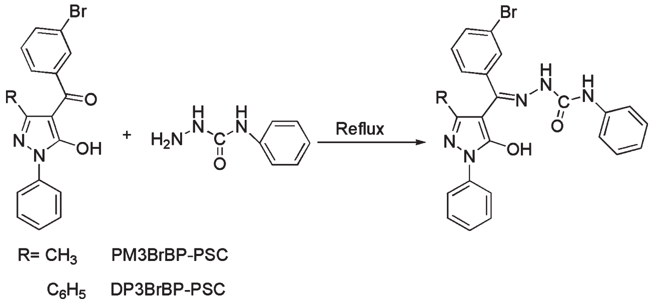
A novel photochromic compound of pyrazolone phenylsemicarbazone exhibits reversible enol−keto photoisomerization upon irradiation of UV light and heating, excellent photostability, and high fatigue resistance. Furthermore, it takes on remarkable modulated fluorescence in the solid state. On the basis of the analysis of crystal structure, the photochromic mechanism of an intermolecular double-proton transfer is proposed. In addition, substituent groups at the 3-position of the pyrazole-ring have an important effect on its structure and properties. Because of a huge steric hindrance of the phenyl group at the 3-position in DP3BrBP-PSC, the phenylsemicarbazide part in the side chain has a tendency of becoming coplanar. Moreover, the conjugation of the molecule obviously increases, which has the advantage of photoisomerization by intermolecular hydrogen bonds.

Experimental Section

Materials. 1,3-Diphenyl-5-pyrazolone (DPP) was synthesized by a literature method.[11] 4-Phenylsemicarbazide (PSC) and 3-bromobenzoyl chloride were purchased from the Aldrich Company, USA. 1-Phenyl-3-methyl-5-pyrazolone (PMP) and all other reagents for synthesis were A. R. grade and were purchased from commercial suppliers and used without further purification.

Synthesis. 1-Phenyl-3-methyl-4-(3-bromobenzoyl)-5-pyrazolone (PM3BrBP) and 1, 3-diphenyl-4-(3-bromobenzoyl)-5-pyrazolone (DP3BrBP) were synthesized according to the literature with a minor modification.[12] (a) PM3BrBP: yield 85.0%; mp 133.3−135.0 °C. Elemental anal. found for $C_{17}H_{13}N_2O_2Br$: C, 56.70; H, 3.66; N, 7.77. Calcd: C, 57.16; H, 3.67; N, 7.84. (b) DP3BrBP: yield 86.9%; mp 105.2−107.3 °C. Elemental anal. found for $C_{22}H_{15}N_2O_2Br$: C, 62.93; H, 3.65; N, 6.70. Calcd: C, 63.02; H, 3.61; N, 6.68.

SCHEME 2. **Synthesis Routine for PM3BrBP-PSC and DP3BrBP-PSC**



1,3-Diphenyl-4-(3-bromobenzal)-5-hydroxypyrazole 4-phenylsemicarbazone (DP3BrBP-PSC) was synthesized by refluxing DP3BrBP (5 mmol) and PSC (5 mmol) in 25 mL of ethanol in the presence of glacial acetic acid (1 mL). The mixture was refluxed for 6 h under magnetic stirring at 80 °C. After cooling to room temperature in the dark, white powders were obtained (Scheme 2). Yield 82.5%; mp 207.5−208.9 °C. Elemental anal. found for $C_{29}H_{22}N_5O_2Br$: C, 63.02; H, 4.07; N, 12.69. Calcd: C, 63.15; H, 4.02; N,12.70. MS *m*/*z* [M + 1] 552.2 (formula weight: 551.10).

PM3BrBP-PSC was prepared with the same method as DP3BrBP-PSC. Yield 93.2%; mp 224.3−225.1 °C. Elemental anal. found for $C_{24}H_{20}N_5O_2Br$: C, 58.69; H, 4.14; N, 14.22. Calcd: C, 58.89; H, 4.12; N,14.32. MS *m*/*z* [M + 1] 490.3 (formula weight: 489.08). The synthesis routine of DP3BrBP-PSC and PM3BrBP-PSC is presented in Scheme 2.

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra, crystallographic data, selected bond lengths, the dihedral angles, CIF files of two compounds, and Instrumentation. This material is available free of charge via the Internet at http://pubs.acs.org.

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