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Synthesis, photoisomerization properties and thermal bleaching kinetics of pyrazolones containing 3-cyanobenzal

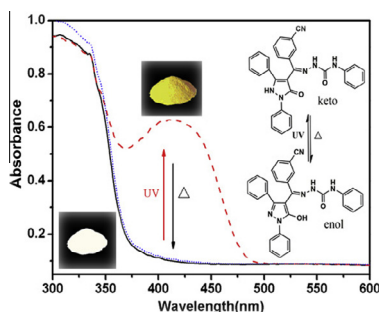
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HIGHLIGHTS

- Pyrazolone containing 3-cyanobenzal has good solid-state photochromic properties.
- Cyano in photochromic pyrazolone derivatives has the halogen-like properties.
- Pyrazolone phenylsemicarbazone exhibits excellent thermal stability.

GRAPHICAL ABSTRACT

Ten new pyrazolone thiosemicarbazone/phenylsemicarbazone derivatives were synthesized. Among them, 1,3-diphenyl-4-(3-cyanobenzal)-5-hydroxypyrazole 4-phenylsemicarbazone (**10**) exhibits excellent photochromic properties and high fatigue resistance. In addition, the decoloration reaction for compound **10** was accelerated with the increase of temperature.



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ABSTRACT

Through the design of molecules and the modification of structures, ten novel pyrazolone derivatives containing 3-cyanobenzal have been synthesized. They are 1-phenyl-3-methyl-4-(3-cyanobenzal)-5-hydroxypyrazole thiosemicarbazone (**1**)/4-methyl-3-thiosemicarbazone (**2**)/4-ethyl-3-thiosemicarbazone (**3**)/4-phenyl-3-thiosemicarbazone (**4**)/4-phenylsemicarbazone (**5**) and 1,3-diphenyl-4-(3-cyanobenzal)-5-hydroxypyrazole thiosemicarbazone (**6**)/4-methyl-3-thiosemicarbazone (**7**)/4-ethyl-3-thiosemicarbazone (**8**)/4-phenyl-3-thiosemicarbazone (**9**)/4-phenylsemicarbazone (**10**), in which seven compounds (**1**, **2**, **3**, **6**, **7**, **8** and **10**) have photoisomerization behaviors. Their structures, photoisomerization properties, and first-order kinetics were investigated. The results show that the compounds **2**, **3**, **7** and **8** exhibit irreversible photoisomerization behaviors, the other three compounds have reversible photoisomerization behaviors under 365 nm light irradiation and heat. But only 1,3-diphenyl-4-(3-cyanobenzal)-5-hydroxypyrazole 4-phenylsemicarbazone (**10**) exhibits good photochromic properties and fatigue resistance. Moreover, effects of various temperatures on the thermal bleaching reaction for **10** and substituent groups on the photochromic phenomenon are discussed.

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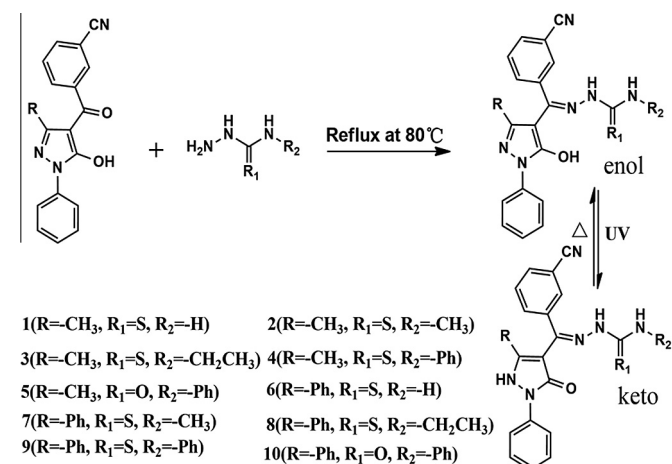
Introduction

Photochromic materials have drawn much attention because of the scientific interests and potential commercial values such as

high-density information storage system, photo-switches and optical memory devices [1,2]. With the increasing demand for materials that can store optical information, more and more researches focus on functional material of photochromism [3–5]. Up to date, among the large number of photochromic compounds such as diarylethenes [6], spiropyrans [7], azobenzenes [8]/overcrowded ethenes [9], and Schiff bases [10], most of them only show reversible photochromic behavior in solution. It is so far rather rare to find single component solid-state photochromism [11–13], whereas solid state photochromic materials are desired for practical applications in constructing optical switches [14,15]. Thus, the design and synthesis of new compounds with photochromic behaviors in the solid state is still an active research area.

In our laboratory, we found that pyrazolone derivatives exhibit the solid-state photochromic properties due to the enol–keto photoisomerization through intermolecular proton transfer upon the irradiation of light and by heating [16–20]. Many works have been focused on pyrazolone derivatives with halogen atoms (F, Cl, Br) substituted phenyl at 4-position of pyrazolone ring, such as 1-phenyl-3-methyl-4-(2-fluorobenzal)-5-hydroxypyrazole methylthiosemicarbazone/ethylthiosemicarbazone [17], 1,3-diphenyl-4-(2-chlorobenzal/4-fluorobenzal)-5-hydroxypyrazole methylthiosemicarbazone/ethylthiosemicarbazone [18] and 1,3-diphenyl-4-(3-fluorobenzal/3-chlorobenzal/3-bromobenzal)-5-hydroxypyrazole phenylsemicarbazone [19,20], which exhibit reversible photoisomerization in the solid state. However, their performances still cannot meet the requirements in optical devices concerning the sensitivity and fatigue resistance. It is still a great challenge to develop new photochromic compounds with high sensitivity and excellent fatigue resistance.

Herein, ten new pyrazolone thiosemicarbazone/phenylsemicarbazone derivatives were synthesized by introducing a 3-cyanobenzal at the 4-position of the pyrazolone ring, in which only one compound **10**, 1,3-diphenyl-4-(3-cyanobenzal)-5-hydroxypyrazole phenylsemicarbazone, exhibits good solid-state photochromic properties under alternating UV light irradiation and heat due to the reversible enol–keto isomerization reaction as shown in Scheme 1. Furthermore, the compound also takes on the good fatigue resistance. In addition, the effects of the substituents at the side chain and 3-position of the pyrazolone ring on their photoisomerization properties are discussed in detail.



Scheme 1. Synthetic route and photoisomerization mechanism of the pyrazolone derivatives.

Experiment

Characterization

Melting point was measured with a TECH XT-5 melting point apparatus without correction. Fourier transform infrared (FT-IR) spectra were recorded in the range 400–4000 cm⁻¹ on a Bruker EQUINOX-55 spectrometer. ¹H NMR and ¹³C NMR were carried out on an INOVA-400 NMR spectrometer. The mass spectra were determined with Waters UPLC-Quattro Premier XE LC MS/MS. UV–Vis spectra were measured on a Hitachi UV-3010 spectrometer equipped with an integrating sphere accessory. A 15 W lamp in ZF-8 Ultraviolet Analysis Instrument is used as the light source for irradiation of solid powders, the reflective filter size is 200 mm × 80 mm, the distance between sample and light source was 15 cm. The elemental analyses were performed on a FLASH EA1112 Series NCHS-O analyzer. All the spectroscopic measurements are carried out at room temperature.

Synthesis

4-Phenylsemicarbazide, 4-methyl-3-thiosemicarbazide, 4-ethyl-3-thiosemicarbazide, 4-phenyl-3-thiosemicarbazide, 3-cyanobenzoyl chloride were purchased from Aldrich Company, USA. All other chemicals and solvents were purchased from commercial suppliers and used directly without additional purification. 1,3-diphenyl-5-pyrazolone [21] and 1,3-diphenyl-4-(3-cyanobenzoyl)-5-pyrazolone [22] were synthesized according to the literature with a minor modification.

Synthesis of 1,3-diphenyl-4-(3-cyanobenzal)-5-hydroxypyrazole 4-phenylsemicarbazone (**10**). To a solution of 1,3-diphenyl-4-(3-cyanobenzoyl)-5-pyrazolone (5.0 mmol, 1.8269g) in ethanol (25 mL) were added 4-phenylsemicarbazide (5.0 mmol, 0.7561 g) and glacial acetic acid (1 mL) at 80 °C. After refluxing for 1 h under magnetic stirring, a large quantity of white precipitates appeared. The precipitates were filtered and washed with ethanol, and recrystallized from ethanol to yield white powders (81%). The other compounds were prepared with the same method as compound **10**. The synthetic route for these compounds is shown in Scheme 1.

1, Yield (white powder, 84%). m.p. 179.8–181.1 °C. ¹H NMR (400 MHz, DMSO-d₆, δ): 1.76 (3H, pz-CH₃), 7.25–7.98 (9H, 2phenyl ring), 8.10, 8.37 (2H, NH₂), 8.74 (1H, NH), 10.74 (1H, Pz-NH). ¹³C NMR (100 MHz, DMSO-d₆) 178.24, 146.36, 137.32, 132.05, 128.80, 125.21, 120.01, 118.73, 111.03, 13.44. FT-IR (cm⁻¹): 3335 ν (NH), 2231 ν (C≡N), 1595 ν (C=N), 1497, 1411 ν (Ph-ring), 1475, 1384 ν (Pz-ring), 1298 ν (C=S). Elemental analysis: (C₁₉H₁₆N₆OS) Calcd (%) C, 60.62; H, 4.28; N, 22.33. Found (%) C, 60.68; H, 4.32; N, 22.40. MS *m/z* [M–1] = 375.14 (formula weight 376.43).

2, Yield (faint yellow powder, 75%). m.p. 215.7–217.1 °C. ¹H NMR (400 MHz, DMSO-d₆, δ): 1.80 (3H, pz-CH₃), 3.07 (3H, –CH₃), 7.29–7.99 (9H, 2phenyl ring), 8.43 (1H, NH), 8.67 (1H, NH), 10.58 (1H, Pz-NH). ¹³C NMR (100 MHz, DMSO-d₆, δ) 178.38, 146.81, 138.82, 133.12, 132.65, 131.36, 129.79, 129.21, 129.07, 125.93, 120.58, 119.02, 111.87, 31.40, 13.43. FT-IR (cm⁻¹): 3342 ν (NH), 2230 ν (C≡N), 1611 ν (C=N), 1515, 1411 ν (Ph-ring), 1499, 1384 ν (Pz-ring), 1254 ν (C=S). Elemental analysis: (C₂₀H₁₈N₆OS) Calcd (%) C, 72.28; H, 4.45; N, 16.86. Found (%) C, 72.32; H, 4.53; N, 16.94. MS *m/z* [M–1] = 389.16 (formula weight 390.46).

3, Yield (white powder, 90%). m.p. 213.1–213.9 °C. ¹H NMR (400 MHz, DMSO-d₆, δ): 1.18 (3H, –CH₃), 1.81 (3H, pz-CH₃), 3.65 (2H, –CH₂), 7.29–7.96 (9H, 2phenyl ring), 8.40 (1H, NH), 8.76 (1H, NH), 10.40 (1H, Pz-NH). ¹³C NMR (100 MHz, DMSO-d₆, δ) 177.34, 146.86, 138.73, 133.02, 132.69, 131.31, 129.80, 129.21,

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