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A novel solid-state photochromic compound containing double heterocycles

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ABSTRACT

A new compound containing double heterocycles of pyrazole and thiophene, i.e. 1,3-diphenyl-4-(2-thienylmethylene)-5-hydroxypyrazole 4-phenylsemicarbazone (I), was synthesized and characterized by elemental analysis, MS, IR, ^{1}HNMR, ^{13}CNMR and X-ray single crystal diffraction. In solid state, it exhibits good photochromic properties under the UV and visible light irradiation. Upon the irradiation of UV light, the keto isomer (II) shows three IR absorption bands at 1697, 3302, 3404 cm^{-1}, which are not observed for the enol isomer. To understand the IR spectral changes, theoretical calculations were carried out using Gaussian 03 program. Based on analysis of the single crystal structure and the results of theoretical calculation, the photochromic mechanism is due to the double-proton transfer by intramolecular and intermolecular hydrogen bonds, leading to the isomerization between the enol and the keto form.

1. Introduction

Photochromism is a reversible transformation between two forms with different chemical structures induced by photoirradiation [1,2]. Structural changes may cause various physicochemical properties, such as absorption, emission, refractive index, dielectric constant, and redox potential. Photochromic compounds attract much attention because of potential applications in optical memories and switches, holographic displays, photochromic lenses, molecular logic gates and light-driven actuators [3]. So far, large amounts of organic photochromic compounds have been reported [4], However, most of them show reversible photochromic behaviors only in solution. It is rather rare to find single component with solid-state photochromism so far [5]. In addition, in many cases of photochromism, photogenerated isomers are thermally unstable. Moreover, solid-state photochromic materials are desired for practice applications of optical switches [6]. Thus, to develop new compounds with photochromic behaviors in solid state is very important for their applications.

In recent years, a series of pyrazolone phenylsemicarbazones have been reported in our lab [7]. These compounds exhibit reversible photoisomerization in solid state due to the transformation between the enol form and the keto form through proton transfers upon the irradiation of light and heating.

Previous works were focused on 1,3-diphenyl-4-arylacyl-5-hydroxypyrazole phenylsemicarbazone derivatives. That is to say, substituted moieties at the 4-position on the pyrazole ring have been phenyl or substituted phenyls. However, the substituted moiety containing thiophene has not been studied. Furthermore, among pyrazolone phenylsemicarbazones hitherto reported, the color varies only between white and yellow during the photochromic process. So their derivatives need to be further developed by the structural modification in order to improve the photochromic properties, richen the photochromic color and establish the relation between structures and properties.

Herein, a novel pyrazolone phenylsemicarbazone, 1,3-diphenyl-4-(2-thienylmethylene)-5-hydroxypyrazole 4-phenylsemicarbazone (**I**), was synthesized by the introduction of thiophene ring, which takes on good solid-state photochromic behaviors in coloration and decoloration upon the irradiation of UV and visible light. Compared with thermal decoloration of pyrazolone phenylsemicarbazones, this is the first example for the pyrazolone phenylsemicarbazone system that the colored form reversibly returns to the original form by the irradiation of visible light [7]. Furthermore, the photochromic color was richened between pink and yellow in comparison with changes of color between white and yellow for the other pyrazolone phenylsemicarbzones [7]. Thus, it has great potential application in optical storage devices. In addition, FT-IR, theoretical calculation and

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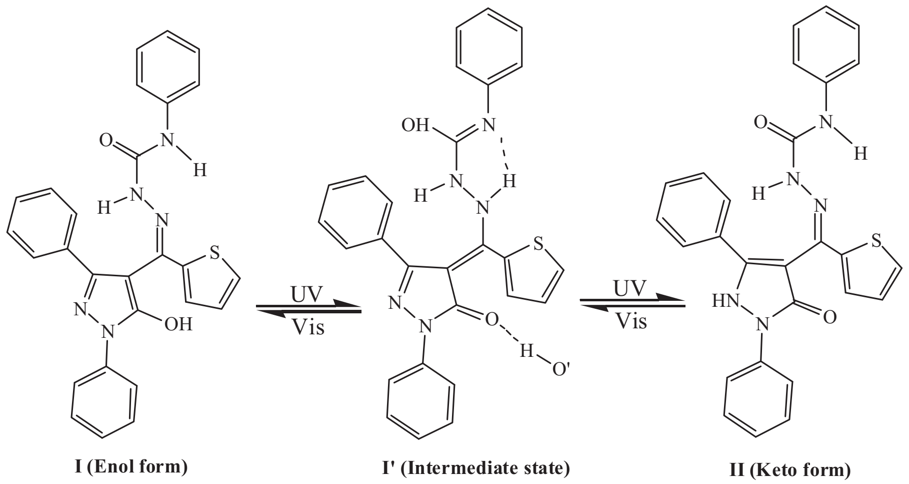

Scheme 1. Photochromic mechanism of the compound.

crystallographic analysis were used to investigate the structure changes of the compound **I** before and after the UV light irradiation and the photochromic mechanism. The results show that the photochromism of the compound is the tautomerization between the enol form and the keto form by the double-proton transfer via intramolecular and intermolecular hydrogen bonds in Scheme 1.

2. Results and discussion

2.1. Photochromic properties in solid state

The absorption spectra of powders **I** (enol form) induced by photoirradiation at room temperature are shown in Fig. 1. Upon the irradiation of 365 nm light, the pink powders (**I**) changed to the yellow (**II**). At the same time, a new broad band centered at 410 nm appears in the range of 370–480 nm, which is attributed to the keto form, and its intensity increases with the irradiation continuation (Fig. 1A). The results indicate that the photoisomerization from the enol form (**I**) to the keto form (**II**) occurs in solid state during the 365 nm light irradiation (Scheme 1). However, the thermal irreversibility is an indispensable property for the applications in some optoelectronic devices for example as memory storage. The yellow powders (**II**) were put in the dark for more than half a year, no changes in its absorption spectra were observed, which shows the yellow form (**II**) is very stable and retain its coloration memory for long time. However, the yellow (**II**) reverted to the pink (**I**) when it was exposed to the visible light ($\lambda > 400$ nm). Obviously, the intensity of the band in the range of 370–480 nm decreases, but it cannot completely restore the initial absorption spectrum (Fig. 1B, red line), and the changes of color can be clearly observed by naked eyes. The results indicate that the keto form (**II**) reversibly isomerizes to the enol form (**I**) in solid state during the visible light irradiation. According to the plot of $\ln[(A_\infty - A_0)/(A_\infty - A_t)]$ against the time (t) [8], the photochromic process is fitted to the first-order, and the kinetic constant for the coloration and decoloration are $1.83 \times 10^{-4}\ \mathrm{s}^{-1}$ and $1.65 \times 10^{-3}\ \mathrm{s}^{-1}$, respectively (see Fig. S1 in Supporting Information). Compared to kinetics of photoisomerization from the enol form to the keto form for 1,3-diphenyl-4-benzal-5-hydroxypyrazole 4-phenylsemicarbazone [7] ($k_{\text{e-k}} = 7.15 \times 10^{-4}\ \mathrm{s}^{-1}$), the coloration reaction of the compound **I** is slower possibly due to the thiophene instead of phenyl at 4-position of the pyrazolone.

In addition, this coloration/decoloration cycle between the pink enol form and the yellow keto form can be repeated at least 10 times with no remarkable attenuation (Fig. S2). So this compound exhibits good fatigue resistance, which indicates it has promising potential for optoelectronic devices such as rewritable optical memory media, optical switches and color displays [9]. It is noted that this

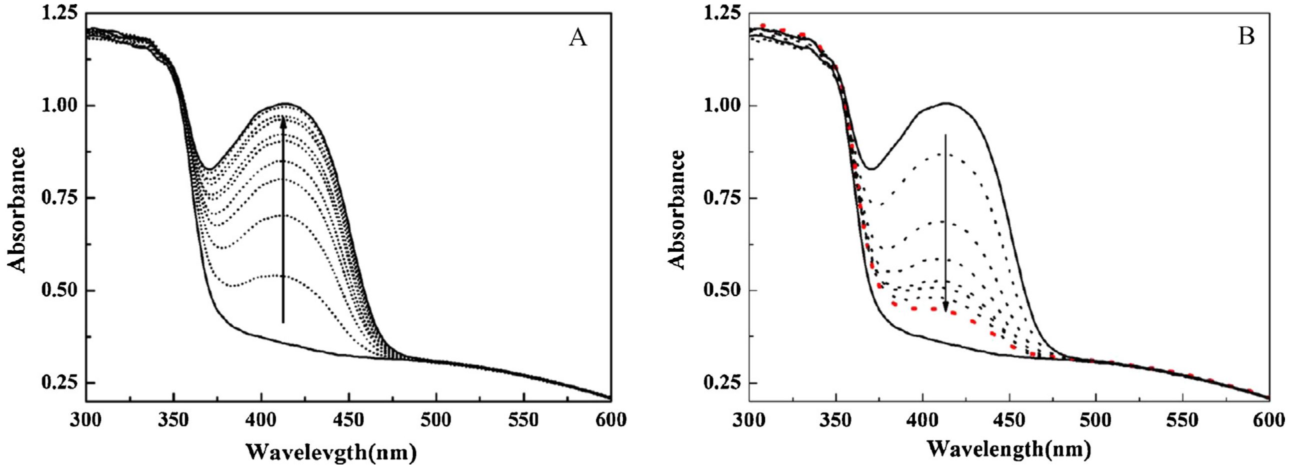

Fig. 1. (A) Absorption spectra of powders **I** with the irradiation of 365 nm light at the interval of 40 min (0, 40, 80, 120, 160, 200, 240, 280, 320, 360, 400 min) and (B) photobleaching spectra of **II** with the irradiation of visible light for 0, 4, 8, 12, 16, 20, 30, 90 min, $\lambda > 400$ nm). (For interpretation of references to color in the text, the reader is referred to the web version of this article)