Solid-State Photochromic Properties and Mechanism of 1-Phenyl-3-methyl-4-(3-chlorobenzal)-5-hydroxypyrazole 4-Methylthiosemicarbazone

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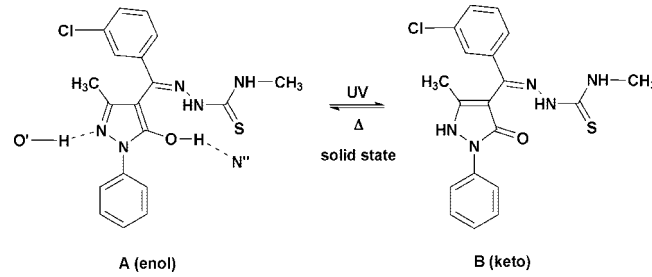
4-Acylhydroxypyrazoles combined with thiosemicarbazide derivants exhibit excellent photochromism in the crystalline state. Upon irradiation with 365 nm light, colorless enol-form isomers are converted to the yellow keto-form isomers. FT-IR, UV/vis, and fluorescence spectra were used to investigate the photochromic behavior of 1-phenyl-3-methyl-4-(3-chlorobenzal)-5-hydroxypyrazole 4-methylthiosemicarbazone. A possible photochromic mechanism has been proposed based on the analysis of the crystal structure of the sample.

Introduction

Proton tautomerization plays an important role in many fields of chemistry and biochemistry.[1] This phenomenon has attracted considerable attention as a potential means for controlling the properties of organic materials because it causes a substantial change in the properties of materials and can be controlled thermally[2] and photochemically.[3] The tautomerization in hydroxypyrazole derivants has been developed to a subject of particular interest because it is closely related to photochromism.[4] Many hydroxypyrazoles combined with thiosemicarbazide derivants exhibit photochromism in the solid state, which is ascribed to the transformation between an enol form and a keto form through hydrogen bonds upon irradiation of UV light. The inter/intramolecular hydrogen bonds contribute significantly to the structural feature and the stability of the molecules. Hydrogen bonds could control the structures of a vast multitude of biomolecules, host−guest complexes, and supramolecular assemblies, and the information on hydrogen bonds is very useful to the understanding of various molecular properties.[1b,5] Renewed interest on the subject has recently arisen because of the discovery of proton-transfer reaction along hydrogen bonds in the solid state.[2e,3e−h,4,6] Because proton transfer in these systems could change their optical properties, these molecules are promising candidates for optical switches and storage devices.[7]

In this paper, we describe a new photochromic compound, 1-phenyl-3-methyl-4-(3-chlorobenzal)-5-hydroxypyrazole 4-methylthiosemicarbazone (**A**), which undergoes reversible photochromism in the solid state. The reversible phenomenon by UV/heat is observed for the first time in this system. The fluorescence spectra are studied, which shows high-contrast fluorescence emission signals. The sample has great potential application in digital optical storage devices. In order to clearly understand the relationship between the structures and properties, a crystallographic analysis of colored crystals has been carried out. Its photochromism is due to proton transfer from the O atom of the hydroxyl group to the N atom of the pyrazole ring in an adjoining molecule through intermolecular hydrogen bonds (Scheme 1); meanwhile, its structure changed from the enol form to the keto form.

SCHEME 1: Photoreaction Mechanism of A



Experimental Section

The melting point was measured with a TECH XT-5 melting point apparatus. Elemental analyses were made on a FLASH EA series 1112 NCHS-O analyzer. Fourier transform infrared (FT-IR) spectra were recorded in the range 400−4000 cm^{-1} on a Bruker EQUINOX-55 spectrometer. ^1H NMR spectra were performed on an INOVA-400 NMR spectrometer with DMSO-d_6 as the solvent. The mass spectrum was determined with a HP1100 liquid chromatograph mass spectrometer. UV/vis absorption spectra were measured at room temperature on a UV-3010 spectrometer equipped with an integrating sphere. The fluorescence behavior of the sample has been studied using a Hitachi F-4500 fluorescence spectrophotometer with a Xe arc lamp (150 W) as the light source at room temperature. A 15 W lamp was used in a ZF-1 ultraviolet analysis instrument as the light source for photocoloration; the distance between the sample and the light source was 15 cm.

1-Phenyl-3-methyl-5-pyrazolone, 4-methylthiosemicarbazide (MTSC), and 3-chlorobenzoyl chloride were purchased from Aldrich Co., USA. The other materials were analytical reagant grade, were obtained from commercial sources, and were used without further purification.

1-Phenyl-3-methyl-4-(3-chlorobenzoyl)-5-hydroxypyrazole (PMCHP) was synthesized according to the literature with a minor modification.[4a,8] Yield: 70%. Mp: 115.6−116.8 °C. Elem

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anal. Calcd for $C_{17}H_{13}N_2O_2Cl$: C, 65.29; H, 4.19; N, 8.96. Found: C, 65.20; H, 4.25; N, 8.78.

1-Phenyl-3-methyl-4-(3-chlorobenzal)-5-hydroxypyrazole 4-methylthiosemicarbazone (**A**) was synthesized by refluxing PMCHP (5 mmol) and MTSC (5 mmol) in 30 mL of an EtOH solution containing glacial acetic acid (1 mL) for ca. 8 h under magnetic stirring at 80 °C in an oil bath. After cooling to room temperature, white precipitate was obtained. The crude product was filtered and purified by recrystallization using EtOH (yield 84%; mp 184.1−185.3 °C).

The chemical structure of **A** was identified by FT-IR, mass spectrometry (MS), ^{1}H NMR spectroscopy, and elemental analysis. The spectroscopic data are as follows. FT-IR (cm^{-1}, the white powder before irradiation of **A**): 3374 ν(N−H), 1667 ν(C═O), 1613 ν(C═N), 1597, 1501 ν(phenyl), 1553, 1456 ν(pyrazole ring), 969 ν(C═S). FT-IR (cm^{-1}, the yellow powder after irradiation of **B**): 3434 ν(N2−H), 3374, 3302, 3274 ν(N−H), 1667 ν(C═O), 1613 ν(C═N), 1597, 1501 ν(phenyl), 1551, 1456 ν(pyrazole ring), 969 ν(C═S). ^{1}HNMR (DMSO-d_6): δ 10.395 (1H, N2−H), 8.667 (1H, N5−H), 7.990−7.606 (4H, C_6H_4Cl), 7.969 (1H, N4−H), 7.552−7.308 (5H, phenyl ring), 3.079−3.067 (3H, $-CH_3$), 1.833 (3H, pyrazole CH_3). MS: $M^+ = 398.00$ (formula weight: 399.44, ^{35}Cl). Elem anal. Calcd for $C_{19}H_{18}N_5OSCl$): C, 57.07; H, 4.54; N, 17.51; S, 8.02. Found: C, 57.15; H, 4.50; N, 17.45; S, 7.99.

Single crystal of **B**: yellowish, $C_{19}H_{18}N_5OSCl$, $M = 399.90$, monoclinic, $P2_1/c$, $a = 7.274(2)$ Å, $b = 24.016(7)$ Å, $c = 11.680(3)$ Å, $\beta = 110.354(1)°$, $V = 1193.11(9)$ Å^3, $Z = 4$, $D_{calcd} = 1.388$ g cm^{-3}, $\mu = 0.328$ mm^{-1}, $F(000) = 832$, and $T = 153$ K. The crystallographic data were collected on an imaging plate system (Rigaku R-AXIS SPIDER) with graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\,73$ Å, ω scans, $3.04° \le \theta \le 27.48°$). Crystal structures was solved by direct methods and refined on F^2 by full-matrix least-squares methods with the *SHELXTL-97* program; 4390 unique measured reflections were used in the refinement. All non-H atoms were refined anisotropically. The H atoms on N atoms were located from the Fourier maps, and all of the other H atoms were placed in geometrically idealized positions. The refinement converged to R1 [observed reflections with $I > 2\sigma(I)$] = 0.0347, wR2 = 0.0973, and $S = 1.017$.

Results and Discussion

Photochromic Properties in the Solid State. The IR spectra of **A** and **B** were measured in the solid state, and some differences between them in the range of 2000−3700 cm^{-1} are clearly observed. Under irradiation of 365 nm light, three new sharp bands attributed to the N−H stretching vibration appear at 3434, 3302, and 3274 cm^{-1} along with the disappearance of a smooth band of 3262 cm^{-1}, which indicates the formation of the keto-form isomer **B** after irradiation of UV light. 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. This phenomenon is similar to the light-induced hydroxypyrazole derivants[4a,b] and other photochromic systems.[9]

Compound **A** shows an interesting photochromic transformation from white to yellow upon UV irradiation. The white crystalline powder (the enol form) changes gradually into yellow (keto form) under irradiation of 365 nm light. Parts a and b of Figure 2 illustrate the absorption and fluorescence spectral changes of **A** upon irradiation with 365 nm light at different times. A new broad absorption band around 400−550 nm appears in Figure 2a, which suggests that the sample exhibits

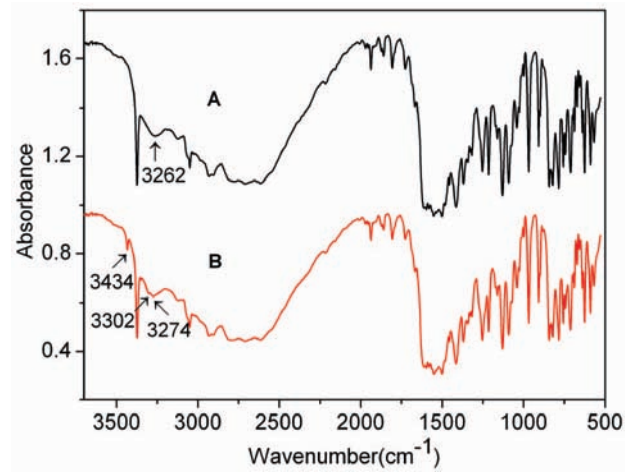

Figure 1. FT-IR spectra of **A** and **B**.

photochromic properties in the solid state. The maximum absorption band at 450 nm is assigned to the keto form.[3b,c] This is in good agreement with the FT-IR spectral analyses above.

The fluorescence of **A** displays one band at 418 nm. Upon irradiation with 365 nm light, the fluorescence is strongly quenched (Figure 2b), and the data of the fluorescence intensity changes versus time are available in the Supporting Information. This quenching is attributed to photoinduced transformation from the enol form to the keto form by proton transfer. The inset in Figure 2d shows the results of a cycling experiment in which the emission of the sample is monitored alternately with UV light irradiation and heating at 120 °C. It is noteworthy that the fluorescence on/off ratio is as high as 6:1. Such a high-contrast switching in the solid state presents a promising application in digital optical storage devices.[10] The white complex **A** is rather sensitive to light and even turns yellow upon irradiation by sunlight for several minutes. The sample **B** reverts slowly to **A** in the dark box at room temperature and more rapidly with heating at >120 °C, but the original spectrum intensity cannot be restored (Figure 2c,d). The dramatic color changes can be explained by the photoinduced proton transfer from one moiety to another. The proton transfer and configuration rearrangement of the π electrons lead to significant absorption spectral changes in the solid state.[3f,11] However, the UV light irradiation has no influence on the absorption spectrum in solution.

Crystal Structure and Mechanism of Photochromism. Because the length of the O−C7 bond is 1.256 Å, which is consistent with the length of the C═O double bond, it can be deduced that the structure of **B** is in the keto form, which is similar to other hydroxypyrazole photochromic compounds.[4] As shown in Figure 3, 1D chains are formed by linking the adjoining molecules through intermolecular hydrogen bonds (N−H···O, 2.649 Å, 159.1°), which provide a convenient channel to transfer protons.[12] Under UV light irradiation, the intermolecular proton transfer from the O atom to the N2 atom by the channel of O−H···N2 forms another intermolecular hydrogen bond (O···H−N2). This process leads to enol−keto photoisomerization through intermolecular proton transfer.

The photochromic process of the title compound is similar to those of other analogous compounds such as 7-hydroxyquinolines and 2-hydroxypyridine[11] but different from those of Schiff base compounds proposed by Cohen et al. The photocoloration process of Schiff bases such as salicylaldehyde and its derivatives was suggested as the mechanism of intramo-

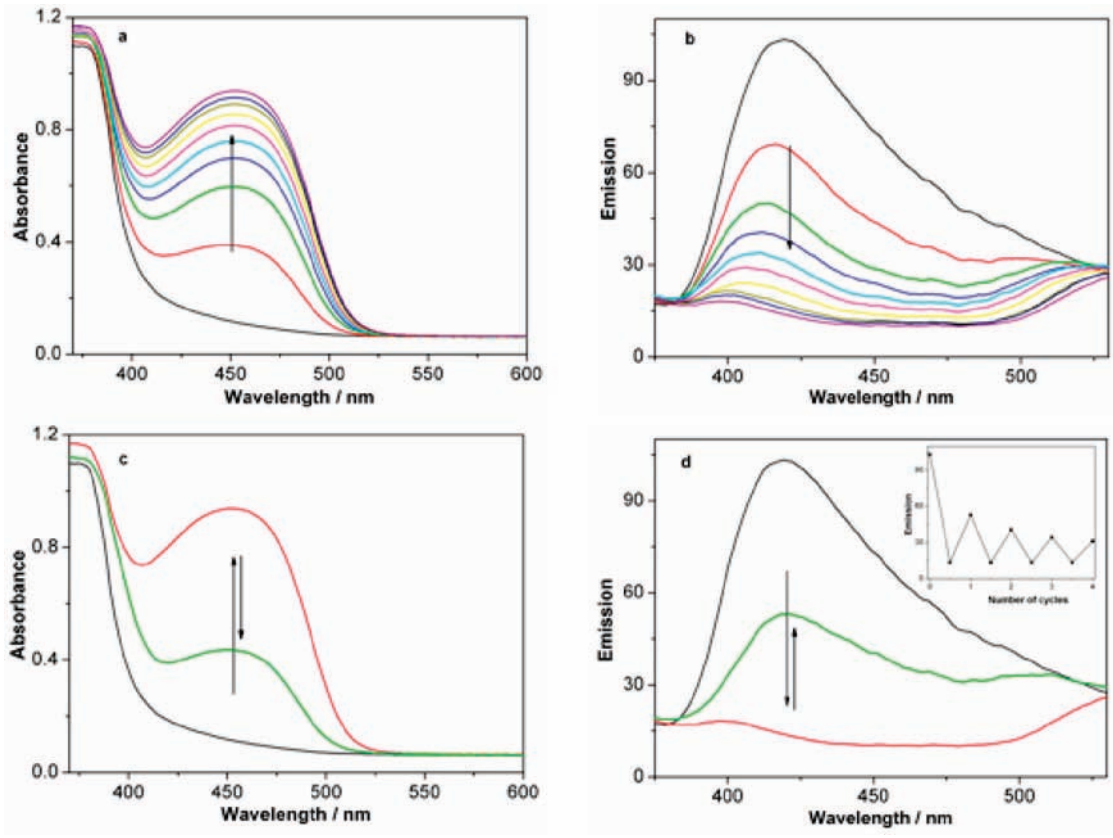

Figure 2. (a) Absorption and (b) fluorescence emission (λ_{ex} = 320 nm) spectral changes of **A** upon irradiation with 365 nm light at room temperature. Irradiated time interval: 3 min. (c) Absorption and (d) fluorescence emission spectral changes of **A** before irradiation (black), after irradiation (red), and after thermal bleaching (green). The inset in part d shows the modulated emission peak intensity of the sample during alternating irradiation of 365 nm light and heating at 120 °C.

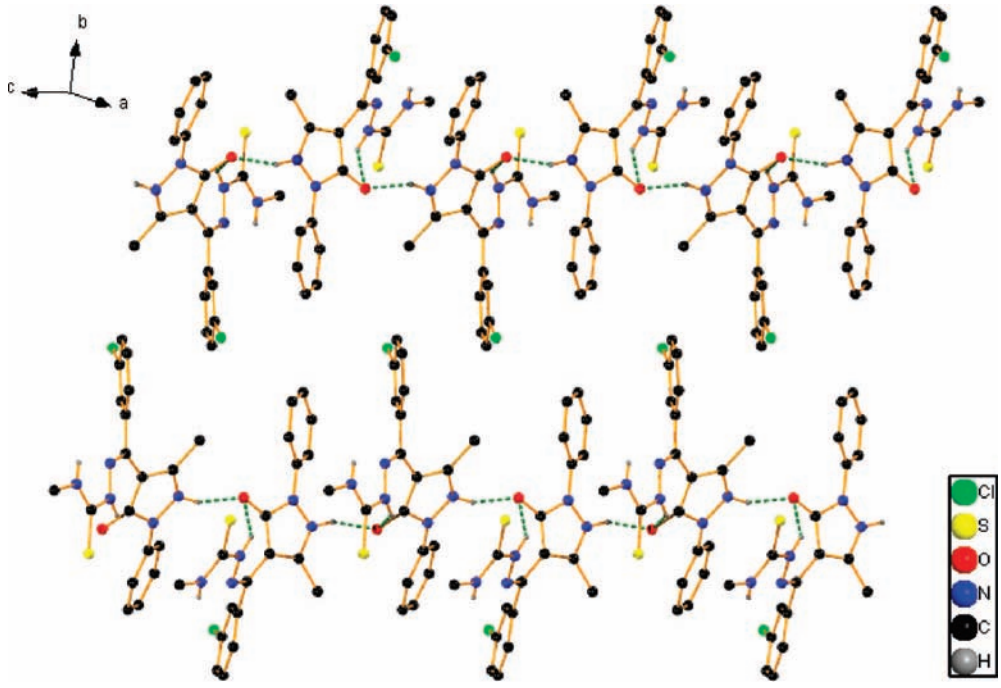

Figure 3. 1D N−H···O hydrogen-bonded chains in the crystal structure of **B**. All H atoms on the C atoms are omitted for clarity.

lecular proton transfer from the hydroxylic group to the N atom in imine (−CH═N−). Because there is not an intramolecular hydrogen bond between the O atom and the imine N atom (N3) in the *trans*-keto form, it is impossible to transfer protons between N3 and O atoms in the title compound.

Conclusion

A new kind of hydroxypyrazole methylthiosemicarbazone with reversible photochromism and high-contrast fluorescence emission signals has been synthesized in this work, which has

great potential as a good candidate for digital optical storage devices. On the basis of the structural analysis, a possible photochromic mechanism of the title compound, proton transfer via the intermolecular hydrogen bond, was proposed. The excellent experimental results provide a new insight for the design and synthesis of other hydroxypyrazole derivatives with tunable properties.

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Supporting Information Available: Figures of powder/yellowish single-crystal photochromism, a timescan of fluorescence spectra, and the molecular structure of **B**, tables of selected bond length and bond angle data and hydrogen bonds, and X-ray crystallographic data in CIF format for **B**. This material is available free of charge via the Internet at http://pubs.acs.org.

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