1230 Chinese Chemical Letters Vol. 14, No. 12, pp 1230 – 1232, 2003
http://www.imm.ac.cn/journal/ccl.html

Synthesis and Properties of a Novel Photochromic Compound

Guang Fei LIU[1], Lang LIU[1], Dian Zeng JIA[1,*] , Kai Bei YU[2]

[1]Institute of Applied Chemistry, Xinjiang University, Urumqi 830046
[2]Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041

Abstract: A new photochromic compound containing pyrazolone-ring was synthesized, and its crystal structure was determined on X-ray singlecrystal diffraction, which belongs to monoclinic crystal system, space group $P2_1/c$. The UV spectrum of the compound is studied.

Keywords: Pyrazolone-ring, crystal structure, photochromism.

Photochromic compounds have attracted considerable attention owing to their potential applications in variable transmitting materials[1] and photonic devices, such as optical disk memory, molecular switching devices, liquid crystal alignment[2,3]. Most organic photochromic compounds such as fulgides, sprirooxazine and spirpyrans[4,7] and their chemistry have been developed and studied comprehensively over the years. A few reports were published about photochromic compounds condensed by pyrazolone with thiosemicarbazide[8,9]. In this paper, a novel thiosemicarbazone compound with photochromism was prepared.

1-Phenyl-3-methyl-4-(4-bromobenzal)pyrazol-5-one N(4)-methyl-3-thiosemicarbazone(PMBbP-mtsc) was synthesized by direct condensation of 1-phenyl-3-methyl-4-(4-bromobenzoyl)-pyrazolone-5(PMBbP)[10] with N(4)-methyl-3-thiosemicarbazide (mtsc) (Aldrich), the other regents and solvents were commercial and used without further purification. General procedure for the preparation of PMBbP- mtsc: A mixture of 5.0 mmol of PMBbP, 5.0 mmol of mtsc, 25 mL methanol and 1.5 mL acetic acid were heated in reflux for 4 h, then cooled to room temperature, the white solid product was filtered and washed with methanol. Yield: 68%, mp 172-173℃. Based on the experimental results, the stoichiometric equations are shown in **Scheme 1**.

Elemental analysis of carbon, hydrogen and nitrogen were carried out with a model 2400-Perkin-Elmer analyzer. Anal. Calcd(%). for PMBbP-mtsc(C19H18BrN5OS): C 51.36, H 4.08, N 15.76; found: C 51.31, H 3.83, N 15.80. Infrared spectrum was recorded from KBr pellets on BRUKER EQUINOX 55 spectrometer. IR(cm-1): 3340-2500 (w, υO-H, υN-H), 1625 (υC=O), 1584 (υC=N), 848 (υCS); 1H NMR was carried on INOVA-400 NMR spectrometer(DMSO, δppm): 10.39 (s, 1H, N4H), 8.58 (s, 1H, N2H), 7.79-7.29 (m, 10H, phenyl and N_5H), 3.05 (d, 3H, CH_3, J=4.4Hz), 1.81 (s, 3H,

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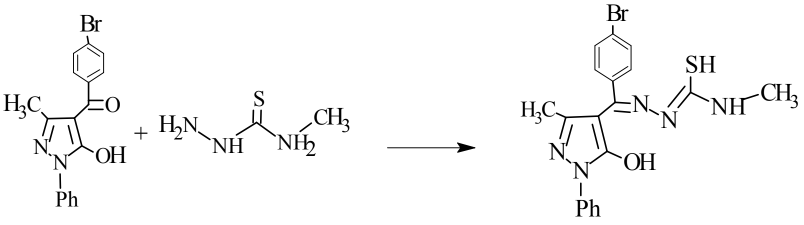
[*] E-mail:jdz@xju.edu.cn (D. Z. Jia)

Scheme 1



CH_3). The crystal structure and the connection of H-bonds were presented in **Figure 1**[11] and **Figure 2**, respectively.

Figure 1 The crystal structure

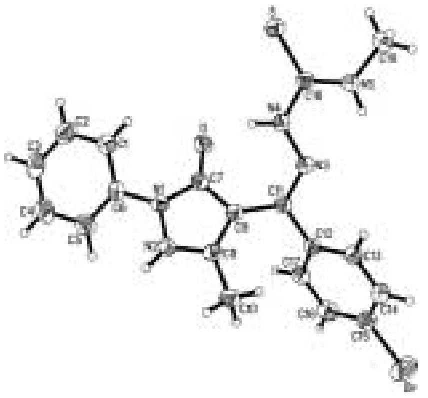
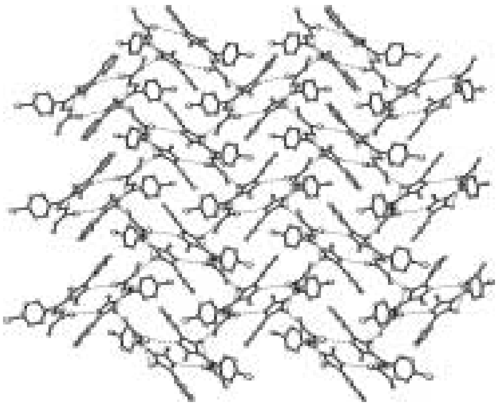


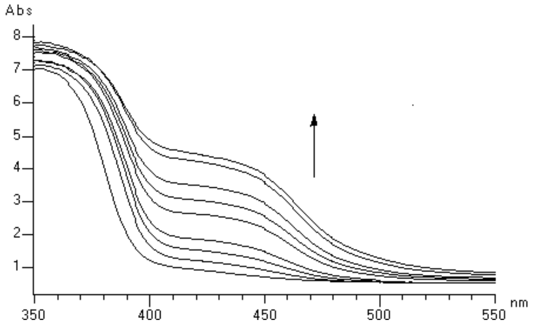
Figure 2 The connection of H-bonds diagram



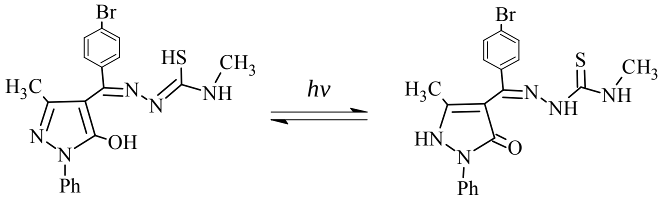
Absorption spectra were monitored on UV-3010 UV-Vis spectrophotometer. **Figure 3** shows the photochromic reaction of the compound. The white compound was irradiated by ultraviolet light 365 nm at room temperature and its color changed to yellow. The absorptions were recorded at different time intervals until spectral variation was no longer evident. Upon irradiation, it can be seen from the spectrum that a new absorption band appeared in the range of 390-470 nm and its intensity grew as measurement continued. When the yellow product was placed in the dark, it could not change back to the original color. If the reversible reaction of the product can occur in the proper wavelength or not, this is not clear yet, and the study on this topic is in process.

By analyzing the crystal structure of PMBbP-mtsc, a possible mechanism was envisioned in Scheme 2, which suggests that before photocoloring, PMBbP-mtsc existed with enol-form I. After irradiation, one H transferred from the mercapto-group to neighboring N2 atom, another H transferred from the hydroxy-group to the N atom at 5 position, *e.g.* the enol-form I converted to the keto-form II, and subsequently, the color of the compound turned from white to yellow. This conclusion was further confirmed by the crystal structure (**Figure 1**) and the connection of H-bonds diagram (**Figure 2**).

Figure 3 UV-Vis absorption spectrum of solid state of PMBbP-mtsc



Scheme 2 Photochromic reaction



(I) (II)

The relevant compounds and their mechanism of the photochromism are under investigation in our laboratory.

Acknowledgment

This work was supported by the National Natural Science Foundation of China(No. 20161003).

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11. Crystallographic parameters have been deposited in the editorial office of CCL.

Received 27 November, 2002