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Synthesis, structure and properties of a novel kind of photochromic compound containing a pyrazolone-ring

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Abstract

Two new organic photochromic compounds containing pyrazolone-ring as photochromic functional unit: 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one thiosemicarbazone (1A) and 1-phenyl-3-methyl-4-benzoylpyrazol-5-one *S*-methylthiosemicarbazone (2A), and some analogous non-photochromic derivatives were synthesized and characterized by elemental analysis, MS, IR Spectra, NMR spectra. The photochromic properties and photocolored kinetics of 1A and 2A were studied by powder-UV reflectance spectra under irradiation of 293 nm light. The crystal structure analysis of photocolored product of 1A showed the photochromic phenomenon was due to the photoisomerization from enol form to keto form. With the addition of the analysis of IR spectra, an intermolecular proton transfer mechanism of the photochemical process was proposed.

Keywords: Synthesis; Pyrazolone-ring; Photochromism; Intermolecular proton transfer mechanism

1. Introduction

The number of investigations for organic photochromic materials has increased considerably in recent years because of their potential commercial applications in several areas, such as high-density optical storage media, optical switching devices, etc. [1–6]. So far, though numerous organic photochromic molecular systems or photoactive devices have been explored, these systems which have been classified according to the photochromic structural units mainly belong to a small number of families, such as fulgides, spiropyrans and spiroxazine, diarylethenes and Schiff bases [7,8]. The great interests have been made to develop new photochromic system and to determine the mechanistic aspects of the photochemical process [9,10].

In this study, five hydrazone compounds (1A, 2A, 3A, 1B and 2B) containing pyrazolone-ring were synthesized and characterized (shown in Scheme 1). It was found that two compounds: 1-phenyl-3-methyl-4-benzoylpyrazol-5-one thiosemicarbazone (1A) and 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one *S*-methylthiosemicarbazone (2A), exhibited photochromic properties by 293 nm light irradiating (or exposed in the sunlight). The general agreement [1,9,11,12] about the photocoloration processes of hydrazone compound such as salicylideneanilines was suggested as the mechanism of intramolecular proton transfer from the O-hydroxyl group to the imine (–CH=N–) nitrogen atom (shown in Scheme 2).

However, the crystal structure of 1A* (colored product of 1A) showed that the photocoloration of 1A involved in an intermolecular proton transfer from O-hydroxyl group to the nitrogen atom of adjoining molecular pyrazolone-ring as shown in Scheme 3.

2. Experimental details

2.1. General comments

All melting points were measured with a TECH XT-5 melting point apparatus and were uncorrected. The elemental analysis were determined on PE-1700 CHN elemental analyzer. IR spectra were recorded as KBr disc on Bio-RAD FTS-40 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were determined on an AC-80 spectrometer with $CDCl_3$ and DMSO-d_6 as mixing solvent. Mass spectra were determined with HP-5988 GC/MS. UV reflectance spectra

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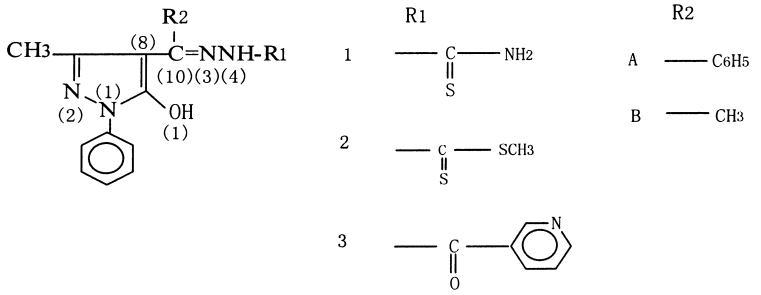
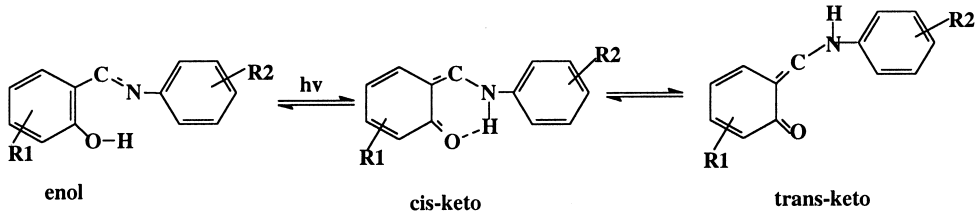


Scheme 1.



Scheme 2.

were recorded on Shimadzu CS-930 thin-layer chromato scanner. The crystal structure of 1A* was obtained by using a Siemens P4 diffractometer and calculations were carried out by using SHELXTL crystallographic software package of molecular structure. The cyclic voltammetric experiments were performed on a CHI660A Electrochemical workstation (CH Instrument Co., USA).

2.2. Materials

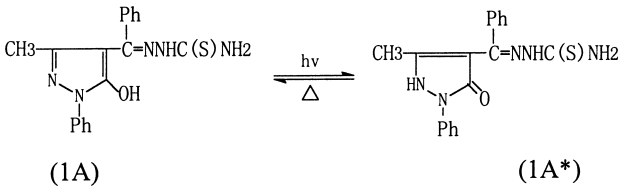
S-methyl-thiosemicarbazine was synthesized by the literature [13] ($C_2H_6N_2S_2$ requires 19.67% C, 4.91% H, 22.95% N; Found: 19.70% C, 4.89% H, 22.86% N).

Nicotinoylhydrazine was synthesized by refluxing the mixture of nicotinic acid (10 g), ethanol (40 ml), benzene (40 ml) and sulfuric acid (98%, 8 ml) for 3–5 h at refluxing temperature. Then benzene and ethanol were removed by evaporation, and the remains were poured into 200 ml of cooling water. After neutralized to pH≅7.0 by using $NaHCO_3$, the solution was extracted three times by ether (30–60 ml). The yellow liquid was mixed with ethanol (60 ml) and hydrazine (20 ml). The mixture was heated to reflux for 4 h, then cooled. The white product was precipitated, the precipitates were suction filtered, washed three times with ethanol, and dried in vacuum ($C_6H_7N_3O$ requires 52.54% C, 5.14% H, 30.48% N; Found: 52.35% C, 4.97% H, 30.48% N).

1-phenyl-3-methyl-4-acetyl-pyrazolone-5 was synthesized by the literature [14] ($C_{12}H_{12}N_2O_2$ requires: 53.96% C, 5.22% H, 24.20% N; Found: 54.05% C, 5.21% H, 24.17% N).

1-phenyl-3-methyl-4-benzoylpyrazol-5-one thiosemicarbazone (1A): 1A was synthesized by mixing 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one (PMBP 5.56 g, 0.02 mol) and thiosemicarbazine (1.82 g, 0.02 mol) in 200 ml of methanol containing 2 ml of glacial acetic acid. The mixture was refluxed on an oil bath at 80°C for 3 h. Then methanol was removed ca. 150 ml by evaporation and the remains were cooled in the dark. Finally the white product was filtered, washed well with ethanol, and dried in vacuum. The other new compounds were prepared with the same method as 1A.

Tetraethylammonium perchlorate [$(C_2H_5)_4N^+ClO_4^-$]: spectra grade. *N*,*N*-dimethylformamide (DMF) was purified as standard method [15]. The other materials used are AR grade.



(1A) (1A*)

Scheme 3.

2.3. Characterization for new compounds

1A: Yield: 78.6%, mp 223°C. The spectroscopic data are as follows. IR: 3467 cm^{-1} (m, ν_{NH_2}), 3347 cm^{-1} [m, $\nu_{N(4)-H}$], 2586 cm^{-1} (br, ν_{O-H}), 1594 cm^{-1} [s, $\nu_{C(10)=N(3)}$], 1475 cm^{-1} (s, $\nu_{pyrazole\text{-}ring}$), 837 cm^{-1} (m, $\nu_{C=S}$). ^1H NMR: δ=10.43 ppm (w, 0.8H, N(2)H), δ=9.65 ppm (w,

0.2H, OH), δ=7.96–7.52 ppm (m, 12H, phenyl and NH_2), δ=2.69 ppm (w, ^{1}H, SH), δ=1.95, 1.64 ppm (s, 3H, CH_3). ^{13}C NMR: δ=11.57, 11.59 ppm (CH_3), δ=96.12, 155.81 ppm (pyrazolone-ring), δ=146.08 ppm [C(10)], δ=177.21 ppm (CS). MS: M^+=351 (formula weight: 351.43). Formula $C_{18}H_{17}N_5OS$ requires 61.52% C, 4.87% H, 19.93% N; Found 61.44% C, 4.67% H, 20.21% N.

2A: Yield 56%, mp 144°C. The spectra data are as follows. IR: 3286 cm^{-1} [m, $\nu_{N(4)–H}$], 2698 cm^{-1} (br, $\nu_{O–H}$), 1596 cm^{-1} [s, $\nu_{C(10)=N(3)}$], 1461 cm^{-1} (s, $\nu_{pyrazole\text{-}ring}$), 1046 cm^{-1} (m, $\nu_{C=S}$). ^{1}H NMR: δ=10.67, 10.58, 10.53 ppm [w, 1H, N(2)H and OH], δ=7.95–7.20 ppm [bs, 11H, phenyl and N(4)H], δ=2.61, 2.63 ppm (s, 3H, SCH_3), δ=1.60, 1.56 ppm (s, 3H, CH_3). ^{13}C NMR: δ=11.92, 16.00 ppm (CH_3), δ=119.85, 157.64 ppm (pyrazolone-ring), δ=146.10 ppm [C(10)], δ=197.62 ppm (CS). MS: M^+=382 (formula weight: 382.31). Formula $C_{19}H_{18}N_4OS_2$ requires 59.66% C, 4.74% H, 14.64% N; Found 60.11% C, 4.72% H, 14.25% N.

3A: 1-phenyl-3-methyl-4-benzoylpyrazol-5-one nicotinoylhydrazone (3A): Yield 95%. The spectra data are as follows. IR: 3133 cm^{-1} [m, $\nu_{N(4)–H}$], 2980–2000 cm^{-1} (br, $\nu_{O–H}$), 1650 cm^{-1} [bs, $\nu_{C=O}$ and $\nu_{C(10)=N(4)}$], 1497 cm^{-1} (s, $\nu_{pyrazole\text{-}ring}$). ^{1}H NMR: δ=13.84 ppm [w, 0.2H, N(2)H], 11.18 ppm (w, 0.8H, OH), δ=8.71–8.65 ppm [1H, N(4)H], δ=8.05–7.64 ppm (4H, pyridine-ring), δ= 7.65–7.15 ppm (bs, 10H, phenyl-ring), δ=2.52–1.44 ppm (s, 3H, CH_3). ^{13}C NMR: δ=19.25 ppm (CH_3), δ=103.48–156.50 ppm (phenyl-ring, pyrazolone-ring, pyridine-ring), δ=142.79 ppm [C(10)]. MS: M^+=397 (formula weight: 397.44). Formula $C_{23}H_{19}N_5O_2$ requires 69.51% C, 4.82% H, 20.30 N; Found: 69.26% C, 4.67% H, 20.34% N.

1-phenyl-3-methyl-4-acetylpyrazol-5-one thiosemicarbazone (1B): Yield 94%, mp 250°C. The spectra data are as follows. IR: 3295 cm^{-1} [m, $\nu_{N(4)–H}$], 3189 cm^{-1} (m, $\nu_{O–H}$), 1592 cm^{-1} [s,$\nu_{C=O}$ and $\nu_{C(10)=N(4)}$], 1491 cm^{-1} (s, $\nu_{pyrazole\text{-}ring}$), 842 cm^{-1} (m, $\nu_{C=S}$). ^{1}H NMR: δ=10.05 ppm (w, 1H, OH), δ=8.01–7.72 ppm [m, 3H, N(4)H and NH_2], δ=7.74–7.19 ppm (5H, phenyl-ring), δ=2.59 ppm [s, 3H, C(10)–CH_3], δ=2.39 ppm (s, 3H, py–CH_3). ^{13}C NMR: δ=12.98 ppm (py–CH_3), δ=15.51 ppm [C(10)–CH_3], δ=116.78–137.55 ppm (phenyl-ring and pyrazolone-ring), δ=145.77 ppm [C(10)]. MS: M^+=289 (formula weight: 289.36). Formula $C_{13}H_{15}N_5OS$ requires 53.96% C, 5.22% H, 24.20% N; Found 54.05% C, 5.21% H, 24.17% N.

1-phenyl-3-methyl-4-acetylpyrazol-5-one *S*-methylthiosemicarbazone (2B): Yield 64%. The spectra data are as follows. IR: 3320 cm^{-1} [w, $\nu_{N(4)–H}$], 2916 cm^{-1} (m, $\nu_{O–H}$), 1594 cm^{-1} [s,$\nu_{C=O}$ and $\nu_{C(10)=N(4)}$], 1496 cm^{-1} (s, $\nu_{pyrazole\text{-}ring}$), 1044 cm^{-1} (m, $\nu_{C=S}$). ^{1}H NMR: δ=8.35–8.25 ppm [2H, N(4)H and OH], δ=7.82–7.49 ppm (5H, phenyl-ring), δ=2.99 ppm [3H, C(10)–CH_3], δ=2.76 ppm (6H, S–CH_3 and py–CH_3). ^{13}C NMR: δ=13.01 ppm (py–CH_3), δ=15.95 ppm (CH_3), δ=117.67–136.71 ppm (phenyl-ring and pyrazolone-ring), δ=145.48 ppm [C(10)]. MS: M^+=320 (formula weight: 320.44). Formula $C_{14}H_{16}N_4OS_2$ requires 52.47% C, 5.03% H, 17.48% N; Found 52.34% C, 5.21% H, 17.17% N.

2.4. Determination of the crystal structure of 1A*

The single crystal of 1A* was obtained by evaporating slowly the methanol solvent at room temperature and whole operation did not avoid the sunlight. The intensity data were collected at 294 K by a Siemens P4 diffractometer using M_O Kα(λ=0.71073 Å) and all calculations were performed by SHELXTL crystallographic software package of molecular structure. Cell constants and orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from reflections in the range 2.73–26.03°. The structure was solved by direct method. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations in their calculated positions. A summary of crystal data, experimental details and refinement results are listed in Table 1.

2.5. Kinetic measurement

The reflectance spectra were recorded by irradiating the samples with 293 nm light at 25°C at appropriate time

Table 1
Summary of crystal data, experimental details and refinement parameters for 1A*

Empirical formula	$C_{18}H_{17}N_5OS$
Formula weight	351.43
T (K)	294(2)
Wavelength (M_O Kα)	0.71073
Crystal system	Monoclinic
Space group	Cc
Unit cell dimensions	a=12.147(2) Å, α=90°; b=20.508(4) Å, β=108.67(3)°; c=11.512(2) Å, γ=90°
Volume	1758.0(6) Å^3
z	4
Density (calc.)	1.328 g cm^{-1}
Absorption coefficient	0.200 mm^{-1}
F(000)	736
Crystal size (mm)	0.42×0.34×0.32
θ range for data collection	2.73–26.03°
Limiting indices	$0\leq h\leq 9$, $0\leq k\leq 25$, $-14\leq l\leq 13$
Reflections collected	1863
Independent reflections	1863 (R_{int}=0.0000)
Refinement method	Full matrix least-squares
Max. and min. transmission	1.000 and 0.923
Absorption correction	Semi-empirical
Data/restraints/parameters	1863/2/295
Goodness-of-fit on F^2	0.897
Final R indices [$I>2\sigma(I)$]	R_1=0.0315, wR_2=0.1004
R indice (all data)	R_1=0.0357, wR_2=0.1054
Absolute structure parameter	−0.05(10)
Largest different peak and hole	0.187 and −0.171 e^{-3}
Extinction coefficient	0.0000(9)

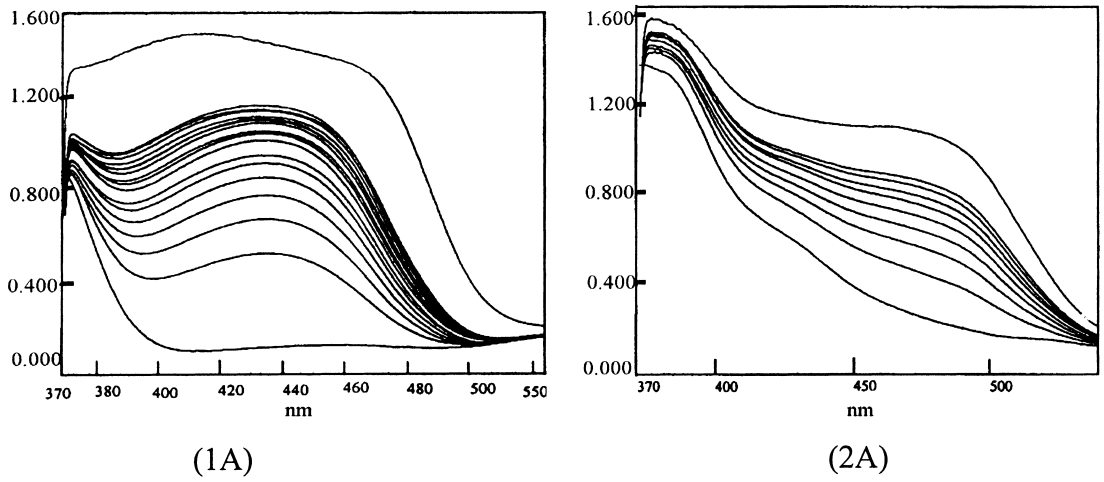


Fig. 1. Photochemical coloration of 1A and 2A with 293 nm light at 298 K, Irradiated time interval: 30 s for 1A and 180 s for 2A, respectively.

intervals. The first-order rate constants (k) were determined essentially as described in the literature [9]. The experimental data were treated with the standard integrated expression:

$$kt = \ln\left[\frac{A_\infty - A_o}{A_\infty - A_t}\right] \quad (1)$$

where A_o, A_∞ and A_t are the observed absorption data measured at the beginning, at the end of the reaction and at time t, respectively. All absorption data are acquired from the reflectance spectra at 435 nm for 1A and at 490 nm for 2A.

2.6. Electrochemical measurement

Pt electrodes were used as working electrode and counter electrode, and saturated calomel reference electrode was separated from the working compartment by a solution bridge fitted with a medium glass frit. Tetraethylammonium perchlorate (0.1 M) was used as supporting electrolyte in DMF solution containing 1×10^{-3} M measured compounds.

3. Results and discussion

3.1. Photochromism and thermochromism

The compounds 1A and 2A (enol form) exhibit photochromic and thermal bleaching phenomena only in the solid state; the color of 1A turned from white to yellow and 2A from yellow to reddish orange under irradiation of the 293 nm light (or exposed in the sunlight). Their powder-UV reflectance spectra at 298 K for different light irradiated times are shown in Fig. 1. A new absorption band appears around 450 nm for 1A and 490 nm for 2A.

However, when the colored compounds of 1A* and 2A* are heated at around 200 and 100°C, respectively, their absorption decreased as shown in Fig. 2. It shows that 1A* (or 2A*) can't be completely restored to 1A (or 2A) as a result of the distortion of crystal lattice during being heated.

However, these compounds do not exhibit the photochromism and thermochromism in the solution state. The data of ^{1}H NMR show the enol form (O–H, ca. 0.2H,

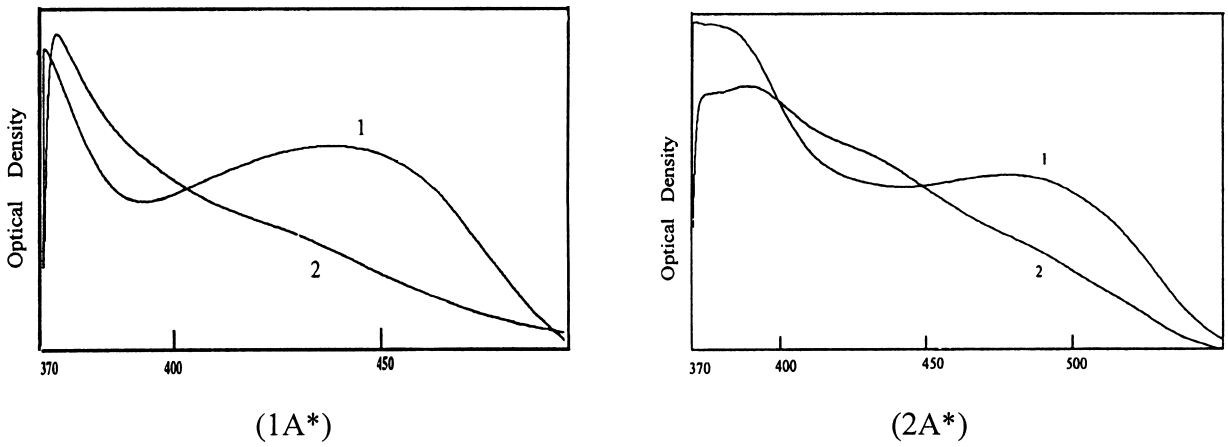


Fig. 2. Thermobleaching spectra of 1A* at 200°C and 2A* at 100°C. 1: before heated; 2: after heated.

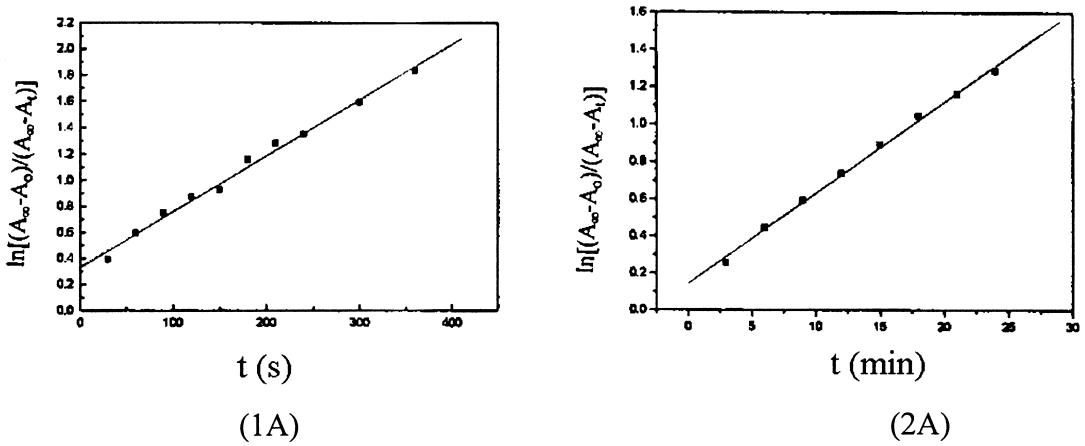


Fig. 3. First-order kinetic plot of photoisomeriztion (enol→keto) reaction of 1A and 2A induced by 293 nm light.

δ=9.65 ppm) and keto form [pyrazolone-ring N(2)–H, ca. 0.8H, δ=10.43 ppm] of 1A are in the equilibrium with ca. 1:4 ratio.

3.2. Kinetics of the photochromic reaction

The kinetic curves (shown in Fig. 3) of 1A and 2A are plotted according to the Eq. (1). The wavelength at which the maximum change in optical density occurred was used for the kinetic measurements. A good linear fit was found for 1A and 2A in the kinetic plots from which the first-order or pseudo-first-order rate constants were obtained as $k_{1A}=7.80\times10^{-3}\,s^{-1}$ and $k_{2A}=1.03\times10^{-3}\,s^{-1}$, respectively. Results show that the photocoloration of 1A is faster 7 times than 2A.

3.3. Mechanism of photochromism

A single crystal X-ray study for 1A* has been undertaken to demonstrate the mechanism of photochromism of this kind compounds. The reliable structure data of 1A are not reported in this paper because the crystalloid of 1A is easily turned into 1A* during measurement though its single crystal has been obtained by evaporating methanol solvent at room temperature in the dark. The spectra analysis in the previous section show that the compounds are enol forms before the photocoloration takes place. The molecular structure and packing in the unit cell of 1A* are shown in Figs. 4 and 5, respectively and the bond lengths and bond angles are given in Table 2.The data show that the structure of colored compound 1A* is the keto form, and an intermolecular hydrogen bond [N(2)–H$\cdots$O(1)] (2.632 Å) exists between neighboring molecules. It suggests that the change of color be due to the photoisomerization from the enol form to the keto form. However, it is almost impossible to transform hydroxyl proton [O(1)–H] to N(2) atom of pyrazolone-ring in molecule itself because the proton must surmount not only the bonding effort with O(1) but also potential barrier, especially when it pass through pyrazolone-ring with great electron cloud density. If 1A is also involved in the intermolecular hydrogen bond [N(2)$\cdots$H–O(1)] could easily take place by a convenient way of intermolecular proton transfer.

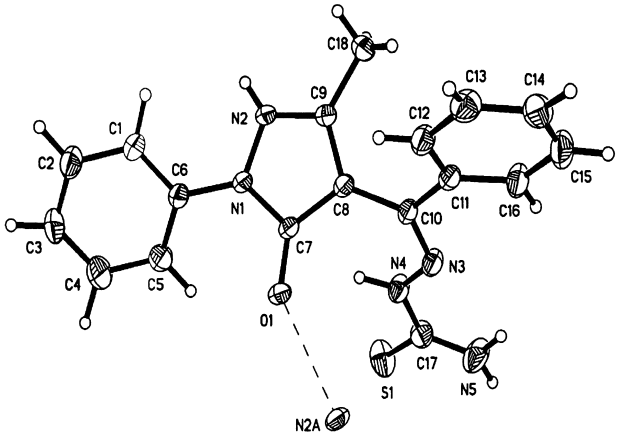


Fig. 4. The crystal structure of 1A*.

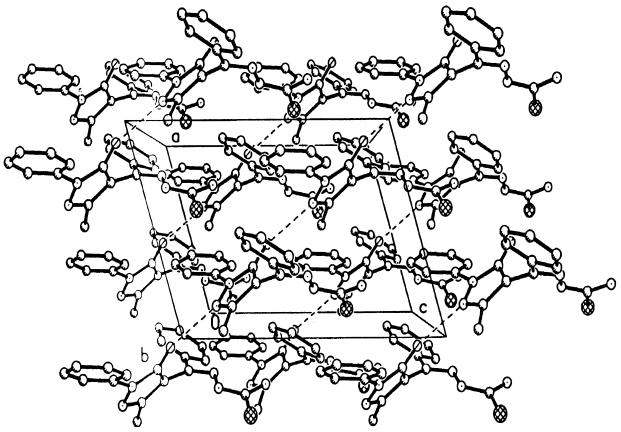


Fig. 5. Packing in unit cell of 1A*.

Table 2
The data of bond length (Å) and bond angle (°) of 1A*

S(1)–C(17)	1.672 (2)	O(1)–C(7)	1.257 (2)
N(1)–N(2)	1.371 (2)	N(1)–C(7)	1.377 (2)
N(1)–C(6)	1.417 (2)	N(2)–C(9)	1.325 (2)
N(3)–C(10)	1.295 (2)	N(3)–N(4)	1.364 (2)
N(4)–C(17)	1.356 (2)	N(5)–C(17)	1.316 (3)
C(1)–C(6)	1.384 (3)	C(1)–C(2)	1.384 (3)
C(2)–C(3)	1.385 (3)	C(3)–C(4)	1.381 (4)
C(4)–C(5)	1.378 (3)	C(5)–C(6)	1.388 (2)
C(7)–C(8)	1.428 (2)	C(8)–C(9)	1.398 (2)
C(8)–C(10)	1.470 (2)	C(9)–C(18)	1.492 (2)
C(10)–C(11)	1.486 (2)	C(11)–C(12)	1.386 (3)
C(11)–C(16)	1.401 (3)	C(12)–C(13)	1.390 (3)
C(13)–C(14)	1.384 (3)	C(14)–C(15)	1.378 (4)
C(15)–C(16)	1.393 (3)		
N(2)–N(1)–C(7)	108.23 (12)	N(2)–N(1)–C(6)	122.21 (12)
C(7)–N(1)–C(6)	128.14 (13)	C(9)–N(2)–N(1)	110.49 (12)
C(10)–N(3)–N(4)	117.38 (14)	C(17)–N(4)–N(3)	121.33 (14)
C(6)–C(1)–C(2)	119.4 (2)	C(1)–C(2)–C(3)	120.3 (2)
C(4)–C(3)–C(2)	119.8 (2)	C(5)–C(4)–C(3)	120.4 (2)
C(4)–C(5)–C(6)	119.6 (2)	C(1)–C(6)–C(5)	120.5 (2)
C(1)–C(6)–N(1)	120.5 (2)	C(5)–C(6)–N(1)	119.0 (2)
O(1)–C(7)–N(1)	122.5 (2)	O(1)–C(7)–C(8)	131.38 (13)
N(1)–C(7)–C(8)	106.11 (12)	C(9)–C(8)–C(7)	106.76 (13)
C(9)–C(8)–C(10)	126.92 (14)	C(7)–C(8)–C(10)	126.27 (13)
N(2)–C(9)–C(8)	108.19 (13)	N(2)–C(9)–C(18)	120.86 (14)
C(8)–C(9)–C(18)	130.9 (2)	N(3)–C(10)–C(8)	123.8 (2)
N(3)–C(10)–C(11)	116.00(14)	C(8)–C(10)–C(11)	120.19 (13)
C(12)–C(11)–C(16)	118.6 (2)	C(12)–C(11)–C(10)	121.1 (2)
C(16)–C(11)–C(10)	120.3 (2)	C(11)–C(12)–C(13)	120.8 (2)
C(14)–C(13)–C(12)	120.4 (2)	C(15)–C(14)–C(13)	119.4 (2)
C(14)–C(15)–C(16)	120.7 (2)	C(15)–C(16)–C(11)	120.1 (2)
N(5)–C(17)–N(4)	116.4 (2)	N(5)–C(17)–S(1)	124.1 (2)
N(4)–C(17)–S(1)	119.56 (14)		

The IR spectra of enol form compounds in the range of 3500–2000 cm^{-1} are shown in Fig. 6. A broad absorption band in range of 3000–2000 cm^{-1} is observed for 1A, 2A, 3A, 1B and 2B, which is attributed to ν[O(1)–H]. L.J. Bellamy [16] has demonstrated that when X–H group

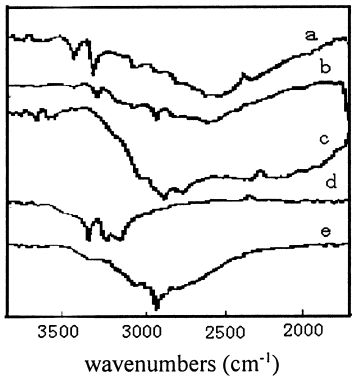


Fig. 6. IR spectra of 1A (a), 2A (b), 3A (c), 1B (d) and 2B (e).

(X=O, N, S and Cl, etc.) is involved in the hydrogen bonding, the absorption band of ν(X–H) will be broadened and red-shifted in the IR spectra. Moreover, the stronger the hydrogen bonding effort is, the greater broadened and red-shifted effect is. Compared the IR spectra of 1A (curve a) and 2A (curve b) with non-photochromic 1B (curve d), the absorption band of ν[O(1)–H] of 1B suggests its O(1)–H group isn't involved in hydrogen bonding, thus 1B can't exhibit photochromic properties. However, 3A and 2B are also found to be non-photochromic though their ν[O(1)–H] are broadened and red-shifted. It suggests the intermolecular hydrogen bonding is not the unique factor effecting their photochromic properties.

It has been reported the compound: 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (PMBP) has tautomer of white enol form and yellow keto form [17], but the enol form can't be photoisomerized into keto form. The crystal structure of PMBP shows the five-member pyrazolone-ring is irregular and the bond length of C(8)–C(10) (1.507 Å) is near to the value of C–C single bond. As shown in Table 2, however, the interior bond angles of the five-member pyrazol-ring of 1A* are about equal to the regular pen-

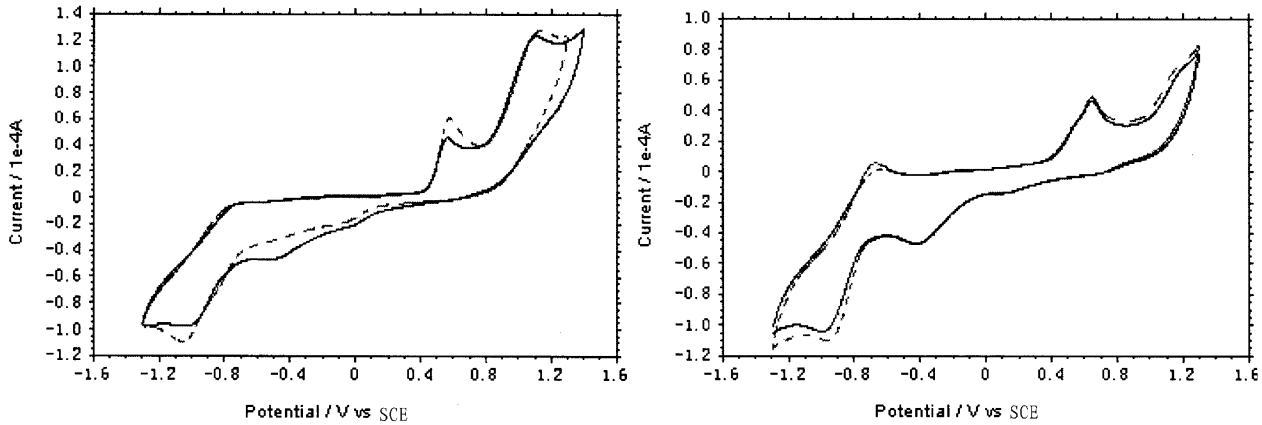


Fig. 7. Cyclic voltammograms of 1A and 3A (v=50 mV s^{-1}, c=1×10^{-3} M) in DMF containing 0.1 M $(C_2H_5)_4N^+ClO_4^-$ as supporting electrolyte. ···: measured in the dark; —: measured under 293 nm light irradiation.

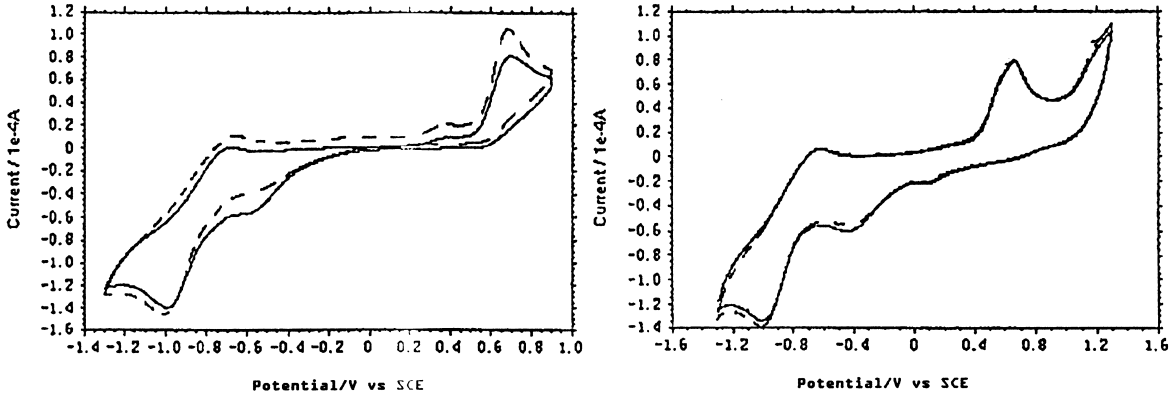


Fig. 8. Cyclic voltammograms of 2A and 3A (v=100 mV s^{-1}, c=1×10^{-3} M) in DMF containing 0.1 M $(C_2H_5)_4N^+ClO_4$ as supporting electrolyte. ···: measured in dark; —: measured under 293 nm light irradiation.

tagon (108°), showing that the pyrazolone-ring of 1A* have favorable coplanarity. The bond length of C(8)–C(10) (1.470 Å) suggests a more large conjugate system is also formed between the pyrazolone-ring and the side chain group [–C(10)=NNHC(S)NH_2]. It suggests that the incorporation of the thiosemicarbazone group greatly improve the systematical conjugacy, which could be advantageous to transform the photon energy into the hydrogen bond [N(2)···H–O(1)] and form the new hydrogen bond [N(2)–H···O(1)] (2.632 Å).

3.4. Electrochemical behavior

An interesting phenomenon has been observed in the cyclovolammetric curves of 1A, 2A and 3A measured in dark and in 293 nm light irradiation (shown in Figs. 7 and 8). It is found that the UV light irradiation influences the electrochemical response of photochromic 1A and 2A much more greatly than that of non-photochromic 3A. Such difference of electrochemical response must be correlated with their properties of transient states formed by absorbing the photon energy. The more detailed demonstration about such correlation will be discussed in the other research paper.

4. Conclusion

As outlined in this paper, a novel kind of photochromic compounds containing the pyrazolone-ring as photochromic functional unit has been developed. Structure analysis suggests their photochromic properties are the result of isomerization from enol form to keto form and the photochromic mechanism is suggested as intermolecular proton transfer by the way of intermolecular hydrogen bond.

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