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Crystal structure and photochromism of 1-phenyl-3-methyl-4-benzyl-5-one-pyrazole *S*-methyl thiosemicarbazone

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Abstract

A new organic photochromic compound containing pyrazolone-ring photochromic functional unit: 1-phenyl-3-methyl-4-benzyl-5-one pyrazole *S*-methyl thiosemicarbazone (PMBP-smtsc) was synthesized. The photochromic properties and photochemical kinetics of PMBP-smtsc have been studied by UV reflectance spectra under irradiation of 365 nm light. The crystal structure analyses of photocolored product show the photochromism is due to the photoisomerization from enol form to keto form through an intermolecular proton transfer.

Keywords: Pyrazolone; Photochromism; Thiosemicarbazone; Intermolecular proton transfer mechanism

1. Introduction

Photochromic molecular materials have been proposed as candidates for applications in optical recording [1–4]. Writing and erasing of data can be achieved by photoconversion ('switching') between different isomers. In recent years, photochromic compounds have attracted numerous scientists to study their properties, mechanisms and applications. Especially, organic photochromic compounds such as spiropyrans [5,6] and spiroxazine [7], fulgides [8,9], diarylethenes [10,11] and Schiff bases [12–14] have been much studied due to their potential importance for the feasibility of information recording and processing [15,16], variable transmitting materials [17] and molecular switching devices [18], etc. Up to now, developing new photochromic system and determining the mechanistic aspects of the photochemical process are still the power to speed the progress of this field.

Thiosemicarbazones and their derivates are widely known as having a large range of biological applications such as antiviral, antibacterial, antimalarial, antifungal, etc [19,20]. Now, a photochromic functional unit is introduced into thiosemicarbazone, we expect that products have doubling functions. However, few photochromic compounds on thiosemicarbazone have been reported previously [21,22].

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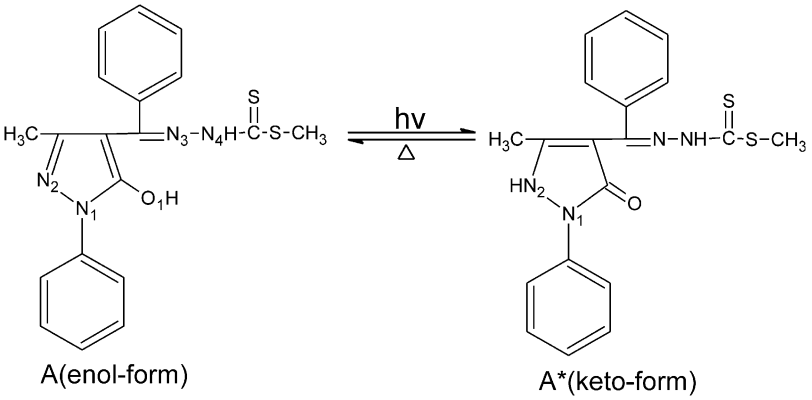


Scheme 1.

An intermolecular H-transfer mechanism was proposed on the basis of the crystal structure of PMBP thiosemicarbazone. It is different from the photochromic properties of Schiff base compounds reported by Cohen and Schmidt [23]. Schiff bases from salicylaldehyde are a typical class of photochromic materials involving both excite-state intramolecular proton transfer and *cis–trans* isomerization to form a colored photoproduct from the colorless molecules upon UV irradiation. In order to interpret further the intermolecular H-transfer mechanism proposed above, we cultivate single crystals of the title compounds. It was found that the title compounds exhibited reversible color changes induced by 365 nm ultraviolet irradiation. And the crystal structure of the title compound showed that the photocoloration of A(enol-form) involved in an intermolecular proton transfer from O-hydroxyl group to the nitrogen atom of adjoining molecular pyrazolone-ring as show in Scheme 1.

2. Experimental details

2.1. Synthesis

S-methyl thiosemicarbazine was synthesized by the literature [24]. 1-phenyl-3-methyl-4-benzyl-5-one-pyrazole *S*-methyl thiosemicarbazone (PMBP-smtsc) was prepared by mixing 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 (PMBP, 5 mmol) and *S*-methyl thiosemicarbazide (smtsc, 5 mmol) in 50 ml of MeOH solution containing 5–6 drops of glacial acetic acid at 70° c for ca 3 h by stirring. The mixture was cooled to room temperature. The yellow crystal suitable for X-ray analysis was obtained by allowing MeOH to evaporate for a few days.

Table 1
Crystal data and structure refinement parameters for A*(keto-form)

Empirical formula	$C_{19}H_{18}N_4\,OS_2$
Formula weight	382.49
Temperature	294(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 11.854(2)$ Å $\alpha = 90°$ $b = 14.852(4)$ Å $\beta = 96.46(2)°$ $c = 21.930(5)$ Å $\gamma = 90°$
Volume, Z	3836.4(15) Å^3, 8
Density (calculated)	1.324 g/cm^3
Absorption coefficient	0.293 mm^{-1}
F (000)	1600
Crystal size	0.48 × 0.40 × 0.12 mm^3
θ range for data collection	1.66° to 24.99°
Limiting indices	$0 \leq h14,\ 0 \leq k17,\ -26 \leq l \leq 25$
Reflections collected	7647
Independent reflections	6751 [R(int) = 0.0212]
Absorption correction	Empirical
Max. and min. transmission	0.9879 and 0.9047
Refinement method	Full matrix least-squares on F^2
Data/restraints/parameters	6751/0/490
Goodness-of-fit on F^2	0.844
Final R indices [$I > 2s(I)$]	$R1 = 0.0465$, $wR2 = 0.0888$
R indices (all data)	$R1 = 0.1085$, $wR2 = 0.1046$
Extinction coefficient	0.00183(19)
Largest diff. peak and hole	0.250 and −0.253 e/Å^3

2.2. Determination of the crystal structure of A*(keto-form)

Data were collected at 294 K by a Siemens P4 diffractermeter with MoKα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct method. All calculations and drawing were performed by the SHELXTL crystallographic software package of molecular structure. The intensities were measured by ω-scans. Cell constants and orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from reflections in the range 1.66–24.99°. Non-H atoms were located in successive ΔF maps and refined anisotropically by full-Δmatrix least-squares on F^2. Hydrogen atoms were found from the difference Fourier map and refined isotropically. The crystal data and structure refinement details are given in Table 1. Non-hydrogen atomic coordinates and thermal parameters are listed in Table 2. The bond lengths and bond angles are listed in Table 3. The molecular structure and the packing arrangement in the unit cell are shown in Figs. 1 and 2, respectively.

3. Results and discussion

3.1. Photochromic properties

The yellow of A(enol form) changes to reddish orange under irradiation of the 365 nm light (or exposed in the sunlight). The color turns back to the original yellow when it is heated. Thus, the compound A has photochromic properties in the solid state. The powder-UV reflectance spectra of A at 298 K for different light irradiated times are recorded on a HITACHI UV-3010 spectrophotometer and shown in Fig. 3. A new absorption band appears around 480 nm, which indicates the title compound exhibits photochromic properties in the solid state. However,

Table 2

Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for A*

Atom	x	y	z	U(eq)	Atom	x	y	z	U(eq)
S(1)	8215(1)	1425(1)	1779(1)	50(1)	S(1′)	13216(1)	6533(1)	2956(1)	71(1)
S(2)	7320(1)	1760(1)	2998(1)	49(1)	S(2′)	12440(1)	5385(1)	3965(1)	61(1)
O(1)	9769(2)	4096(2)	2672(1)	53(1)	O(1′)	14768(2)	3893(2)	2567(1)	51(1)
N(1)	11663(2)	4046(2)	2483(1)	36(1)	N(1′)	16689(2)	4064(2)	2539(1)	37(1)
N(2)	12595(2)	3561(2)	2724(1)	38(1)	N(2′)	17629(2)	4163(2)	2961(1)	36(1)
N(3)	9536(2)	2190(2)	3398(1)	42(1)	N(3′)	14517(2)	4572(2)	3979(1)	39(1)
N(4)	9384(2)	2030(2)	2772(1)	43(1)	N(4′)	14365(3)	5233(2)	3541(1)	46(1)
C(1)	12601(3)	4518(3)	1611(2)	68(1)	C(1′)	17641(3)	3915(2)	1623(2)	48(1)
C(2)	12565(3)	4927(3)	1041(2)	83(2)	C(2′)	17703(3)	4114(3)	1013(2)	70(1)
C(3)	11596(3)	5311(3)	772(2)	61(1)	C(3′)	16864(4)	4606(3)	688(2)	79(1)
C(4)	10646(3)	5285(2)	1065(2)	57(1)	C(4′)	15966(3)	4906(3)	965(2)	65(1)
C(5)	10663(3)	4878(2)	1631(2)	51(1)	C(5′)	15904(3)	4728(2)	1578(2)	48(1)
C(6)	11649(3)	4495(2)	1908(1)	36(1)	C(6′)	16751(2)	4231(2)	1902(1)	34(1)
C(7)	10740(3)	3768(2)	2784(1)	36(1)	C(7′)	15743(3)	3995(2)	2845(1)	36(1)
C(8)	11173(2)	3102(2)	3211(1)	33(1)	C(8′)	16141(2)	4069(2)	3481(1)	35(1)
C(9)	12306(3)	3014(2)	3165(1)	34(1)	C(9′)	17300(3)	4148(2)	3522(1)	34(1)
C(10)	13179(3)	2419(2)	3488(2)	55(1)	C(10′)	18161(3)	4257(2)	4066(1)	52(1)
C(11)	10429(3)	2633(2)	3605(1)	36(1)	C(11′)	15389(3)	4054(2)	3971(1)	34(1)
C(12)	10634(3)	2692(2)	4284(1)	36(1)	C(12′)	15562(3)	3392(2)	4479(1)	34(1)
C(13)	11508(3)	3205(2)	4576(2)	49(1)	C(13′)	16260(3)	2654(2)	4445(2)	49(1)
C(14)	11688(3)	3249(3)	5213(2)	65(1)	C(14′)	16387(3)	2028(3)	4915(2)	62(1)
C(15)	10989(4)	2793(3)	5559(2)	70(1)	C(15′)	15832(4)	2142(3)	5428(2)	65(1)
C(16)	10097(4)	2289(3)	5279(2)	67(1)	C(16′)	15137(3)	2872(3)	5468(2)	58(1)
C(17)	9931(3)	2235(2)	4647(2)	54(1)	C(17′)	15003(3)	3495(2)	5003(2)	48(1)
C(18)	8379(3)	1744(2)	2510(1)	36(1)	C(18′)	13410(3)	5721(2)	3469(2)	45(1)
C(19)	6074(3)	1505(3)	2490(2)	67(1)	C(19′)	11263(3)	6099(3)	3730(2)	118(2)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected bond lengths (Å) and angles (°) for A*

S(1)C(18)	1.661(3)	S(1′)C(18′)	1.648(3)
S(2)C(18)	1.740(3)	S(2′)C(18′)	1.743(3)
S(2)C(19)	1.787(3)	S(2′)C(19′)	1.782(4)
O(1)C(7)	1.248(3)	O(1′)C(7′)	1.254(3)
N(1)N(2)	1.374(3)	N(1′)N(2′)	1.374(3)
N(1)C(7)	1.401(4)	N(1′)C(7′)	1.374(3)
N(1)C(6)	1.425(4)	N(1′)C(6′)	1.429(4)
N(2)C(9)	1.338(4)	N(2′)C(9′)	1.331(4)
N(3)C(11)	1.285(4)	N(3′)C(11′)	1.290(3)
N(3)N(4)	1.385(3)	N(3′)N(4′)	1.371(3)
N(4)C(18)	1.332(4)	N(4′)C(18′)	1.338(4)
C(7)C(8)	1.418(4)	C(7′)C(8′)	1.426(4)
C(8)C(9)	1.364(4)	C(8′)C(9′)	1.372(4)
C(8)C(11)	1.478(4)	C(8′)C(11′)	1.471(4)
O(1)–C(7)–N(1)	122.9(3)	O(1′)–C(7′)–N(1′)	121.9(3)
O(1)–C(7)–C(8)	131.3(3)	O(1′)–C(7′)–C(8′)	132.1(3)
N(1)–C(7)–C(8)	105.8(3)	N(1′)–C(7′)–C(8′)	105.9(3)
N(4)–C(18)–S(1)	120.6(2)	N(4′)–C(18′)–S(1′)	121.9(3)
N(4)–C(18)–S(2)	113.7(2)	N(4′)–C(18′)–S(2′)	112.4(3)
S(1)–C(18)–S(2)	125.7(2)	S(1′)–C(18′)–S(2′)	125.7(2)
N(2)–N(1)–C(7)	107.5(2)	C(7′)–N(1′)–N(2′)	108.8(2)
C(9)–N(2)–N(1)	109.6(3)	C(9′)–N(2′)–N(1′)	108.7(2)
N(2)–C(9)–C(8)	109.2(3)	N(2′)–C(9′)–C(8′)	109.7(3)
C(9)–C(8)–C(7)	107.8(3)	C(9′)–C(8′)–C(7′)	106.7(3)
N(1)–C(7)–C(8)	105.8(3)	N(1′)–C(7′)–C(8′)	105.9(3)

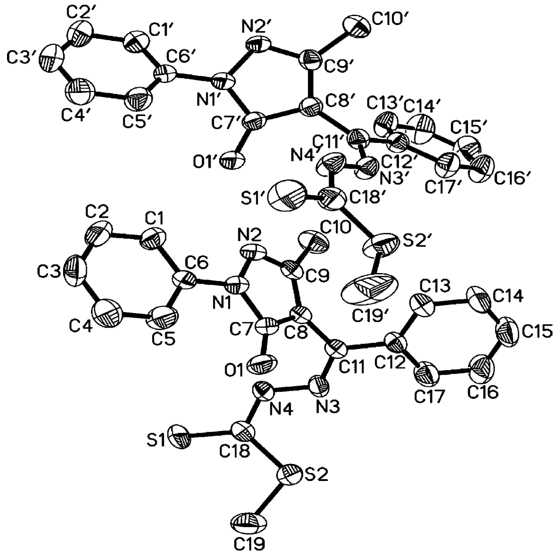


Fig. 1. Crystal structure of A*.

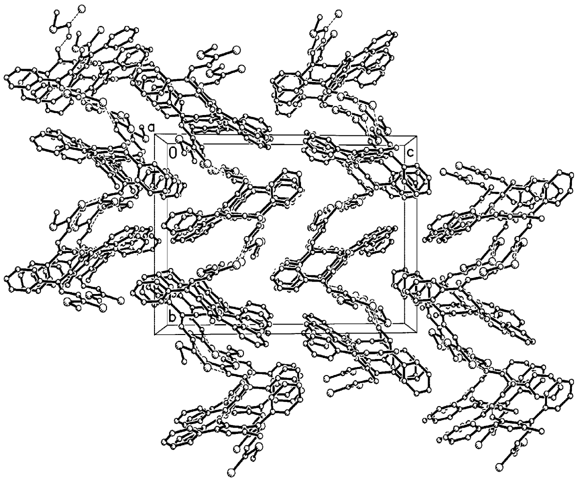


Fig. 2. Molecular packing of A*.

the title compound does not exhibit the photochromism in the solution.

3.2. Kinetics of the photochromic reaction

The first-order rate constant of A(enol-form) was determined essentially as described in the literature [25]. The experimental data were treated with the standard integrated expression:

$$\ln\frac{A_\infty - A_0}{A_\infty - A_t} = kt \qquad (1)$$

where A_0, A_t, A_{00} are the observed absorption data corresponding to 480 nm wavelength at the beginning, at time t, and at the end of the reaction, respectively.

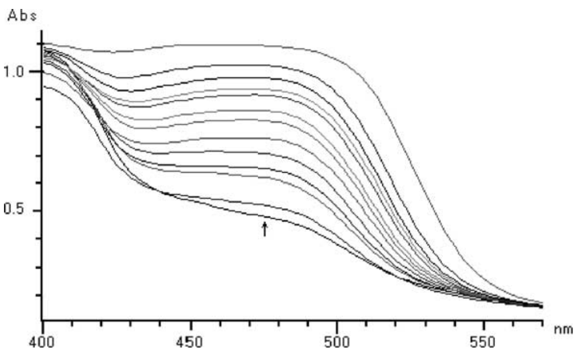


Fig. 3. UV reflectance spectra of photochemical coloration of A with 365 nm light at 298 K.

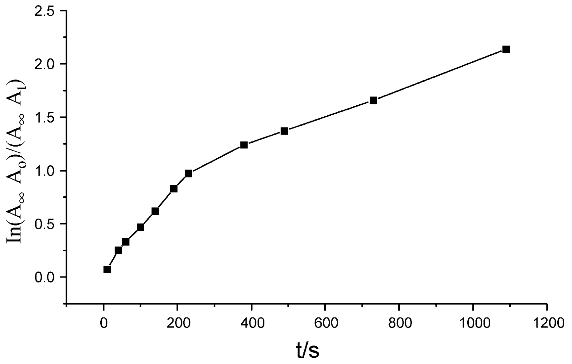


Fig. 4. kinetic plot of photoisomerization (enol → keto) reaction of A induced by 365 nm light.

The kinetic curve of the photochromic reaction for the title compound is plotted according to the Eq. (1) and shown in Fig. 4. It is observed that the photoisomerization is not proceeded at the certain speed during the whole reaction. For comparison purpose, the whole plot is spited into two parts (Figs. 5 and 6). Initially, the spectral changes of A under UV irradiation mainly occurred in the 400–550 nm region giving rise to fast change of the color and increase of the absorbance. Which is corresponding to the first part of the kinetic curve in Fig. 4. A good linear fit as found in the kinetic plot (Fig. 5) from which the first-order or preudo-first-order rate constant was obtained as $3.98 \times 10^{-3}\ s^{-1}$. For longer irradiation times of A, the absorbance increased slowly. A good line was found in Fig. 6, from which the first-order rate constant was obtained as $1.26 \times 10^{-3}\ s^{-1}$. The results indicate that the photochemical reaction for A(enol-form) before 250s is faster 3 times than after 250s, and is faster 3–10 times than the analogous compound reported previously [22], which is in agreement with the phenomena observed. The reason is that the photochemical reaction before 250s occurs in the surface of the compound and the reaction after 250s occurs in the inner. So the rate constants of two parts are different.

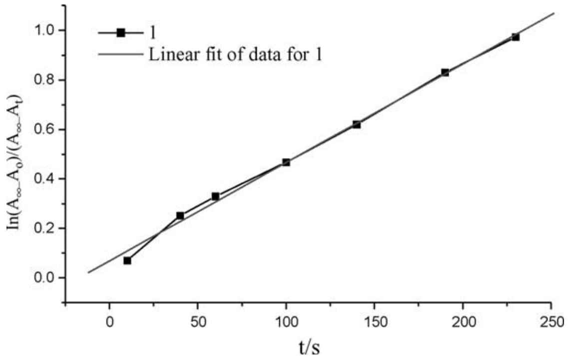


Fig. 5. First-order kinetic plot of photoisomerization reaction of A induced by 365 nm light before 250s.

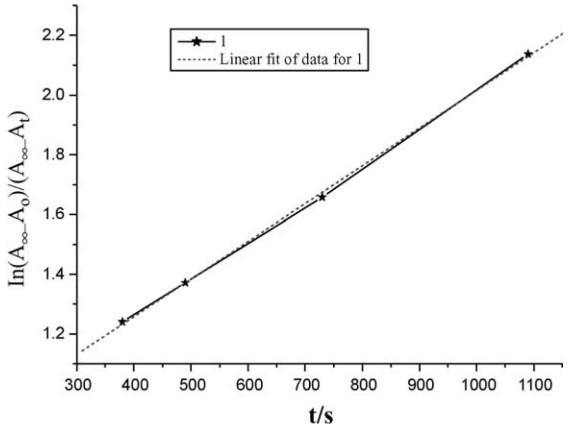
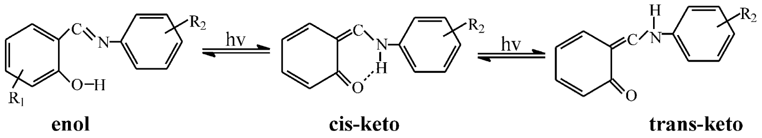


Fig. 6. First-order kinetic plot of photoisomerization reaction of A induced by 365 nm light after 250s.

3.3. Analyses of crystal structure

The reliable structure data of A are not obtained because the crystal of A is easily turned into A* during measurement. Thus, the crystal structure data of photocolored product are only reported in this paper. From Fig. 1, it is observed that there are two crystallographically independent molecules in an asymmetric structure unit, not related one to another by symmetry, but associated by an intermolecular H-bond (N2–H…O1′, 2.683 Å, 174°). The H-bond distance is slightly longer than that of PMBP thiosemicarbazone (2.632 Å) and slightly shorter than the value for PMBP methyl thiosemicarbazone (2.701 Å) reported previously [22]. The corresponding bond lengths and angles in the two molecules are nearly similar. There are also intermolecular H-bonds[N4–H…S1′, 3.495 Å, 155°; N4′–H…S1, 3.509 Å, 157°] between the neighboring molecules. The hydrogen bonds assembled the moieties into a supramolecule with infinite long-chain structure along



Scheme 2.

b axle as shown in Fig. 2. It is interaction of these hydrogen bonds that contribute to the stabilization of the title compound. Finally, it is important to mention that two molecules in Fig. 1 display different configuration. The dihedral angles between pyrazolone-ring and phenyl ring of N(1), C(11) are 17.2°, 61.7°, respectively. In the other molecules, the dihedral angles between pyrazolone-ring and phenyl-ring of N(1)′, C(11)′ are 39.0°, 64.8°, respectively.

3.4. Mechanism of photochromism

The IR spectra analysis in [21] show that the yellow compound (A) is the enol form before the photocoloration takes place. The C7–O1 and C7′–O1′ band distances are 1.248(3) nm and 1.254(3) nm, respectively, which is indicative of significant double character. So the reddish orange compound is the keto-form. The structure of A* shows that an intermolecular hydrogen bond [N2–H…O1′] exists between neighboring molecules. It suggests that the change of color is due to the photoisomerization from the enol form to the keto form. It is different from the photochromic processes of Schiff base compounds proposed by Cohen and Schmidt. The photocoloration processes of Schiff bases such as Salicylaldehyde and its derivatives was suggested as the mechanism of intramolecular proton transfer from the hydroxylic group to the imine (–CH=N–) nitrogen atom (shown in Scheme 2). However, it is almost impossible for A to transfer hydroxyl proton (O–H) to N2 atom of pyrazolone-ring in molecule itself because the proton must surmount not only the bonding effort with N2 but also potential barrier, especially when it pass through pyrazolone-ring with great electron cloud density. According to the results of structure analyses, the photochromic process of A is considered to be similar to that of analogous compounds with the same environment reported previously. So the intermolecular proton transfer mechanism of the photochromism postulated previously [21] is further supported by crystal structure analyses of PMBP S-methyl thiosemicarbazone carried out in this paper.

4. Supplementary data

Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, deposition number 188947.

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