Available online at www.sciencedirect.com

Journal of Photochemistry and Photobiology A: Chemistry 171 (2005) 243–249

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Photochromism in solid state and acidichromism in solution of 1-phenyl-3-methyl-4-(4′-methylbenzal)-pyrazolone-5 thiosemicarbazone

Bang-Hua Peng[a], Guang-Fei Liu[a], Lang Liu[a], Dian-Zeng Jia[a,*], Kai-Bei Yu[b]

[a] *Institute of Applied Chemistry, Xinjiang University, Urumqi 830046, PR China*
[b] *Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu 610041, PR China*

Received 20 July 2004; received in revised form 12 October 2004; accepted 13 October 2004
Available online 8 December 2004

Abstract

1-Phenyl-3-methyl-4-(4′-methylbenzal)-pyrazolone-5 thiosemicarbazone (PM4MBP-TSC) has been synthesized and its single crystal has also been developed. Its photochromism is investigated in the solid state through the analyses of its UV–vis reflection spectra and the mechanism is proved to be intermolecular proton transfer by the structure analysis. The acidichromic properties were also studied from the absorption and fluorescence spectra by adding acetic acid to the methanol solution of the compound. The observed phenomena can be explained by the solute–solvent complex of PM4MBP-TSC and the acetic acid constituted in the solution that destroyed the former conjugated structure.

Keywords: Pyrazolone; Proton transfer; Photochromism; Acidichromic properties

1. Introduction

Photochromism is defined as a reversible transformation between two isomers having different absorption spectra by photoirradiation [1]. Up to date among the large number of photochromic molecules investigated, few have been found to be photochromic in the crystalline state. Photochromic organic crystals are interesting not only for the design of new materials for optical data processing and storage, but also because the photoinduced molecular transformations might be used to gain control over other physical properties in the solid state [2,3]. The crystalline photochromic materials also show a fatigue resistant character and have a promising potential for optoelectronic devices. For instance, the photoswitching of NLO properties has been recently achieved in photochromic organic crystals [4].

Hydrogen transfer is a possible mechanism for the crystalline photochromism. There have been many studies of proton transfer (PT) in the solid state and solution [5–7]. The dynamics of the photoinduced PT is of great interest from basic and application point of view. Its mechanism has been discussed to verify whether or not a quantum mechanical tunneling takes place [8]. PT reaction (proton tautomerism) is central to several fields of chemistry and biochemistry, and plays a key role in pharmaceutical action, enzyme activity, and the stabilization of base pairs in duplex DNA. Schiff-bases are an interesting class of compounds possessing O–H···N hydrogen bond and the PT reaction can proceed through it. These compounds are often thermo- or photochromic, undergoing reversible PT (tautomerism) in the solid state. Generally, the enol-imine (OH) form is the most stable form at room temperature and is in equilibrium with the keto-enamine (NH) form. As a result, the OH form of Schiff-bases has been well characterized. However, until recently, no NH form had been structurally characterized [9,10].

In our earlier studies, we reported results on photochromic thiosemicarbazones derived from 4-acyl pyrazolone [11,12]. Here, we report a solid-state photochromic compound: 1-phenyl-3-methyl-4-(4′-methylbenzal)-pyrazolone-5 thiosemicarbazone (PM4MBP-TSC). Its photochromic properties are due to intermolecular proton transfer. We also analyzed the acidichromic properties by means of UV–vis absorption and fluorescence spectra in its methanol solution.

---

[*] Corresponding author. Tel.: +86 991 858 2887; fax: +86 991 858 1006.
E-mail address: jdz@xju.edu.cn (D.-Z. Jia).

1010-6030/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2004.10.011

We found that there existed an acid–base equilibrium in solution. When a neutral methanol solution is made acidic by adding acetic acid, the absorption and fluorescence spectra are substantially changed, which can be recovered by adding base solution to it. This suggests that the spectral characteristics of photochromic species are reversibly changed by pH value variance. We believe that research in the area of acidichromism will become more active, as the absorption and emission characteristics of such chromophoric species may be tuned by adjusting the pH value. The purpose of this investigation is to identify the nature of this species' photochromic properties in the solid state and acidichromic properties in solution.

2. Experimental

The preparation of 1-phenyl-3-methyl-4-(4′-methylbenzoyl)-pyrazolone-5 (PM4MBP) was according to literature [13].

1-Phenyl-3-methyl-4-(4′-methylbenzal)-pyrazolone-5 thiosemicarbazone (PM4MBP-TSC) was synthesized from stoichiometric mixtures of particular PM4MBP and thiosemicarbazide (TSC) in ethanol at refluxing temperature under a constant stirring, which condensed to the solid state. The white solid products were then recrystallized from ethanol. Elemental analyses of $C_{19}H_{19}N_5SO\cdot C_2H_5OH$: found (%)—C, 61.36; H, 6.45; N, 16.85; calculated (%)—C, 61.29; H, 6.12; N, 17.02. The elemental analyses were determined on model PE-2400C elemental analyzer. ^1H NMR (DMSO-d_6) were carried out on INOVA-400^1H NMR Spectrometer. ^1H NMR (DMSO-d_6): $\delta = 10.227$ (0.6H, Pz-NH), $\delta = 9.769$ (0.4H, Pz-OH), $\delta = 7.295$–7.965 (m, 10H, 2Ph + NH), $\delta = 7.180$ (d, 2H, NH_2), $\delta = 2.383$ (s, 3H, Pz-CH_3), $\delta = 1.794$ (s, 3H, Ph-CH_3). All the other solvents, such as ethanol and methanol are analytical grade and were used without further purification. Room temperature absorption and fluorescence spectra were recorded by a Hitachi UV-3010 spectrometer and LING GUANG 970-CRT spectrofluorophotometer, respectively. Irradiation of microcrystalline sample of PM4MBP-TSC was carried out using a pressed pellet. The pH values were determined by using the METTLER TOLEDO DELTA 320 pH meter, which was calibrated by standard buffer solutions of pH 4.01 and 6.82. The pH value of solution was adjusted by dropwise addition of acetic acid solution to its methanol solution. X-ray diffraction data were collected at 296 K on a Siemens *P*4 four-circle diffractermeter using graphite monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å). The crystal structure was solved by direct method and refined by full-matrix least squares on F^2. Empirical absorption was applied. The intensity was measured by ω-scans. The diffraction data were collected from reflections in the range of 2.06–25.25°. Hydrogen atoms were added theoretically and refined isotropically. All calculations and drawings were performed by the *SHELXTL*-97 crystallographic software package of molecular structure.

3. Results and discussion

3.1. Photochromic properties in solid state and the crystallographic explanation

White solid products of I (Scheme 1) changes its color to yellow (II) under the irradiation of 365 nm light. The dramatic color changes can be explained by the different electronic states (proton tautomerism) resulting from the photoirradiation. Photoinduced proton transfer (PT) from one moiety to another is of great interest. The proton transfer change and the configuration rearrangement of the π–electrons lead to large spectral changes [14]. Particularly, the striking feature in the experiment is that the relative intensity of UV–vis reflection band increases after UV light irradiation. The powder-UV reflection spectra at 298 K for different irradiation time intervals are recorded and shown in Fig. 1. A new broad reflection band between 350 and 450 nm was observed and it continuously increased as measurement continued, which suggests that the title compound exhibits photochromic properties in the solid state.

But the ultraviolet irradiation has no influence on the absorption spectrum recorded in solution and the thermal-decoloration reaction cannot occur when the solid sample was heated.

The kinetic curve (Fig. 2) is plotted according to Eq. (1) [3,4,15]

$$kt = \ln[(A_\infty - A_0)/(A_\infty - A_t)] \qquad (1)$$

where k is the first-order rate constant. A_0, A_∞ and A_t are the observed reflection data measured at the beginning, at the end and at time t of the reaction, respectively. All reflection data are acquired from Fig. 1 at 390 nm, at which the maximum changes in optical density occurred. From Fig. 2, it can be seen that it represents a good linear fit. The photochromic reaction process follows the first-order kinetics and the pseudo-first-order rate constant is obtained from the slope as $k = 8.4 \times 10^{-5}\ s^{-1}$. To obtain more information about the coloration process, an absorbance diagram (E-diagram) [16] of the system is formulated (Fig. 3). The re-

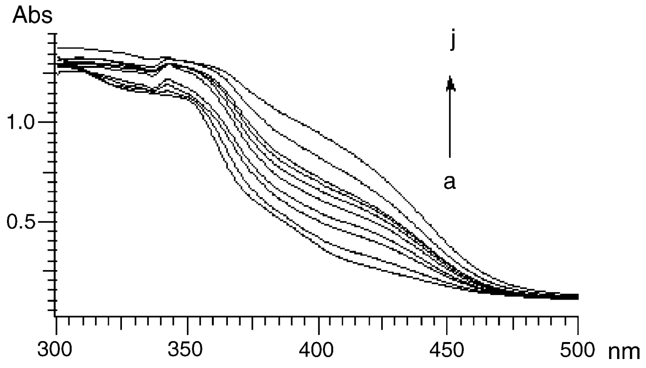
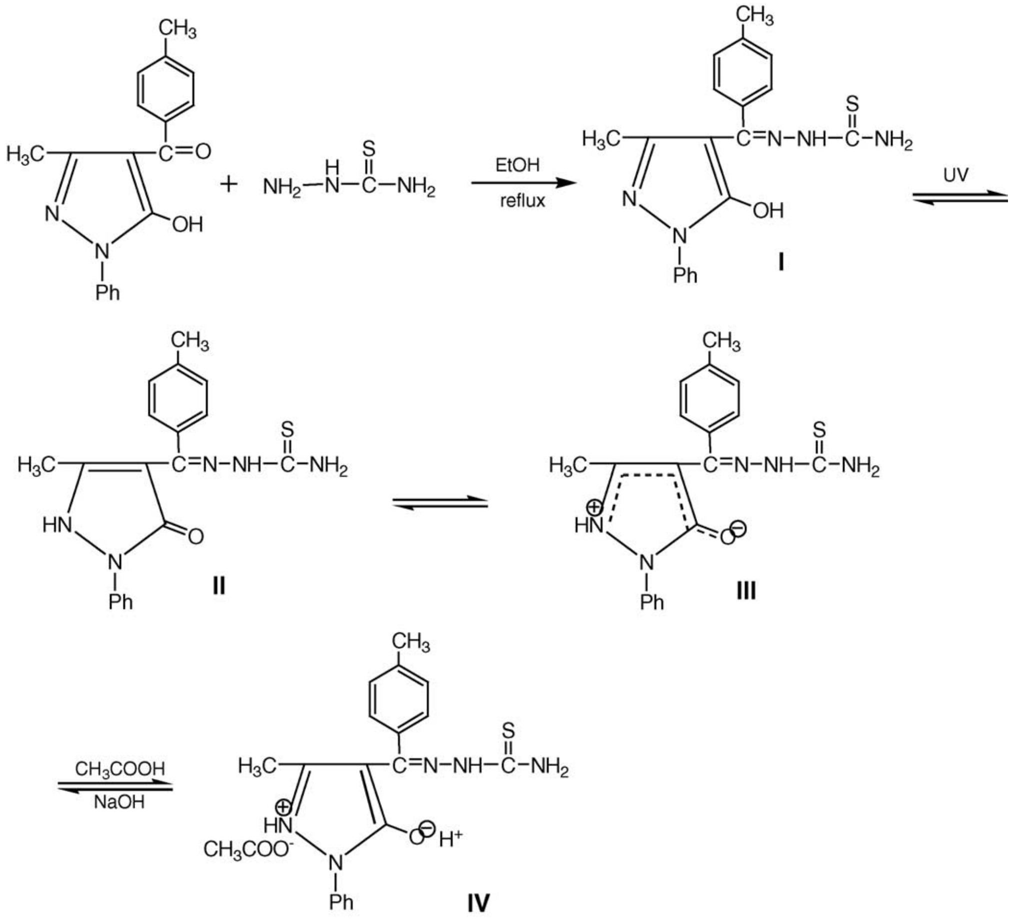


Fig. 1. UV–vis reflection spectral changes in the solid state of PM4MBP-TSC. From a to j, each irradiation time (min) is 0, 15, 45, 70, 105, 135, 165, 195, 315, 516.



Scheme 1. Reaction equation and tautomerization for PM4MBP-TSC.

flection at λ = 390 nm is plotted against those at 420, 410, and 370 nm during the coloration of the compound. The straight lines in the E-diagram indicate that the reaction is a uniform one. In other words, only one linear independent step is contained in the photo-coloration process [17].

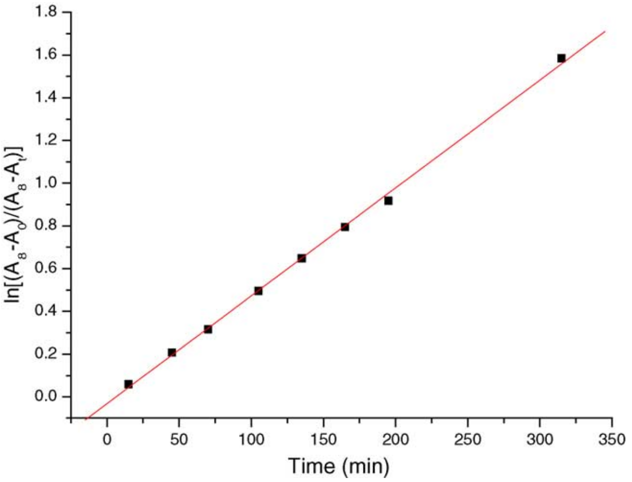


Fig. 2. First-order kinetic plot of photoisomerization reaction of PM4MBP-TSC induced by 365 nm light.

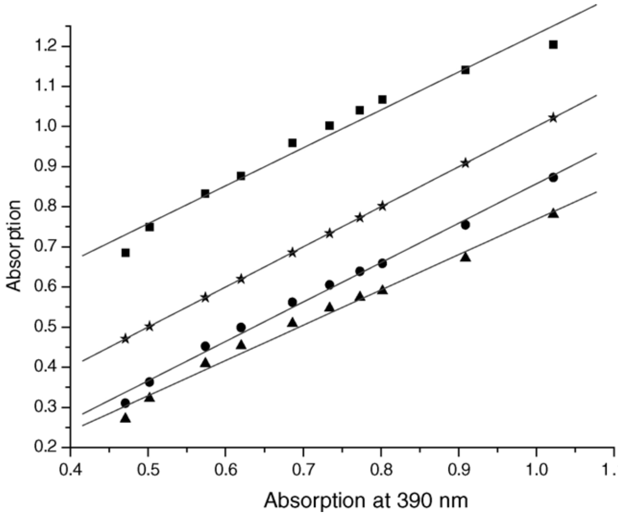


Fig. 3. E-diagram of PM4MBP-TSC. The reflection at 390 nm (*) is plotted against those at 370 nm (■), 410 nm (●) and 420 nm (▲).

By slowly evaporating the mixture solution of ethanol–chloroform (1:1) without avoiding the sunlight at room temperature, we obtained the yellowish, transparent single crystal of PM4MBP-TSC. The molecular structure, atomic labeling

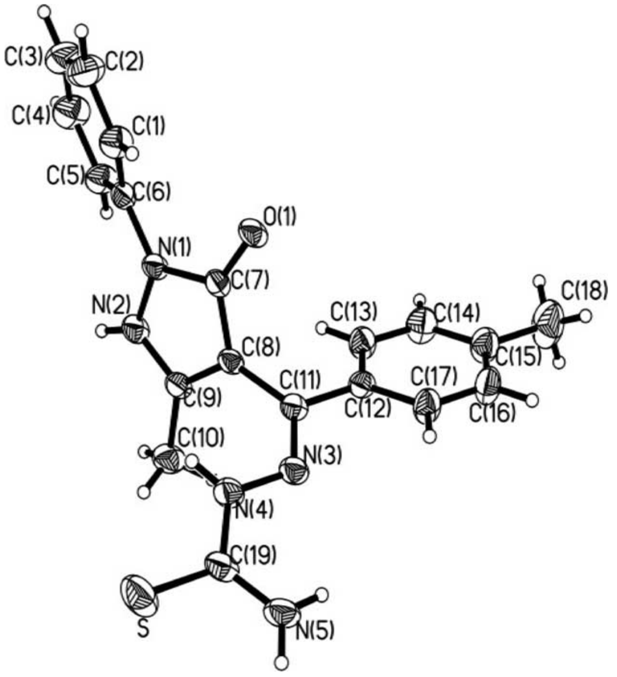


Fig. 4. Crystal structure of the title compound.

Table 1
Selected bond lengths (Å) and bond angles (°) for PM4MBP-TSC

Bond length		Bond angles	
S–C(19)	1.666(2)	C(11)–N(3)–N(4)	117.10(2)
O(1)–C(7)	1.259(2)	C(19)–N(4)–N(3)	119.93(2)
N(1)–N(2)	1.378(2)	N(5)–C(19)–N(4)	116.0(2)
N(1)–C(7)	1.392(2)	N(2)–N(1)–C(7)	108.49(2)
N(2)–C(9)	1.335(2)	C(9)–N(2)–N(1)	109.12(2)
N(3)–C(11)	1.293(2)	N(1)–C(7)–C(8)	105.38(2)
N(3)–N(4)	1.369(2)	N(2)–C(9)–C(8)	108.99(2)
N(4)–C(19)	1.358(2)	C(9)–C(8)–C(7)	107.87(2)
N(5)–C(19)	1.316(3)	N(3)–C(11)–C(8)	124.20(2)
C(8)–C(11)	1.477(3)	N(3)–C(11)–C(12)	116.34(2)

and possible configurations of the compound are shown in Figs. 4 and 5. Selected bond lengths and bond angles are compiled in Table 1. X-ray structure determination reveals that the C–O bond length of 1.259 Å (Table 1) is more characteristic of ketone than C–OH bond. Similarly, we can see that the C11–N3 (1.293 Å) is consistent with a C=N double bond, and that C9–N2 with a distance of 1.335 Å is apparently single bond. The bond distances around C19, which is 1.358, 1.316, and 1.666 Å for N4, N5 and S, respectively, are partial double-bond characters. Thus, the elongation of the C=S bond and shrinkage of C19–N5 are observed. Such conformation would be expected to increase the strength of the intermolecular hydrogen bonds, which stabilizes the keto form in the crystal state [18]. In PM4MBP-TSC, the dihedral angle between mean plane C7–C8–C9–N1–N2 (mean deviation 0.0138 Å) (I) and the plane C12–C13–C14–C15–C16–C17 (mean deviation 0.0054 Å) (II) is 80.3°. The dihedral angle of plane II with the plane N3–N4–C19–N5 (mean deviation 0.0048 Å) (III) is 34.2°, which indicates the non-coplanarity of the molecule probably induced by steric hindrance effect of phenyl substituent on C11 and the hydrogen bonding requirement. In the compound, there are intermolecular hydrogen bonds N2–H···O (2.765 Å), N5–H···O (3.008 Å), N4–H···O (3.108 Å), but there was no intramolecular hydrogen bond in the crystal.

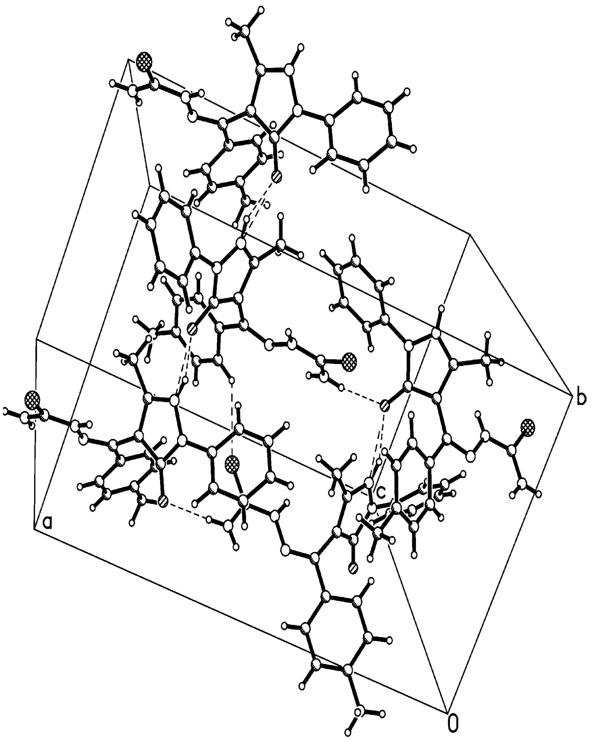


Fig. 5. Crystal packing in the unit cell.

The X-ray structure of the yellow crystal has several important implications [19] for the proposed reaction mechanism in PM4MBP-TSC photochromics (Scheme 1): (a) the structure of the photoproduct represents the first direct evidence that the yellow coloration of PM4MBP-TSC exposed to UV-light can be assigned to the NH tautomer (II). Pyrazolones exist mainly in several tautomers, in the OH and NH forms [20,21], and analyzing the ^{1}H NMR, the ratio between NH form and the OH form of the compound is 3:2 in solution, all of which show there is a balance between different tautomers in solution. (b) The color change of the compound may be due to the molecular configurational transformation between their isomers, as in this compound, there are *enol* and the *keto* tautomers, so that the transformation may occur between them through PT reaction. Since there are no significant intramolecular interactions in the crystal structure of the NH form, the PT in the solid state clearly is an intermolecular process. (c) The PT reaction can proceed despite the unfavorable donor–acceptor orientation in the reactant of OH form like any other Schiff-bases. Finally, it is worth pointing out that the color change was not accompanied by any significant structure changes.

Based on the analysis above, it is concluded that the white products (I) changed into the yellowish ones after irradiation which is a keto form (II). Therefore, a photoisomerization reaction must have taken place during irradiation process. This proves that photoexcitation was followed by a rapid PT and subsequently rearranged to form the II colored products. The rules governing the photo equilibrium are determined not only by chemical factors but also depended on the crystal structure as well, as crystal packing plays a crucial role in photochromism, i.e., on the ability of the independent moieties to perform the required conversion from enol form to keto form [7]. In the ground state, the enol form is more stable than the keto form, however, in the excited state, the keto form is more stable than the enol form. Hence, the enol form changed into the keto form, along with the proton moving spontaneously after photoexcitation [22]. This can be interpreted as intermolecular PT mechanism. From the hydrogen connection diagram, we can see that there exists intermolecular hydrogen bond between N2–H and O1 (2.765 Å). Concerning the bond distance, the proton donor and the proton acceptor site is sufficiently close in intermolecular hydrogen bond. The sum of the Vander Waals radii of N and O (3.07 Å) [23] is significantly longer than this hydrogen bond length of 2.765 Å, which enables direct tunneling of the proton between them, so that the enol form I tautomerized to the keto form II through hydrogen transfer when irradiated by UV-light (Scheme 1).

3.2. *Absorption and fluorescence spectra in acidic and basic media*

It has been pointed out earlier that the photochemistry of Schiff-bases compounds in solution is quite different from that of solid state sample [24]. This must be due to some packing arrangement in the solid sample, but this rigid arrangement does not exist in solution. To date, however, there has been no report of a detailed investigation of the effect of pH on the spectral properties of thiosemicarbazones in solution. Therefore, we studied the effect on the spectral properties by varying the pH value of PM4MBP-TSC in methanol solution. It was observed that PM4MBP-TSC is quite sensitive to solution pH value. When a neutral methanol solution of PM4MBP-TSC is made acidic by adding acetic acid, the absorption and fluorescence characteristics are substantially changed. We coined the phrase acidichromism to indicate such a phenomenon, wherein the spectral characteristics of an acidichromic species are reversibly changed by pH variance. Results described herein include pH-dependent acidichromic processes of PM4MBP-TSC in methanol solution.

The strength of the hydrogen bond relates to the equilibration of the amount of the resonance structures, and consequently to the equilibration of bond length. It is shown that the flow of electrons through the coupled bonds compensates for the increase of the atomic charges caused by the PT process, and leads to strengthening of the intermolecular hydrogen bond. Effectiveness of resonance was characterized by different factors based on bond length. It has been proposed that the resonance enhancing of the hydrogen bond strength is the most effective in symmetrical O–H–O and N–H–N bonds [22]. Schiff-bases are reported to be in the zwitterionic form as the resonant existence of the keto form [9]. Therefore, in methanol solution of PM4MBP-TSC, form III (Scheme 1) may exist along with other tautomers, and perhaps, the large stabilization of the zwitterionic form brought about by the resonance seems to be an important factor in permitting solution acidichromism.

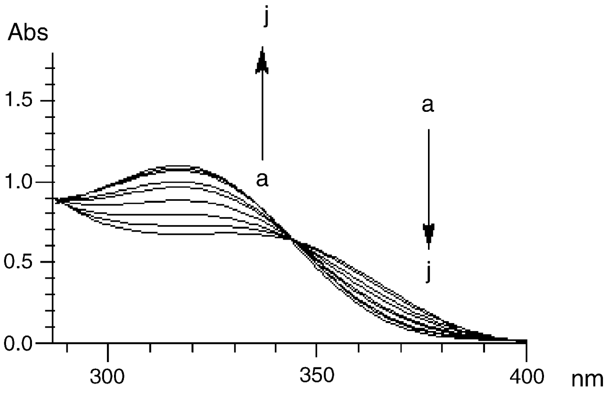


Fig. 6. Absorption spectra of PM4MBP-TSC in methanol solution. The values of pH from a to j are: 7.92, 5.74, 5.28, 5.09, 4.97, 4.76, 4.56, 4.35, 4.04, 3.66.

Fig. 6 shows the acidichromic effects in 5.0×10^{-5} M PM4MBP-TSC methanol solution. The curve a represents the absorption spectrum of PM4MBP-TSC in pure methanol solution. The absorption band was found to be relatively sensitive to the presence of acetic acid. When adding acetic acid, the optical density of the region around 360 nm decreased noticeably. However, a new absorption band appeared around 320 nm, and its intensity increased as the pH value was lowed. The solution pH value, as determined by pH electrode, ranged from value 7.92 (curve a) to 3.66 (curve j). Under acidic conditions, the first band ($\lambda = 360$ nm) decreases while the second band ($\lambda = 320$ nm) develops with decreasing pH value, and this change is not obvious when the concentration of acid reach some extent. This suggests there is a balance between the new compound and the former one. The acidichromic product PM4MBP-TSC·CH_3COOH (IV), which is generated upon addition of acetic acid, spontaneously changes to the former form at room temperature through addition of NaOH solution (Fig. 7). However, there are some discrepancies compared to Fig. 6: the bands around 360 nm did not restore by adding base solution. This is, perhaps, because of the formation of CH_3COONa, which changes the solution condition to lead to the discrepancy. From Fig. 6, we can calculate the pK_a of PM4MBP-TSC according to Eq. (2):

$$A = A_{A^-} + [((A_{HA} - A)[H^+])/K_a] \qquad (2)$$

Curve is plotted (Fig. 8), where A is the solution absorbance of different pH, A_{HA} and A_{A^-} the absorbance of conjugated

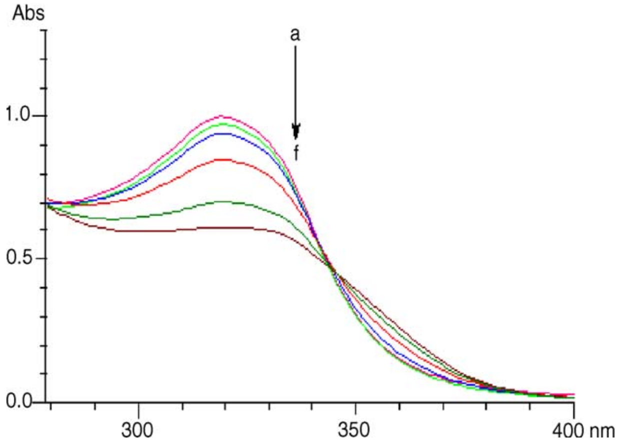


Fig. 7. Absorption spectra of PM4MBP-TSC acidic methanol solution continuing to add base solution. From a to f, the values of pH are: 3.30, 3.73, 4.15, 4.58, 4.87, 5.18.

acid and conjugated base in their maximal concentrations (all absorbance data observed at 320 nm). From the slope, we can get the $pK_a = 5.16$, and the A_{A^-} is 0.636.

The phenomenon can also be explained as follows: these pH-induced changes can be attributed to the enolic moiety functioning as an acid–base group. The acid–base equilibrium of the PM4MBP-TSC can be defined by $R–OH + CH_3COOH = R–OH \cdot CH_3COOH$, where the $R–OH \cdot CH_3COOH$ (structure IV in Scheme 1) denotes the acid form and the R–OH (structure III in Scheme 1) denotes the base form. One highly reactive functional group in the solution is the enolic anion, and thus in the presence of acid the form III may steadily transform into the protonated form IV.

The band around $\lambda = 360$ nm is characterized by a gradual blue shift with decreasing pH value, indicating the transformation from one form to another. This behavior indicates that the band is due to the ionized form, whereas the band around $\lambda = 320$ nm is due to nonionized form of the compound [25].

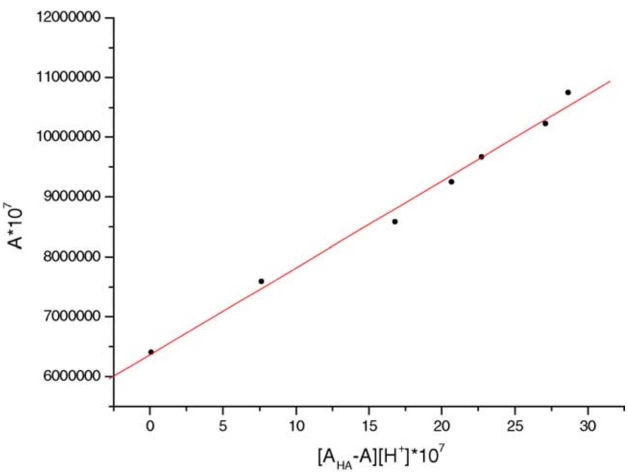


Fig. 8. $A–(A_{HA} - A)[H^+]$ plot of different pH.

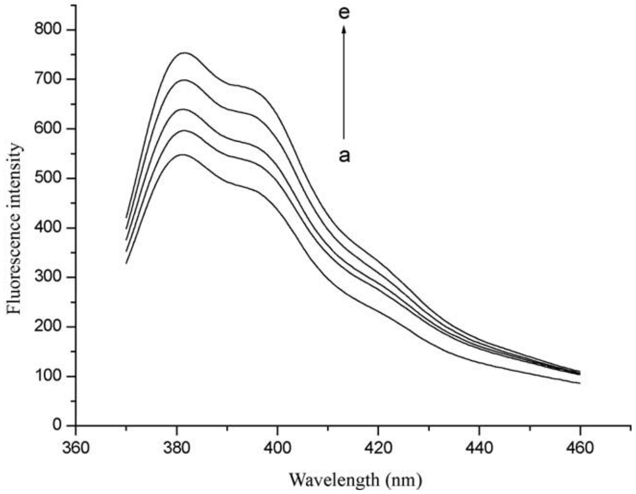


Fig. 9. Fluorescence spectra of PM4MBP-TSC in methanol solution upon addition of acetic acid. From a to e, the pH value decreases continuously.

Over this pH value range, an isosbestic point was observed, indicating that only two distinct species are involved in the acidichromic process associated with these curves. It also indicates that an acid–base equilibrium occurs between the nonionized and ionized species of PM4MBP-TSC [26]. The acidichromic products IV has a new absorption band centered at 320 nm, a hypsochromic shift of 40 nm compared with curve a. This result may be interpreted as following: In form III, the enolic oxygen is a good electron donor, while the nitrogen atom bound to the pyrazolone-ring is a good electron-withdrawing species, form III may exists as a fully conjugated structure having an extensive delocalized π–electron system which results from the donor–acceptor resonance structure shown in Scheme 1. When acetic acid begins to complex with the conjugated system, the donor–acceptor system is destroyed through the formation of an internal salt (IV). The loss of the donor–acceptor system is associated with reduced π-system delocalization and a concomitant hypsochromic shift in the absorption spectrum for the IV with respect to III [25].

The fluorescence spectra of the compound were studied in methanol solution of different pH values (Fig. 9). It can be seen that as the pH values decreased, there was an increase in fluorescence intensity around 380–400 nm, also indicating the acidichromic properties of title compound.

4. Conclusions

In this study, we analyzed the solid state photochromism of PM4MBP-TSC, which is mainly due to the intermolecular hydrogen transfer from the enol form to the keto form. We also observed its acidichromic properties by adding acetic acid solution to its methanol solution. The absorption and fluorescence spectra also are presented to illustrate these properties.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 20262005 and 20366005).

References

[1] Y.C. Liang, A.S. Dvornikov, P.M. Rentzepis, J. Photochem. Photobiol. A: Chem. 125 (1999) 79.

[2] T. Yamada, S. Kobatake, K. Muto, M. Irie, J. Am. Chem. Soc. 122 (2000) 1589.

[3] S.H. Kim, H.J. Suh, J.Z. Cui, Y.S. Gal, S.H. Jin, K. Koh, Dyes Pigm. 53 (2002) 251.

[4] S. Bénard, P. Yu, Chem. Commun. (2000) 65.

[5] M. Irie, T. Lifka, S. Kobatake, N. Kato, J. Am. Chem. Soc. 122 (2000) 4871.

[6] R. Casalegno, A. Corval, K. Kuldová, O. Ziane, H.P. Trommsdorff, J. Lumin. 72 (1997) 78.

[7] E. Hadjoudis, A. Rontoyianni, K. Ambroziak, T. Dziembowska, I.M. Mavridis, J. Photochem. Photobiol. A: Chem. 162 (2004) 521.

[8] T. Kobayashi, T. Sekikawa, T. Inabe, J. Lumin. 72 (1997) 508.

[9] J.H. Chong, M. Sauer, B.O. Patrick, M.J. Maclachlan, Org. Lett. 21 (2003) 3823.

[10] A. Grabowska, K. Kownacki, J. Karpiuk, S. Dobrin, Ł. Kaczmarek, Chem. Phys. Lett. 267 (1997) 132.

[11] X.C. Tang, D.Z. Jia, K. Liang, X.G. Zhang, X. Xia, Z.Y. Zhou, J. Photochem. Photobiol. A: Chem. 134 (2000) 23.

[12] L. Liu, D.Z. Jia, Y.L. Ji, K.B. Yu, J. Photochem. Photobiol. A: Chem. 154 (2003) 117.

[13] B.S. Jensen, Acta Chem. Scand. 13 (1959) 1668.

[14] O. Ziane, R. Casalegno, A. Corval, Chem. Phys. 250 (1999) 199.

[15] L. Liu, D.Z. Jia, Y.L. Ji, K.B. Yu, J. Mol. Struct. 655 (2003) 221.

[16] Y.T. Li, J.W. Zhou, Y.Q. Wang, F.S. Zhang, X.Q. Song, J. Photochem. Photobiol. A: Chem. 113 (1998) 65.

[17] X.J. Zheng, J.Y. Zhuang, L.P. Jin, Z.M. Wang, C.H. Yan, L.G. Zhu, Y.H. Mei, J. Mol. Struct. 595 (2001) 201.

[18] E.M. Jouad, M. Allain, M.A. Khan, G.M. Bouet, J. Mol. Struct. 604 (2002) 205.

[19] P. Naumov, A. Sekine, H. Uekusa, Y. Ohashi, J. Am. Chem. Soc. 124 (2002) 8540.

[20] R. Schobert, S. Iegfried, M. Nieuwenhuyzen, W. Milius, F. Hampel, J. Chem. Soc., Perkin Trans. 1 (2002) 1723.

[21] G.A. Chmutova, O.N. Kataeva, H. Ahlbrecht, A.R. Kurbangalieva, A.I. Movchan, A.T.H. Lenstra, H.J. Geise, I.A. Litvinov, J. Mol. Struct. 570 (2001) 215.

[22] A. Mandal, D. Fitzmaurice, E. Waghorne, A. Koll, A. Filarowski, S. Quinn, S. Mukherjee, Spectrochim. Acta A 60 (2004) 805.

[23] H. Ünver, M. Kabak, D.M. Zengin, T.N. Durlu, J. Chem. Crystallogr. 31 (2001) 203.

[24] M. Belletate, M. Leclerc, G. Durocher, J. Phys. Chem. 98 (1994) 9450.

[25] X.D. Sun, M.G. Fan, X.J. Meng, E.T. Knobbe, J. Photochem. Photobiol. A: Chem. 102 (1997) 213.

[26] C.J. Drummond, D.N. Furlong, J. Chem. Soc., Faraday. Trans. 86 (1990) 3613.