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ARTICLE TYPE

Photochromism and fluorescence modulation of pyrazolone derivatives in the solid state

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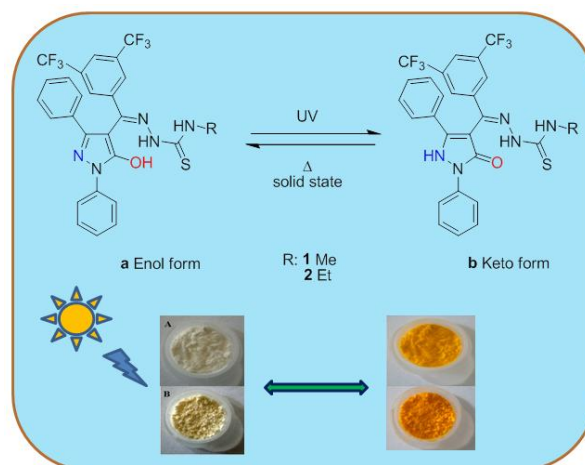
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Two novel photochromic compounds derived from pyrazolones, which displayed photochromic reaction in the solid state, have been synthesized and their photochromic and fluorescence properties were investigated. Their fluorescence emission can be efficiently modulated by photoisomerization of pyrazolones almost up to 90% upon UV light irradiation. Importantly, the fluorescence emission of **1** can be reversibly switched “on” and “off” upon alternative UV light irradiation and heating. These compounds exhibited photochromic coloration from white *E*-form to yellow brown *K*-form. On the basis of molecular structure determined by X-ray single crystal analysis, there are intermolecular hydrogen bonds which provide suitable proton transfer channels for enol-keto transformation. The colored *K*-form isomers which are very stable under ambient temperature may be due to the reverse reaction happen at a high temperature.

1. Introduction

Organic photochromic materials, as a class of important multifunctional materials, are of great current interest because of their potential applications in many fields, such as high-density optical data storage,¹ molecular switches,² sensors³ and so on. Studies at present time mainly focus on the derivatives of spiroopyrans,⁴ diarylethene,⁵ azobenzenes,⁶ fulgides,⁷ quinones⁸ and Schiff bases,⁹ but most of these compounds only showed photochromic properties in solution phase,¹⁰ which restricted their applications to a great extent. Therefore, the design, synthesis, and study of novel photochromic system are the goal that scientists constantly pursue. It is worthy of notice that solid-state photochromic compounds are still rather rare. Compounds in the solid state are very useful for special applications such as 3-D homographic memory.¹¹ Pyrazolones, which show reversible photochromic reactions in the solid state, possess potential actual application to optical memories and switches. The ability to predictably control these properties by varying the structure will be essential to develop photochromic materials for various applications.¹² Great efforts have been done to improve their performance by mainly changing the substituent groups at the 4-position on the pyrazolone ring.¹³ Although some organic compounds containing pyrazolone ring exhibit good photochromic properties and a high fatigue resistance,¹⁴ their properties still could not meet the growing demands for application in optical data storage. Whatever, the properties of pyrazolones required for a specific application can be optimized by varying substituent on their skeleton.

In this work, two novel compounds, 1,3-diphenyl-4-(3,5-bis(trifluoromethyl)benzal)-5-hydroxypyrazole (1a) and 4-methylthiosemicarbazone (1b) and 1,3-diphenyl-4-(3,5-bis(trifluoromethyl)benzal)-5-hydroxypyrazole 4-ethylthiosemicarbazone (2a), were synthesized successfully



Scheme 1. Photochemical reactions of **1** and **2**.

by introducing trifluoromethyl substituent onto the phenyl of 4-position of pyrazolone-ring as shown in scheme 1. Their reversible photochromic performances were detailed examined in the solid state. The observed on/off fluorescence modulation was reversibly switched upon alternative UV light irradiation and heating. In order to understand the relationship between the molecular structure and their photochromic behaviors of as-synthesized compounds, the crystal structure analysis were carried out by X-ray diffraction. The results showed that photochromic coloration reaction occurred in the solid state by an intermolecular proton transfer through hydrogen bonding under 365 nm light irradiation.

2. Experimental

2.1 Measurements

The TECH XT-6 melting point apparatus was used to measure melting point of compounds. ^1H NMR spectra were carried at room temperature on an INOVA-400 NMR Spectrometer with DMSO- d_6 as the solvent. The elemental analyses were made on FLASH EA 1112 Series NCHS-O analyzer. The FI-IR spectra were performed in the range of 400-4000 cm^{-1} on a BRUKER VERTEX 70 Spectrometer. The UV-Vis absorption spectra were measured by using a Hitachi U-3900H spectrometer equipped with an integrating sphere accessory. The Fluorescence spectra were studied by using a Hitachi F-4500 fluorescence spectrophotometer with a Xe arc lamp (150 W) as the light source at room temperature, and the breadths of excitation and emission slits were both 5.0 nm. A ZF-1 ultraviolet analysis instrument equipped with an ultraviolet lamp (15 W cm^{-2}) as the light source was used to study the powders' photocoloration, the distance between the sample and the light source was 15 cm.

Single crystals of **1** suitable for X-ray crystallographic work were grown by slow evaporation of their ethanol solution at room temperature. The data were collected by the ω -scan mole using a graphite monochromatized Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) on an imaging plate system (Rigaku R-AXIS SPIDER) at 298 K. Crystal structures was solved by direct methods and refined on F^2 by full-matrix least-squares methods with the SHELXTL-97 program. All non-H atoms were refined anisotropically. H atoms on nitrogen atoms were located from Fourier maps, and all of the other H atoms were placed in geometrically idealized positions and refined using riding model.

2.2 Materials

1,3-Diphenyl-5-pyrazolone was synthesized with the method described in literatures.¹⁵ 4-Methylthiosemicarbazide (MTSC), 4-ethylthiosemicarbazide (ETSC) and 3,5-bis(trifluoromethyl)benzoyl chloride were purchased from the J&K Company, the other reagents were AR grade, were purchased from commercial sources and used without further purification.

1,3-Diphenyl-4-(3,5-bis(trifluoromethyl)benzal)-5-pyrazolone was synthesized by the method according to the literature.¹⁶

2.3 Synthesis of compound 1a

1,3-Diphenyl-4-(3,5-bis(trifluoromethyl)benzal)-5-hydroxypyrazole 4-methylthiosemicarbazone (**1a**) was synthesized by refluxing of 1,3-Diphenyl-4-(3,5-bis(trifluoromethyl)benzal)-5-pyrazolone (3 mmol) and MTSC (3 mmol) in 4 mL of ethanol solution in the presence of glacial acetic acid (about 15 drops). And the mixture was refluxed for 2 h under magnetic stirring at 80 $^{\circ}\text{C}$ in an oil bath. After cooling to room temperature, filtration and purification of the crude product were carried out by recrystallization from ethanol in the dark. The white powder 1a was obtained. Yield 46%; M.p. 239.6-240.9 $^{\circ}\text{C}$; MS (m/z): 562.1 [M]. Elemental analysis calcd for $\text{C}_{26}\text{H}_{19}\text{N}_5\text{OSF}_6$: C, 55.41; H, 3.40; N, 12.43%. Found C, 55.52; H, 3.38; N, 12.30%; ^1H NMR (400 MHz, DMSO- d_6): δ 10.393 (1H, N2-H), 8.921 (1H, N4-H), 8.259 (1H N5-H), 7.946-7.147 (13H phenyl-ring) 3.171-3.084 (3H CH_3); ^{13}C NMR (100 MHz, DMSO- d_6): δ 178.44, 148.18, 141.11, 140.01, 139.09, 138.03, 130.95, 130.63, 130.29, 129.96, 129.24, 129.15, 129.01, 128.92, 128.61, 127.85, 127.42, 126.70, 126.52, 124.70, 122.32, 122.05, 121.99, 121.71, 119.06, 31.56;

IR (ν , cm^{-1}): (the white powders before irradiation): 3597 $\nu(\text{O-H})$, 3373 $\nu(\text{N-H})$, 1664 $\nu(\text{C=O})$, 1613 $\nu(\text{C=N})$, 1558, 1497, $\nu(\text{phenyl})$, 1462, 1414, 1390 $\nu(\text{pyrazole-ring})$, 1187, 1137 $\nu(\text{C=S})$; (the orange powders after irradiation): 3597 $\nu(\text{O-H})$, 3373 $\nu(\text{N-H})$, 1664 $\nu(\text{C=O})$, 1613 $\nu(\text{C=N})$, 1549, 1498, $\nu(\text{phenyl})$, 1462, 1414, 1390 $\nu(\text{pyrazole-ring})$, 1140 $\nu(\text{C=S})$. From the IR data before and after irradiation, we can speculate that the enol form and the keto form exist together before and after irradiation, respectively.

2.4 Synthesis of compound 2a

According to the synthetic method of **1a**, compound **2a** was prepared. Yield: 38.1%; M.P. 256.0-257.3 $^{\circ}\text{C}$; MS (m/z): 576.1 [M]. Elemental analysis calcd for $\text{C}_{27}\text{H}_{21}\text{N}_5\text{OSF}_6$: C, 56.14; H, 3.67; N, 12.13%. Found C, 56.10; H, 3.59; N, 12.21%; ^1H NMR (400 MHz, DMSO- d_6): δ 10.421 (1H, N2-H), 8.921(1H, N4-H), 8.314(1H, N5-H), 8.234-7.190 (13H, phenyl-ring), 3.646-3.612 (2H, CH_2), 1.206-1.170 (3H, CH_3); ^{13}C NMR (100 MHz, DMSO- d_6): δ 177.44, 148.22, 141.16, 140.03, 139.27, 138.08, 130.93, 130.60, 130.27, 129.94, 129.29, 129.22, 129.06, 128.96, 128.64, 127.95, 127.46, 126.78, 126.52, 124.70, 122.36, 122.30, 120.03, 121.67, 119.02, 102.91, 14.60; IR (ν , cm^{-1}): (the white powders before irradiation): 3352 $\nu(\text{N-H})$, 1663 $\nu(\text{C=O})$, 1609 $\nu(\text{C=N})$, 1547, 1493 $\nu(\text{phenyl})$, 1414, 1391 $\nu(\text{pyrazole-ring})$, 1136 $\nu(\text{C=S})$; (the orange powders after irradiation): 3353 $\nu(\text{N-H})$, 1663 $\nu(\text{C=O})$, 1612 $\nu(\text{C=N})$, 1551, 1497 $\nu(\text{phenyl})$, 1416, 1391 $\nu(\text{pyrazole-ring})$, 1140 $\nu(\text{C=S})$.

3. Results and discussion

Photochromic pyrazolones containing bis(trifluoromethyl)phenyl ring were easily prepared by Schiff base reaction to afford the target products, which were characterized by NMR spectra and elemental analysis as well as single crystal X-ray diffraction. Detailed below are their photochromic performances and mechanism in the solid state.

3.1 UV-Vis absorption spectra

The UV-Vis spectra of the two new compounds **1** and **2** in the solid state upon 365 nm light irradiation at room temperature were recorded, as shown in Fig. 1. From Fig. 1, we know that a new broad absorption band appears around 400-550 nm for **1** and **2**, respectively. With the irradiation time extending, their absorption intensities are increased gradually. Subsequently, the white powder changed to orange. The results indicate that the photochromic reaction occurs from the white *E*-form to the orange *K*-form during prolong irradiation time in the solid state. Fig. 2 showed that compound **1** retrieve by subsequent heating, indicating that pyrazolones thermal-bleaching to the *E*-form isomer, however, not fully recover to the original state when heated it at 180 $^{\circ}\text{C}$ (the degree of photobleaching is ca. 71.6% based on their absorption values). For compound **2**, no matter it is heated or irradiated by visible light, the photogenerated orange form of **2b** can't return to the original form, which suggests that the colored form is very stable and the photoisomerization of **2** is irreversible.

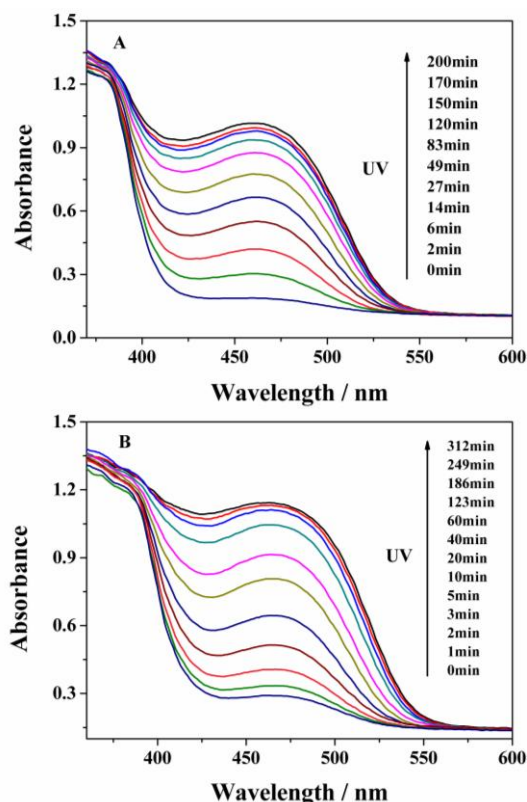


Fig. 1. Absorption spectra of **1** (A) and **2** (B) powders upon irradiation with 365 nm light at room temperature.

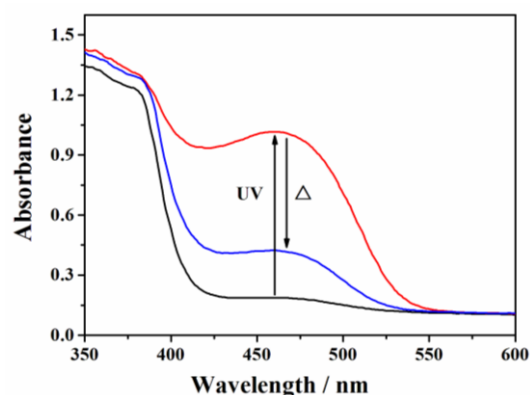


Fig. 2. Absorption spectral changes of **1** before UV irradiation (black line), after irradiation (red line) and after thermal bleaching (blue line).

3.2 The kinetics of photochromic reaction

The corresponding first-order rate constants of photoisomerization were determined by fitting the experimental data to the following equation,¹⁷

$$kt = \ln [(A_{\infty} - A_0) / (A_{\infty} - A_t)]$$

Where k is the first-order rate constant, and A_0 , A_{∞} , and A_t are the observed absorbance measured at the beginning, end, and time t , respectively. All absorption data are acquired at the wavelength of 460 nm for **1** and 463 nm for **2**, where the maximum changes in optical density. From the Fig. 3, it can be seen that they display a good linear fit. The two new compounds from *E*-form to *K*-form followed the first-order kinetics, and the pseudo-first-order rate constants are obtained from the slope as $k_1 = 2.82 \times 10^{-3} \text{ s}^{-1}$ and $k_2 = 2.79 \times 10^{-3} \text{ s}^{-1}$. Their photoreaction rates

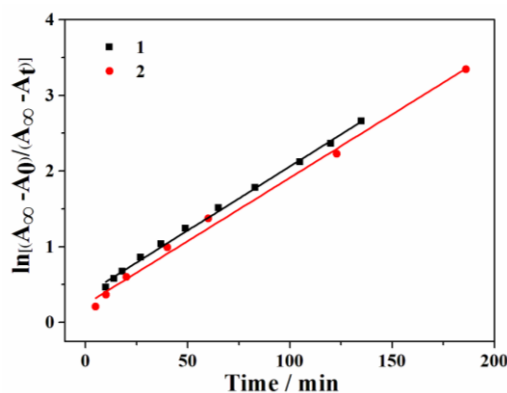


Fig. 3. First-order kinetic plots of photoisomerization reaction of compounds **1** and **2**.

are very similar, which suggest that substituents (methyl- or ethyl-) on the unit of thiosemicarbazide have a little effect on their photoisomerization rates.

3.3 Modulation of fluorescence spectra

The fluorescent emission spectra of the two compounds were investigated by 365 nm light irradiation at room temperature, their spectra changes with UV irradiation at different times are shown in Fig. 4. It can be seen that a characteristic fluorescence band was observed at 422 nm when excited by 300 nm light for the *E*-form **1a**. Upon irradiation with 365 nm light, the intensity of the fluorescence band decreased gradually with prolonged irradiation time, and it reached the photostationary state of *K*-form **1b** after 180 min, and the intensity returned its maximum value by heating at 180 °C, which indicated that this material exhibited good property of optical switch. For compound **1**, the fluorescence contrast ratio between the *E*-form and *K*-form isomers was 6:1. In comparison, compound **2a** showed a similar emission behavior after irradiation with 365 nm light, but its characteristic fluorescence band appeared at 427 nm when excited at 360 nm light for the *E*-form **2a**, and it reached its photostationary state of *K*-form **2b** only need 123 min. It should be noted that the ratio of fluorescence contrast between the *E*-form and *K*-form isomers is 8:1. The ratios were much higher than that of our reported previously.¹⁴ Thus they have potential applications for optical storage or optical switches. Why does photoisomerization reaction modulate fluorescence emission so effectively? The one reason may be that the absorbance band of *K*-form well overlapped with the emission spectra of *E*-form, respectively. The photoinduced energy transfer can be efficiently happened between *K*-form and *E*-form for modulation of their fluorescence emission. Another reason, the fluorescence quenching of **1** and **2** may be simply due to the increasing of the *K*-form upon irradiation of UV light, which shows weak or no fluorescence emission. We think that they all should be responsible for the quenching of emission.

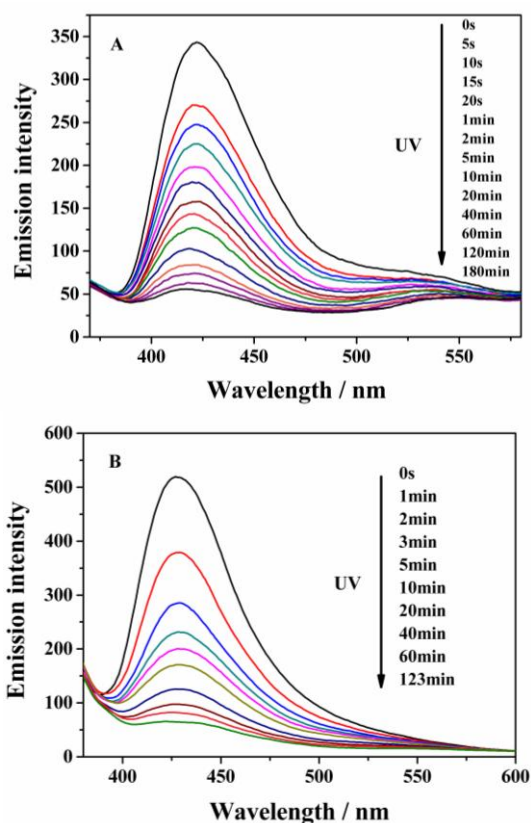


Fig. 4. Fluorescent emission spectra of powders **1** (A) and **2** (B) by 365 nm light ($\lambda_{\text{ex}} = 300$ nm for compound **1** and 360 nm for **2**) irradiation at room temperature.

3.4 Crystal structure analysis and mechanism of photochromic reactions

Single crystals of compound **1** were obtained by slow evaporation of ethanol solutions at room temperature keeping out of the light. In order to obtain the molecular structure of compound **1** and study its relationship between molecular structure and photochromic behaviors of the compound **1**, X-ray crystallographic analysis was carried out. The crystal data and molecular structure refinement details of compound **1** are given (Table S1, ESI[†]). It crystallize into monoclinic crystal system with centrosymmetric space group of $P2_1/c$ with $a = 8.2512(3)$ Å, $b = 30.1101(10)$ Å, $c = 11.6340(5)$ Å, $\beta = 102.2120(10)^\circ$; $Z = 4$. The bond length of C(7)–O is 1.2562 Å, which is considerably shorter than the standard length of the C–O bond [1.350 Å] and longer than the length of the C=O bond [1.222 Å] (Table S2, ESI[†]).¹⁸ These results suggest that the two isomers (*E*-form and *K*-form) might coexist in the crystal of **1**.

From Fig. 5A, it can be seen that one ethanol molecule in the asymmetric unit of **1**. There are intramolecular [N(4)–H(4N) \cdots O1] (2.818(4) Å) and intermolecular [N(2)′–H(2N) \cdots O1] (2.720(4) Å) hydrogen bonds existing in compound **1** as shown in Fig. 5B and Table 1. At the same time, there also has a hydrogen bond [N(5)–H \cdots O2′] (2.988(7) Å) between the molecules **1** and the solvent molecules to meet the crystal symmetry. In light of the above analysis, a reasonable photochromic mechanism was proposed. Upon UV light irradiation, the intermolecular proton transfers from O atom to the N2′ atom by the channel of [N(2)′–H–O1] forming another

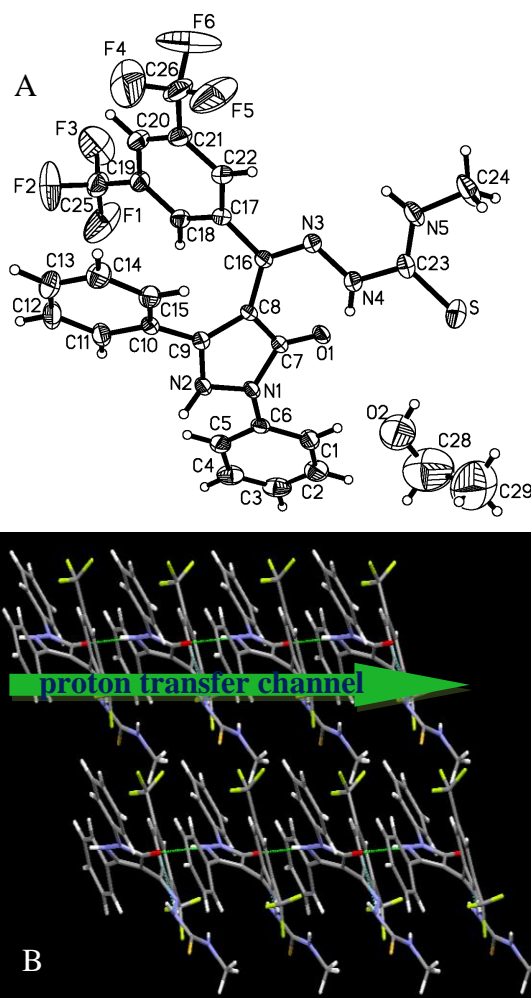


Fig. 5. (A) Molecular structure and (B) hydrogen bond connection diagrams of compound **1**, solvent molecules were omitted for clarity in B. intermolecular hydrogen bond [N(2)′–H \cdots O1]. Thus, it is credible for us to make a conclusion that photochromic mechanism is tautomerization between *E*-form to *K*-form isomers due to the proton transfer through intermolecular hydrogen bonds. The conclusion further evidence the mechanism proposed by our groups previously.¹⁹

Table 1. Hydrogen Bonds Geometry for **1**.

D–H \cdots A	d(D–H) (Å)	d(H \cdots A) (Å)	d(D \cdots A) (Å)	(D–H \cdots A) ($^\circ$)
N(4)–H(4N) \cdots O1	0.865(10)	2.11(3)	2.818(4)	138(4)
N(2)–H(2N) \cdots O1	0.866(10)	1.867(2)	2.720(4)	168(5)
N(5)–H(5N) \cdots O2	0.862(10)	2.37(4)	2.975(7)	128(4)

⁴⁵ symmetry codes: #1 $x, -y+1/2, z-1/2$ #2 $x, -y+1/2, z+1/2$

4. Conclusions

We have prepared a novel reversible photochromic compound by introduction of trifluoromethyl substituent onto the phenyl of 4-position of pyrazolone-ring. Their photochromic reactivity and fluorescence modulation studies have shown that properties of **1** were significantly improved compared with our previously reported pyrazolones. The ratios of fluorescence contrast between the *E*-form and *K*-form isomers can be reached to 6:1 for **1**. On the basis of the crystal structure analysis, intermolecular proton transfer should be responsible for photochromic mechanism of

the title compounds. The photochromic tautomerization between *E*-form and *K*-form isomers is realized by proton transfer via intermolecular hydrogen bonds between O atom of one molecule and N atom of another molecular. It is critical for understanding photochromic mechanism and useful for the design other pyrazolone derivatives with tunable properties.

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Notes and references

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†Electronic Supplementary Information (ESI) available: Tables of crystal data, structure refinement, selected bond length, bond angles data. Crystallographic data set for the structure **1** is available through the Cambridge Structural Data base with deposition number, CCDC: 1027744. See DOI: 10.1039/b000000x/

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