

Isolation, Characterization and X-ray Structure Determination of the Schiff Base Ligand: 5-Methyl-2-phenyl-4-[phenyl-(4-phenyl-thiazol-2-ylamino)-methylene]-2,4-dihydro-pyrazol-3-one

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ABSTRACT

The structure of the amine tautomer of the new Schiff base derived from 4-benzoyl-5-methyl-2-phenyl-2,4-dihydro-pyrazol-3-one (**2**) and 4-phenyl-thiazol-2-ylamine (**3**) was confirmed by means of single crystal X-ray diffraction. The title compound (**4**) was synthesized and crystals were grown from a mixture of dichloromethane and n-hexane (1:3). Single crystal X-ray diffraction analysis show that the structure is primarily stabilized by strong intramolecular N3–H3A...O1 hydrogen bonds [$N3-H3A = 0.883(19)$ Å, $H3A...O1 = 1.925(18)$ Å, $N3...O1 = 2.6901(13)$ Å, with an angle for $N3-H3A...O1 = 144.1(17)$ °] and this leads to the formation of a pseudo nine-membered hydrogen bonded pattern. Elemental analysis, FTIR and NMR analyses have been employed to characterize the crystal.

KEYWORDS

Pyrazolone, thiazole, Schiff base, tautomer, X-ray structure.

1. Introduction

The chemistry of pyrazolone derivatives has attracted much attention because of their interesting structural properties and applications in diverse areas.¹ They can be used in laser materials, as ¹H NMR shift reagents, in chromatographic studies and in the petrochemical industry.² Furthermore, they are useful reagents for the extraction and separation of various metal ions.³ Moreover, particular interest exists due to the ability of these compounds to exhibit several tautomeric forms: keto-imine, imine-ol and keto-amine.⁴ These Schiff base ligands have been studied extensively due to their ease of synthesis and their ability to be readily varied both sterically and electronically. On the other hand, the aminothiazole ring system is a useful structural element in medicinal chemistry.⁵ We have reported substituted pyrazolones with various amino thiazoles and their molecular structures were determined.⁶ The ligands can exist in three tautomeric forms but the keto-amine form is predominant in the solid state.⁷ In Schiff base compounds, the imine nitrogen can act as an inter- or intramolecular hydrogen bond acceptor. We are interested in exploring the essence of inter- and intra-molecular interactions of the ligand in metal stabilization, extraction and fluorescence effects in green chemistry.

As a part of our ongoing studies into the structure and utility of Schiff base ligands synthesized from pyrazolone and thiazole, we report the synthesis (Scheme 1), spectral properties, crystal structure, tautomerism (Scheme 2), and weak interactions of the Schiff base prepared from the condensation of 4-benzoyl-5-methyl-2-phenyl-2,4-dihydro-pyrazol-3-one (**2**) and 4-phenyl-thiazol-2-ylamine (**3**).

2. Experimental

2.1. Materials and Measurements

The compound 5-methyl-2-phenyl-2,4-dihydro-pyrazol-

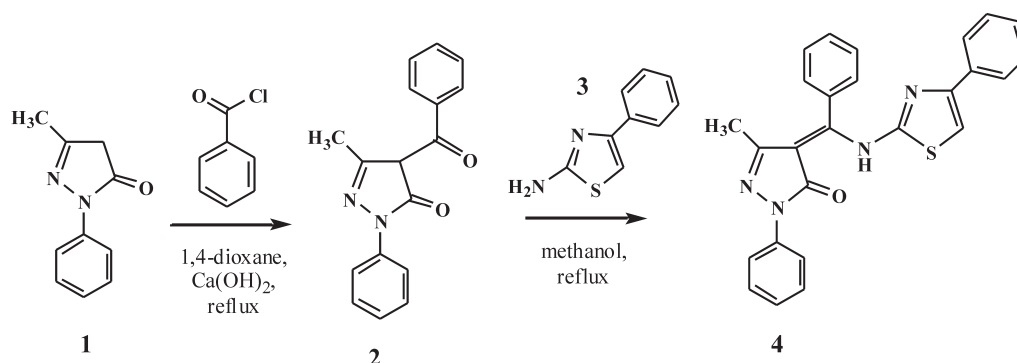
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3-one (**1**) was obtained from Prima Chemicals, Ahmedabad, India. Methanol and dioxane were obtained from SD's Fine Chemical Ltd., India. Absolute alcohol was obtained from Baroda Chem. Industry Ltd. and was used after distillation. Calcium hydroxide and benzoyl chloride were obtained from Samir Tech. Chem. Pvt. Ltd. All the chemicals used were of AR grade. Solvents used in this study were purified following standard procedures. For the synthesis of compound **2**, the benzoylation step was carried out in the presence of calcium hydroxide as per a literature method.⁸

The elemental analysis was obtained by using a Flash Elemental Analyzer-1112. Infrared spectra (IR) were measured with a PerkinElmer Precisely 100 FTIR spectrometer. ¹H and ¹³C NMR spectra were measured at 400.22 and 100.63 MHz, respectively, with a Bruker Avance III 400 MHz spectrophotometer by using TMS (tetramethylsilane) as the internal reference. Melting points were recorded on an Ernst Leitz Wetzlar hot stage melting point apparatus. Reactions were monitored by thin layer chromatography (TLC) on aluminum-backed plates coated with Merck Kieselgel 60 F254 silica gel. TLC plates were visualized by UV radiation at a wavelength of 254 nm. Crystals suitable for X-ray diffraction were obtained by slow evaporation of the title compound in a combination of dichloromethane with n-hexane (1:3) at room temperature. The data collection and cell refinement were achieved by using Bruker APEX2 and SAINT-Plus respectively.⁹ The data reduction was performed with SAINT-Plus and XPREP.⁹ The program used to solve and refine the structure was SHELXS 97.¹⁰ For molecular graphics ORTEP-3¹¹ and OLEX2¹² were employed to prepare the material for publication.¹²

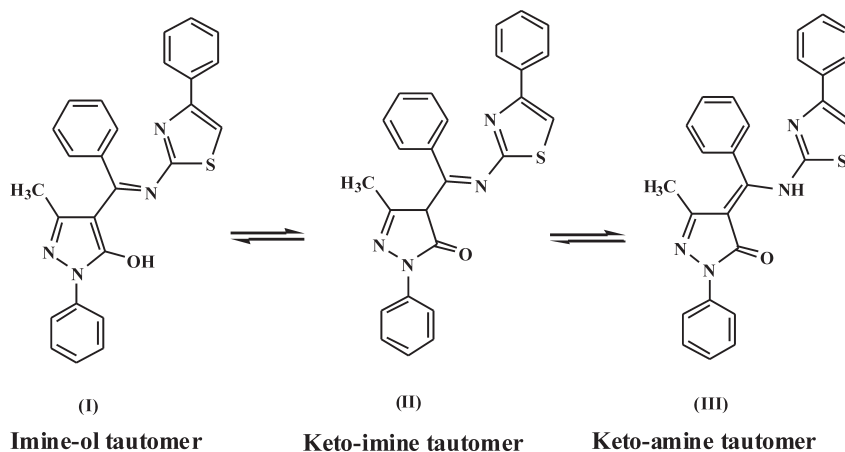
2.2. Synthesis of Schiff Base Ligand

5-Methyl-2-phenyl-2,4-dihydro-pyrazol-3-one (**1**) (2 g, 11.5 mmol) was dissolved in hot dioxane (20 mL) in a flask



Scheme 1

Synthetic pathway for the Schiff base ligand.



Imine-ol tautomer

Keto-imine tautomer

Keto-amine tautomer

Scheme 2

The possible tautomeric forms of the Schiff base.

equipped with a stirrer, separating funnel and reflux condenser. Calcium hydroxide (1.7 g, 23 mmol) was added to this solution, followed by benzoyl chloride (3.23 g, 11.5 mmol) added dropwise with precaution, as this reaction was exothermic. During this addition the reaction mass was converted into a thick paste. After the complete addition, the reaction mixture was refluxed for half an hour and then it was poured into dilute hydrochloric acid (50 mL, 2 M). The crude product 4-benzoyl-5-methyl-2-phenyl-2,4-dihydro-pyrazol-3-one (2) obtained was separated by filtration and recrystallized from n-hexane to give a bright yellow crystalline solid (2.5 g, 80 %).

A solution of 2 (1 g, 3.6 mmol) in methanol (30 mL) was added to another solution of 4-phenylthiazol-2-ylamine (3) (0.63 g, 3.6 mmol) in methanol (20 mL) under an inert atmosphere. The reaction mixture was refluxed for three hours. Completion of the reaction was monitored by TLC using hexane/ethyl acetate (8:2). The reaction was allowed to cool to room temperature and stirred overnight. A yellow precipitate formed which was then filtered and washed with methanol (10 mL). The crude product was purified by crystallization from ethanol to give brown crystals of the desired product 5-methyl-2-phenyl-4-[phenyl-(4-phenylthiazol-2-ylamino)-methylene]-2,4-dihydro-pyrazol-3-one (4)

(1.2 g, 77 %), mp. = 199 °C. IR (cm⁻¹): 3153, 1616, 1591, 1540, 1516, 1490, 1385, 1353, 1209, 1196, 839, 821, 724, 688; δ_{H} (400 MHz, CDCl₃): 13.73 (0.5H, s, NH), 7.97 (2H, d, *J* = 7.84 Hz, ArH), 7.71 (2H, d, *J* = 7.28 Hz, ArH), 7.57 (3H, m, ArH), 7.44 (2H, d, *J* = 7.24 Hz, ArH), 7.36 (2H, t, *J* = 7.92 Hz, ArH), 7.32 (2H, t, *J* = 7.42 Hz, ArH), 7.25 (2H, d, *J* = 7.16 Hz, ArH), 7.12 (t, *J* = 6.36 Hz, ArH), 6.84 (1H, s, CH), 4.71 (0.5H, s, OH), 1.48 (3H, s, CH₃) ppm; δ_{C} (100 MHz, CDCl₃): 165.04, 160.88, 159.27, 153.04, 147.55, 138.42, 136.09, 134.47, 131.15, 129.47, 129.34, 126.04, 119.39, 107.58, 103.39, 15.97 ppm.

3. Results and Discussion

3.1. Characterization of the Ligand

The compound was stable at room temperature, non-hygroscopic, insoluble in n-hexane, petroleum ether and toluene, and soluble in chloroform, dichloromethane and ethyl acetate. Analytical data are shown in Table 1.

The general structure of these ligands is such that they can exist in three tautomeric forms as shown in Scheme 2. Detailed solution and solid-state studies of the ligand were carried out to establish the predominant tautomer.

Table 1 Analytical data of the Schiff base and precursor.

Compound	M.F.	M.Wt.	Yield/%	M.p./°C	Elemental analysis/% (found/calcd.)			
					C	H	N	S
2	C ₁₇ H ₁₄ N ₂ O ₂	278.31	80	85	73.28 (73.37)	5.12 (5.07)	10.13 (10.07)	–
4	C ₂₆ H ₂₀ N ₄ OS	436.53	77	199	77.67 (77.54)	4.59 (4.62)	12.80 (12.83)	7.31 (7.35)

M.F. - molecular formula, M.Wt. - molecular weight, M.p. - melting point.

3.2. IR and NMR Spectroscopy

The IR spectra of this family of ligands exhibit two characteristic bands at 3135 and 1616 cm^{-1} , which can either be assigned to ν O-H and ν C=N, respectively, for the tautomeric imine-ol form (Scheme 2, I) or ν N-H and ν C=O respectively for the keto-amine form (Scheme 2, III) of the ligand. We assigned these two peaks to ν N-H and ν C=O, respectively, for the latter form in conjunction with the information obtained from crystallographic studies (discussed below).

The ^1H and ^{13}C NMR spectra of the ligand were recorded in CDCl_3 at room temperature and the data are presented in the experimental section. The signals due to methyl protons appear as singlets at δ 1.48 ppm. Another singlet was observed at δ 6.84, which corresponds to the only proton of the thiazole ring. In the aromatic region between δ 7.13 and 7.98 ppm overlapping doublets and multiplets are observed. One broad singlet, corresponding to a single proton, is observed at δ 13.73 ppm. This signal disappeared when a D_2O exchange experiment was carried out and integrates exactly for one proton, which suggests that only one tautomeric form of the ligand exists in solution under the experimental conditions. Although no temperature dependent experiments were carried out, comparing with the solid state study, this signal was assigned to NH. However, assignment of this peak to OH cannot be ruled out, provided the solid state structural evidence is not considered. This assignment is not without contention as several researchers have reported the determination of the imine-ol (I) tautomer in solution. For example, in the case where an *N*-oxime derivative was made, the imine-ol molecule is present exclusively. A mixture of the two tautomers has also been reported in solution.¹³ However it is important to note that in the vast majority of examples where X-ray data are shown, the crystal structure is invariably the keto-amine isomer (III).^{7,14}

In the ^{13}C NMR spectrum the carbon atom of the methyl group appears at δ 15.97 ppm. The singlet appearing at δ 103.39 ppm is assigned to the carbon atom of the C-N moiety; the significant upfield shift is due to the electron donating phenyl group attached to it. The signal appearing at δ 107.58 ppm can be assigned to the C-H of the thiazole ring. The correlation between carbon and hydrogen can be seen from the HSQC data (see online supplement). The carbon atoms of the three benzene rings exhibit signals in the range of δ 119–139 ppm. In the low field region, five signals were observed at δ 147.55, 153.04, 159.27, 160.88 and 165.04 ppm, which are associated with the carbon atoms of the heterocyclic ring. The most deshielded signal at δ 165.04 ppm can be assigned to the C=O carbon and the next signal at δ 160.88 ppm was assigned to the carbon of C=N.

3.3. X-ray Crystallography Studies

Crystal data collection parameters are given in Table 2.

The molecular structure of the ligand (Fig. 1) was determined from single crystal X-ray studies.

This structure determination gives evidence for the existence of the keto-amine form (in the solid state). An analysis of the structural data shows that the C10-O1 distance in the pyrazolone moiety is 1.244(15) Å, which is significantly shorter than the distances found for C-OH in some pyrazolone derivatives, 1.341, 1.346 Å¹⁵ and 1.331 Å,¹⁶ however, they are close to the distances found for C=O in similar compounds, 1.262 Å.¹⁵ The C10-N1 distance of the imine moiety is at 1.376(15) Å, which is significantly longer than those found for C=N in pyrazolone compounds, 1.298(2) Å¹⁷ and 1.383(2) Å,¹¹ but similar to that found for C-N (1.339(3) Å).¹⁸ It should also be noted that the proton associated with N3 can be located from the Fourier

Table 2 Crystal data and structure refinement of the new Schiff base.

Empirical formula	$\text{C}_{26}\text{H}_{20}\text{N}_4\text{O}_5$
Formula weight	436.52
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P_{21/c}$
Unit cell dimensions	a = 13.9867(3) Å b = 21.2378(4) Å, $\beta = 95.7990(10)^\circ$ c = 7.22470(10) Å
Volume	2135.09(7) Å ³
Z	4
Density (calculated)	1.358 Mg/m ³
Absorption coefficient	0.179 mm ⁻¹
F(000)	912
Crystal size	0.46 × 0.25 × 0.23 mm ³
Theta range for data collection	1.75–28.41
Reflections collected	58780
Independent reflections	5358 [R(int) = 0.0260]
Completeness to theta = 28.41 °	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9600 and 0.9223
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5358 / 0 / 294
Goodness-of-fit on F ²	1.035
Final R indices [I > 2sigma(I)]	R1 = 0.0373, wR2 = 0.0913
R indices (all data)	R1 = 0.0476, wR2 = 0.0978
Largest diff. peak and hole	0.572 d –0.285 e. Å ⁻³

difference map. The bond between the C9 and C11 carbon atoms is a double bond and it further concludes that the resulting Schiff base is present as a keto-amine (III in Scheme 2) tautomeric form, rather than the imine-ol (I in Scheme 2) in the solid state. However, the N-H proton is clearly hydrogen bonded with the O1 atom, the N3...O1 distance is 2.690(13) Å and the N3-H3A...O1 angle is 144.1(17) ° (Table 3). The possibility of the attachment of H3A with C9 (imine-one form-II) is ruled out on the basis of the angles around C9. The summation of the three angles C7–C9–C10, C7–C9–C11 and C10–C9–C11 is 359.91 and is close to the ideal value of 360 expected from the coplanar C7, C9, C10 and C11 atoms. Selected bond angles and bond lengths are summarized in Table 4.

Thus, the crystal structure study conclusively proves the existence of this compound in the keto-amine (III) form.

With the help of XRD analysis, the possible weak interactions of the resulting Schiff base were also studied (Fig. 2). The molecular structure is primarily stabilized by a strong intra molecular N3–H3A...O1 hydrogen bond [N3–H3A = 0.883(19) Å, H3A...O1 = 1.925(18) Å, N3...O1 = 2.6901(13) Å, and the angle N3–H3A...O1 = 144.1(17) °] and this leads to the formation of a

Table 3 Intramolecular hydrogen-bond distances (Å) and angles (°) for the ligand in the crystal lattice.

DH...A	D–H/Å	H...A/Å	D...A/Å	D–H...A/°
N3–H3A...O1	0.88	1.93	2.6901(13)	144.1
C6–H6...O1	0.95	2.34	2.9626(15)	122
C2–H2...N2	0.95	2.43	2.7706(16)	101
C26–H26...N4	0.95	2.54	2.8728(16)	100
C17–H17...O1 ^a	0.95	2.42	3.2954(16)	153
C23–H23...N2 ^b	0.95	2.61	3.5437(16)	166

^a x, $\frac{1}{2}$ –y, $\frac{1}{2}$ +z, ^b –1+x, $\frac{1}{2}$ –y, $\frac{1}{2}$ +z.

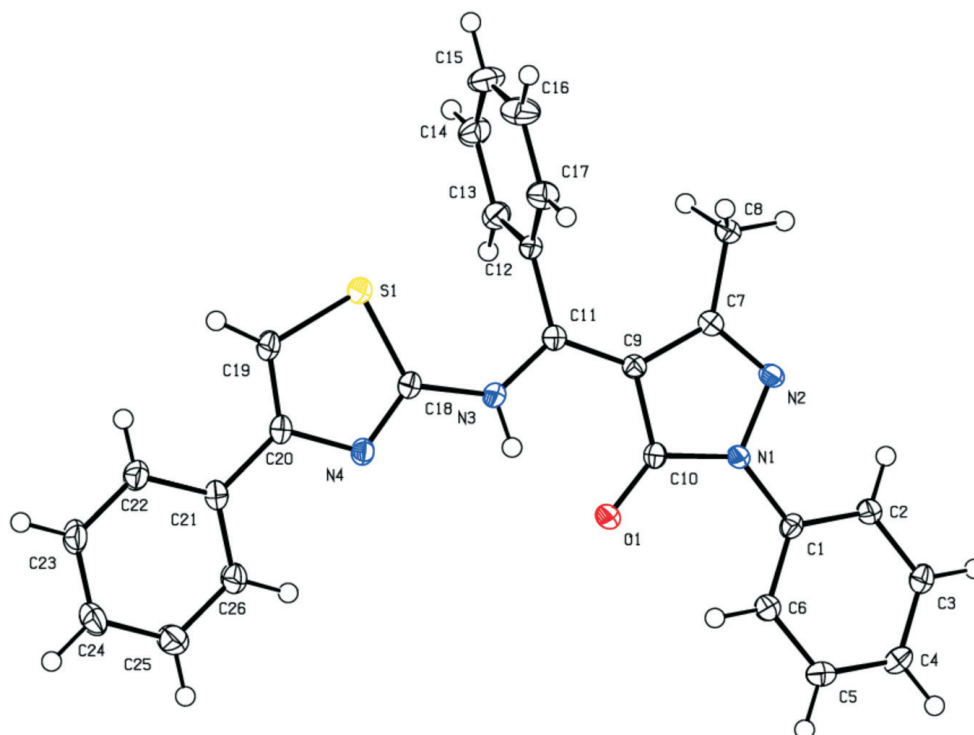


Figure 1 ORTEP diagram of the ligand showing the atom numbering scheme (50 % probability factor for the thermal ellipsoids).

Table 4 Summary of selected bond lengths (Å) and bond angles (°) of ligand.

Bond	Bond length	Bond	Bond angle
C1–N1	1.4165(15)	N2–C7–C9	111.46(10)
N3–H	0.883(19)	N2–C7–C8	119.56(10)
N1–N2	1.4086(14)	C9–C7–C8	128.94(11)
C10–O1	1.2441(15)	C7–C8–H(8A)	109.5
C10–N1	1.3762(15)	C7–C9–C10	105.19(10)
C7–C8	1.4940(16)	N3–C11–C9	117.68(11)
C9–C11	1.3799(16)	C11–N3–C18	130.59(11)
C11–N3	1.3499(15)	C11–N3–H(3A)	113.7(12)
C18–N3	1.3919(15)	C19–S1–C18	88.32(6)
S1–C18	1.7316(13)		

pseudo nine-membered (N1–N2–C7–C9–C11–N3–H3A...O1–C10) hydrogen bonded pattern, thus locking the molecular conformation and eliminating conformational flexibility. However, intermolecular interaction involves C–H...O interactions [the C17–H17...O1, C...O distance being 3.2954(16) Å, and the C–H...O angle being 153°, Fig. 2] which stabilize the packing. Table 4 show the intramolecular and intermolecular hydrogen bond geometry, respectively, for the ligand.

4. Conclusion

There are three possible tautomers for this broad family of compounds. The Schiff bases produced by the reaction between 4-benzoyl-5-methyl-2-phenyl-2,4-dihydro-pyrazol-3-one (2) and 4-phenyl-thiazol-2-ylamine (3) are shown to exist in the

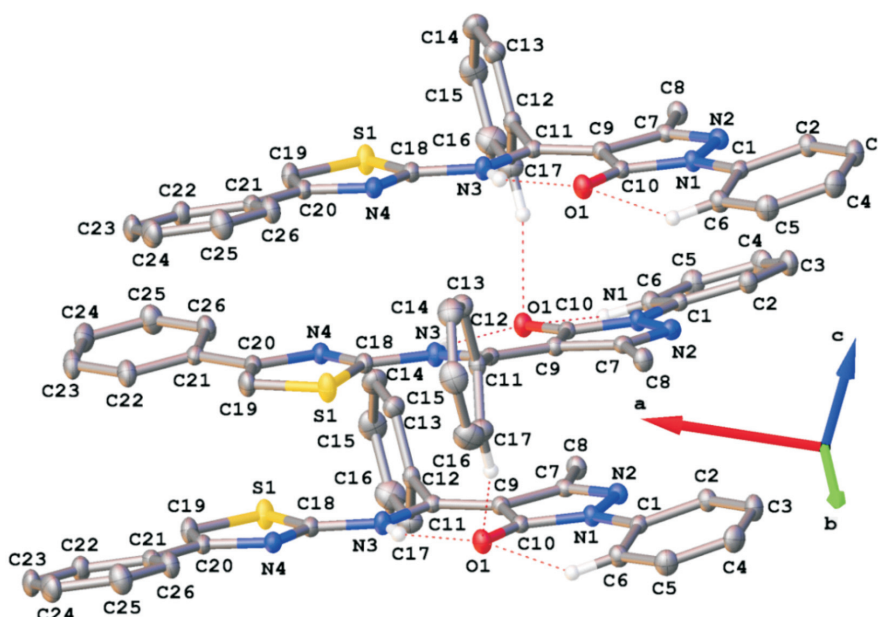


Figure 2 Intramolecular and intermolecular hydrogen-bond for the ligand in the crystal lattice.

keto-amine (III in Scheme 2) form in deuterated chloroform solutions at room temperature by assigning the NMR signal at 13.73 ppm to the NH, although assignment of this signal to OH cannot be ruled out if the solid state structural evidence is not considered. The crystal structure of 5-methyl-2-phenyl-4-[phenyl-(4-phenyl-thiazol-2-ylamino)-methylene]-2,4-dihydro-pyrazol-3-one (4) showed that the synthesized Schiff base exists also in the keto-amine form in the solid state. Furthermore, this solid state structure shows that strong hydrogen bonding between the amine hydrogen and the pyrazolone C10 carbonyl oxygen helps to stabilize the structures of these compounds in the keto-amine form.

Supplementary material

Copies of ^1H NMR, ^{13}C NMR, HSQC, HMBC, COSY and IR spectra are given in the online supplement. CCDC 953343 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieval.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223/336 033; e-mail: deposit@ccdc.ac.uk.

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