ЖУРНАЛ СТРУКТУРНОЙ ХИМИИ

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STRUCTURAL TAUTOMERISM OF 4-ACYLPYRAZOLONE SCHIFF BASES AND CRYSTAL STRUCTURE OF 5-METHYL-2-PHENYL-4-{1-[(PYRIDIN-2-YLMETHYL)-AMINO]-ETHYLIDENE}-2,4-DIHYDRO-PYRAZOL-3-ONE

© 2009 **A.S. Amarasekara[1]*, O.S. Owereh[1], K.A. Lyssenko[2], T.V. Timofeeva[3]**

[1]*Department of Chemistry, Prairie View A&M University, Prairie View, TX 77446, USA*
[2]*Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russia*
[3]*Department of Natural Sciences, New Mexico Highlands University, Las Vegas, NM 87701, USA*

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The Schiff base derivatives prepared from 4-acetyl-5-methyl-2-phenyl-2,4-dihydro-pyrazol-3-one and alkyl amines are shown to remain exclusively in the amine-one(I) tautomeric form in chloroform solutions at room temperature using a combination of ^{1}H, ^{13}C, APT, COSY, HMQC, and HMBC NMR spectroscopic methods. The crystal structure of 5-methyl-2-phenyl-4-{1-[(pyridin-2-ylmethyl)-amino]-ethylidene}-2,4-dihydro-pyrazol-3-one showed that this 4-acylpyrazolone Schiff base stays in the amine-one(I) form in the solid state as well, and the solid state structure supports the fact that strong hydrogen bonding between amine hydrogen and the pyrazolone C_3 carbonyl oxygen helps to stabilize the amine-one(I) tautomer.

K e y w o r d s: 4-acylpyrazolone, Schiff-base, tautomerism.

1. INTRODUCTION

4-Acylpyrazolones are a well known class of β-diketone ligands forming complexes with various metal ions [1]. The lanthanide complexes of 4-acylpyrazolones are renowned for their interesting fluorescence properties [2, 3] and have recently attracted renewed attention due to useful applications in biochemistry [4], electronics and in spent fuel re-processing technology. On the other hand the chemistry of the Schiff base derivatives of 4-acylpyrazolones are less explored, even though these ligands are also known to show appealing complexation properties [5—8]. Furthermore, the Schiff base formation extend the scope of the classical β-diketone system and provides an opportunity for constructing tridentate and tetradentate ligands from the initial bidentate 4-acylpyrazolone. There are limited attempts to produce tridentate [9—12] and tetradentate [7, 8] ligands from 4-acyl pyrazolone Schiff base derivatives and synthesis of their complexes. Jia has reported [10] the preparation of a tridentate salicylidene hydrazone derivative of 4-acylpyrazolone, which form complexes with trivalent lanthanides Sm, Eu and Gd, all showing blue fluorescence in the solid state. The synthesis of symmetrical tetradentate ligands are also reported with 4-acylpyrazolone system using diamines such as 1,2-ethylenediamine and 1,2-phenylenediamine and these ligands are shown to complex with Cr(III) [7] and Ni(II) [8]. Thiosemicarbazone of 4-acylpyrazolones are another interesting group of Schiff base derivatives showing photochromism and acidichromism properties [13—15] due to tautomerism in their molecular structures. The pyrazolones and 4-acylpyrazolones are known to exhibit interesting keto-enol tautomerism, and in principle Schiff base derivatives of 4-acylpyrazolones can exist in five possible tautomeric forms; imine-ol, imine-one(I), imine-one(II), amine-one(I) and amine-one(II) forms as shown in Fig. 1. The solution state tautomeric molecular structures are usually assigned by using NMR methods and this can be often difficult due to simultaneous presence of several tautomeric

* E-mail: asamarasekara@pvamu.edu

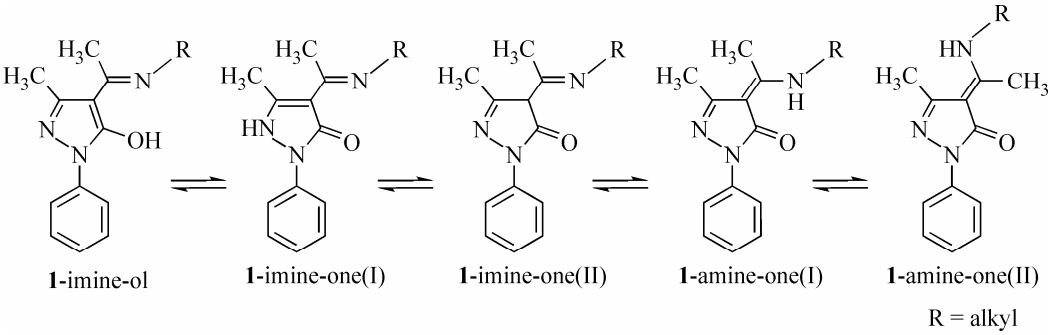


Fig. 1. Structural tautomerism of 4-acylpyrazolone Schiff base **1** with *N*-alkyl group

forms or observation of average signals due to rapid interconversions. Holzer has recently reported [16] a spin coupling constant based approach for the assignment of tautomeric forms of 4-acylpyrazolones, excluding the Schiff base derivatives.

During our studies on multidentate 4-acylpyrazolone Schiff base ligands grafted on silica surfaces and their complexation with lanthanides, we required the synthesis of a variety of 4-acylpyrazolone Schiff base derivatives. Identification of the possible tautomeric forms is an important aspect in the understanding of the molecular structures of the multidentate ligands with selective chelation characteristics, and as far as we are aware the tautomerism has not been studied in detail for the 4-acylpyrazolone Schiff base systems formed from the reaction between 4-acylpyrazolones and alkylamines. Therefore we have undertaken to study the structures of these compounds by spectroscopic and X-ray crystallography methods to explore the tautomerism of these multidente systems. In this publication we describe the synthesis of five 4-acylpyrazolone Schiff base compounds by condensation of 4-acetyl-5-methyl-2-phenyl-2,4-dihydro-pyrazol-3-one with different alkylamines (Fig. 2) and their solution state structure determination using NMR methods. Furthermore, we report the solid state structure determination of the multidentate ligand 5-methyl-2-phenyl-4-{1-[(pyridin-2-ylmethyl)-amino]-ethylidene}-2,4-dihydro-pyrazol-3-one using single crystal X-ray crystallography to support the structural data obtained using spectroscopic methods.

2. EXPERIMENTAL

2.1. Instrumentation and measurements. ^{1}H NMR Spectra were recorded in $CDCl_3$ on a Varian Mercury plus spectrometer operating at 400 MHz and chemical shifts are given in ppm downfield from TMS ($\delta = 0.00$). ^{13}C NMR spectra in $CDCl_3$ were recorded in the same spectrometer operating at 100 MHz; chemical shifts were measured relative to $CDCl_3$ and converted to δ(TMS) using $\delta(CDCl_3) = 77.00$. FT-IR spectra were recorded on a JASCO-470 PLUS IR spectrometer using KBr pellets. A Bruker SMART APEX2 CCD diffractometer was used for the single crystal X-ray crystallography. Elemental analysis were performed at QTI laboratories, New Jersey.

2.2. General procedure for the preparation of 4-acylpyrazolone Schiff bases (1a—e). A mixture of 4-acylpyrazolone [17] **2** (0.432 g, 2.0 mmol) and amine **3a—c** (2.0 mmol) in 10 mL of ethanol was refluxed for 30 minutes. Upon cooling of the solution 4-acylpyrazolone Schiff bases were separated as microcrystalline precipitates after one day at room temperature. The crude products were recrystallized with ethanol to give pure 4-acylpyrazolone Schiff bases. Compounds **1d**,**e** were prepared

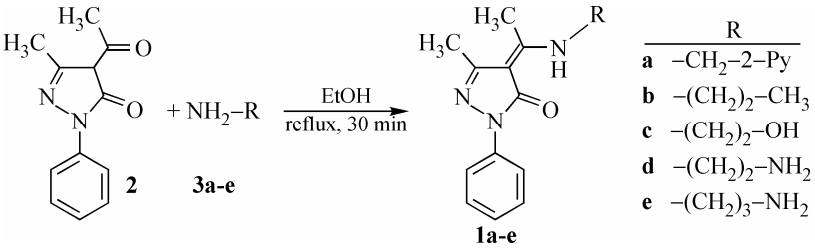
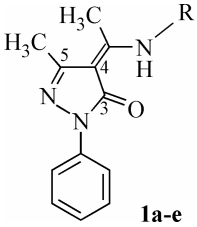


Fig. 2. Synthesis of 4-acylpyrazolone Schiff bases **1a—e**

Table 1

^{1}H *NMR Data of compounds* **1a—e** ($CDCl_3$, 23 °C)



1a-e

	R
a	$-CH_2-2-Py$
b	$-(CH_2)_2-CH_3$
c	$-(CH_2)_2-OH$
d	$-(CH_2)_2-NH_2$
e	$-(CH_2)_3-NH_2$

	2×CH_3	N—H	N—Ph	N—R
1a	2.39 (s)	12.00 (bs)	7.12 (*t*, *J* = 7.2 Hz, 1H)	4.75 (*d*, *J* = 6.0 Hz, 2H),
	2.41 (s)		7.37 (*t*, *J* = 7.2 Hz, 2H)	7.23 (*d*,*d*, *J* = 4.8, 7.6 Hz, 1H)
			7.98 (*d*, *J* = 7.2 Hz, 2H)	7.29 (*d*, *J* = 7.6 Hz, 1H)
				7.69 (*d*,*d*,*d*, *J* = 2.0, 7.6, 7.6 Hz, 1H)
				8.60 (*d*,*d*, *J* = 2.0, 4.8 Hz)
1b	2.33 (s)	11.50 (bs)	7.13 (*t*, *J* = 7.2 Hz, 1H)	1.03 (*t*, *J* = 7.6 Hz, 3H)
	2.38 (s)		7.37 (*t*, *J* = 7.2 Hz, 2H)	1.72 (m, 2H)
			7.97 (*d*, *J* = 7.2 Hz, 2H)	3.36 (m, 2H)
1c	2.24 (s)	11.56 (bs)	7.14 (*t*, *J* = 7.2 Hz, 1H)	1.68 (bs, 1H)
	2.36 (s)		7.39 (*t*, *J* = 7.2 Hz, 2H)	3.53 (m, 2H)
			7.96 (*d*, *J* = 7.2 Hz, 2H)	3.83 (m, 2H)
1d	2.39 (s)	11.85 (bs)	7.12 (*t*, *J* = 7.2 Hz, 1H)	0.45 (bs, 1H)
	2.41 (s)		7.37 (*t*, *J* = 7.2 Hz, 2H)	3.04 (m, 2H)
			7.98 (*d*, *J* = 7.2 Hz, 2H)	3.49 (m, 2H)
1e	2.39 (s)	11.50 (bs)	7.12 (*t*, *J* = 7.2 Hz, 1H)	1.39 (bs, 1H)
	2.40 (s)		7.37 (*t*, *J* = 7.2 Hz, 2H)	1.87 (m, 2H)
			7.97 (*d*, *J* = 7.2 Hz, 2H)	2.87 (*t*, *J* = 6.8 Hz, 2H)
				3.55 (m, 2H)

by using excess (20 mmol) of the corresponding amines (**3d,e**) to prevent the formation of bis-Schiff base products and the desired products were isolated after removal of excess amine under reduced pressure in the rotavapor.

1a 0.453 g, 74 % yield. Found: C, 70.35; H, 6.03; N, 18.20 %. Calc. for $C_{18}H_{18}N_4O$: C, 70.57; H, 5.92; N, 18.29 %. IR (KBr) 653, 695, 752, 831, 1009, 1127, 1351, 1485, 1588, 1641, 2975, 3060, 3406 cm^{-1}.

1b 0.422 g, 82 % yield. Found: C, 69.85; H, 7.54; N, 16.15 %. Calc. for $C_{15}H_{19}N_3O$: C, 70.01; H, 7.44; N, 16.33 %. IR (KBr) 652, 694, 760, 839, 1092, 1352, 1491, 1535, 1592, 1637, 2893, 2910 cm^{-1}.

1c 0.368 g, 71 % yield. Found: C, 64.62; H, 6.82; N, 16.00 %. Calc. for $C_{14}H_{17}N_3O_2$: C, 64.85; H, 6.61; N, 16.20 %. IR (KBr) 652, 696, 761, 839, 1085, 1353, 1491, 1535, 1592, 1630, 2893, 2919, 3452 cm^{-1}.

1d 0.372 g, 72 % yield. Found: C, 64.95; H, 7.11; N, 21.62 %. Calc. for $C_{14}H_{18}N_4O$: C, 65.09; H, 7.02; N, 21.69 %. IR (KBr) 652, 694, 758, 836, 1349, 1488, 1535, 1591, 1635, 2855, 2920, 3392 cm^{-1}.

1e 0.370 g, 68 % yield. Found: C, 66.27; H, 7.55; N, 20.30 %. Calc. for $C_{15}H_{20}N_4O$: C, 66.15; H, 7.40; N, 20.57 %. IR (KBr) 653, 693, 758, 836, 1350, 1488, 1535, 1590, 1635, 2853, 2926, 3389 cm^{-1}. ^{1}H and ^{13}C NMR data of compounds **1a-e** are shown in Tables 1 and 2.

2.3. Crystal structure determination of compound 1a. The single crystals suitable for X-ray crystallography were obtained from the slow evaporation of a solution of **1a** in ethanol at room temperature. Crystals of **1a** ($C_{18}H_{18}N_4O$, M = 306.36) are monoclinic, space group $P2_1/n$, at 100 K:

Table 2

^{13}C NMR *Data of compounds* **1a—e** ($CDCl_3$, 23 °C)

	2×CH_3	C_3	C_4	C_5	=C—N	N—Ph	N—R
1a	16.2	165.5	147.1	166.0	99.9	119.5, 124.4	48.9, 121.5, 123.1
	17.9					128.9, 139.4	137.5, 150.1, 155.9
1b	15.8	165.1	146.9	165.9	99.9	119.5, 124.4	11.6, 23.0, 45.3
	17.8					128.9, 139.4	
1c	16.0	165.7	147.4	166.2	99.3	119.6, 124.6	45.9, 61.3
	17.8					129.0, 139.3	
1d	16.0	165.3	146.9	165.9	99.4	119.5, 124.4	41.5, 46.4
	17.9					128.9, 139.4	
1e	15.8	165.3	146.9	166.9	99.1	119.6, 124.4	32.9, 39.3, 41.1
	17.9					128.9, 139.4	

a = 11.7945(19), b = 6.7731(11), c = 18.975(3) Å, β = 97.507(3)°, V = 1502.8(4) Å^3, Z = 4 (Z' = 1), d_{calc} = 1.354 gcm^{-3}, μ(MoK_α) = 0.88 cm^{-1}, F(000) = 648. Intensities of 13517 reflections were measured with a Bruker SMART APEX2 CCD diffractometer [λ(MoK_α) = 0.71072 Å, ω-scans, 2θ < 58°] and 3609 independent reflections [R_{int} = 0.0759] were used in further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic-isotropic approximation. The H atom of the —NH group was localized in the difference Fourier map and refined isotropically. The other H atoms were placed in calculated positions and refined within riding model with fixed thermal parameters. For **1a** the refinement converged to $wR2$ = 0.1513 and GOF = 1.027 for all independent reflections ($R1$ = 0.0650 was calculated against F for 2126 observed reflections with $I > 2\sigma(I)$). Data reduction and further calculations were performed using the Bruker SAINT+ [18] and the SHELXTL NT [19] program packages. CCDC 704439 contains supplementary crystallographic data for this paper.

3. RESULTS AND DISCUSSION

3.1. Identification of the tautomeric structures of 1a—e. Solution state structure of the compound **1a** in $CDCl_3$ was identified as the **1a** amine-one(I) form by using a combination of ^{1}H, ^{13}C, APT, COSY, HMQC, and HMBC NMR spectroscopic methods. The ^{1}H NMR spectrum of **1a** displayed a two proton doublet (J = 6.0 Hz) at δ 4.75 corresponding to the CH_2 group attached to the pyridine ring. The single proton broad peak at δ 12.00 was assigned to the NH group and the ^{1}H—^{1}H COSY spectrum of **1a** showed a cross peak indicating the coupling of these CH_2 and NH protons. The ^{13}C NMR spectrum exhibited 16 carbons, assigned by APT experiment as six quaternary sp^2, one CH_2, two CH_3 and eight CH carbons. The HMQC experiment was used to establish that three CH carbon signals at δ 119.5, 128.9 and 124.4 corresponds to the phenyl ring. Furthermore, the carbon resonances at δ 121.5, 123.1, 137.5 and 150.1 were assigned to the pyridine ring CH carbons by using the ^{1}H—^{13}C cross-peaks in the HMQC spectrum. The quaternary signals were assigned by using the HMBC spectrum; for instance sp^2 quaternary carbon signal at δ 155.9 showed three distinct cross peaks with proton signals at δ 4.75 (CH_2), 7.29 (C-3, Py) and 7.69 (C-4, Py) thus confirming as C-2 carbon of the pyridine ring. The sp^2 quaternary carbon signal at δ 139.4 showed two cross peaks with δ 7.98 (C-2, C-6, Ph) and 7.37 (C-3, C-5, Ph) in the HMBC spectrum, therefore δ 139.4 peak was assigned to C-1 in the phenyl ring. The carbon -13 signal at δ 99.9 was attributed to the olefinc carbon attached to NH (=C—NH) as this signal indicated the coupling to δ 4.75 (N—CH_2) and one of the methyl group signals (δ 2.39) in the HMBC spectrum. The imine carbon in the pyrazolone ring was assigned to δ 166.0 signal in the carbon spectrum, based on the fact that this carbon showed one cross peak to the directly attached methyl group at δ 2.41 in the HMBC spectrum. The only remaining quaternary carbon signal

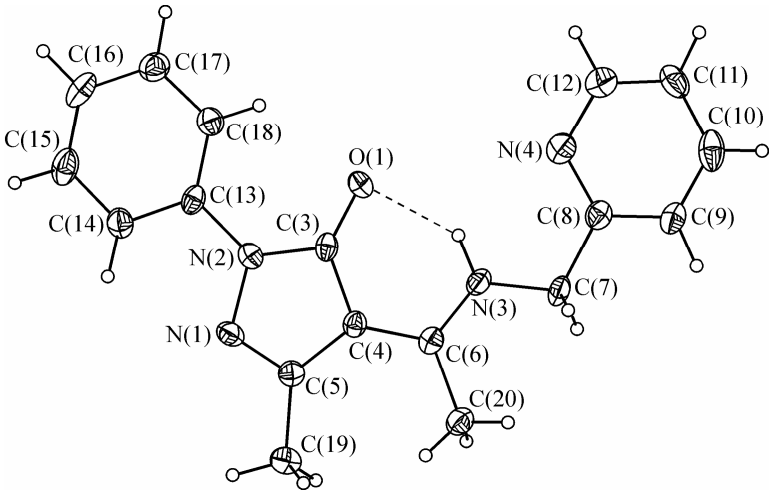


Fig. 3. Single crystal X-ray structure of **1a**, representation of atoms by thermal ellipsoids (p = 50 %)

at δ 165.5 which did not show any long range couplings in the HMBC spectrum was assigned to the C-3 carbonyl carbon of the pyrazolone ring.

The tautomeric structures of the related compounds **1b—e** were also established as amine-one(I) forms by comparison of the ^{1}H and ^{13}C NMR data shown in Tables 1 and 2. For instance, the C_3, C_4 and C_5 pyrazolone ring carbon atoms resonate at δ 165.5, 147.5, δ 165.5, 147.1 and 166.0 in the compound **1a** and these ^{13}C resonances are observed in the ranges of δ 165.1—165.7, 146.9—147.4 and 165.9—166.9 respectively for related compounds **1b—e** (Table 2). In addition to this ^{1}H NMR signal of the hydrogen bonded amine N—H of the compound **1a** was observed as a broad peak at δ 12.00 and the corresponding hydrogen signals of compounds **1b—e** were found as similar broad peaks in the δ 11.50—12.00 region (Table 1), further supporting the structural similarity of the five Schiff bases studied. It is interesting to note that a possible weaker hydrogen bonding from the nitrogen (**1a**, **d**, **e**) or oxygen (**1c**) atoms in the alkyl group of the Schiff base moieties has little or no effect on the geometry and the tautometric form of these molecules. Furthermore, no NMR signals from other four possible tautomeric forms were observed for any of the compounds studied, confirming that compounds **1a—e** exclusively remain in the amine-one(I) tautomeric form in the chloroform solution.

3.2. Identification of the solid state structure of 1a. The solid state structure of **1a** obtained by single crystal X-ray crystallography is shown in Fig. 3. This structure clearly points out that compound **1a** exists as the amine-one(I) tautomeric form in the solid state, which is the same tautomeric form found in the solution state. Structural data in Table 3 show that the O(1)—C(3) bond distance in the pyrazolone system is 1.253 Å, which is comparable to the pyrazolone C=O bond distance of 1.254 Å

T a b l e 3

Selected bond distances and bond angles for **1a**

Bond length	Å (esd)	Bond length	Å (esd)	Bond length	Å (esd)
O(1)—C(3)	1.253(3)	N(2)—C(13)	1.417(3)	C(3)—C(4)	1.438(3)
N(1)—C(5)	1.309(3)	N(3)—C(6)	1.328(3)	C(4)—C(6)	1.400(3)
N(1)—N(2)	1.403(2)	N(3)—C(7)	1.452(3)	C(4)—C(5)	1.435(3)
N(2)—C(3)	1.393(3)	N(3)—H(3N)	0.91(3)	C(7)—C(8)	1.514(3)
Bond angle	deg. (esd)	Bond angle	deg. (esd)	Bond angle	deg. (esd)
C(5)—N(1)—N(2)	106.28(18)	C(6)—N(3)—H(3N)	115.4(16)	N(2)—C(3)—C(4)	104.44(18)
C(3)—N(2)—N(1)	111.81(18)	C(7)—N(3)—H(3N)	119.3(16)	C(6)—C(4)—C(5)	132.3(2)
C(3)—N(2)—C(13)	128.92(19)	O(1)—C(3)—N(2)	125.6(2)	C(6)—C(4)—C(3)	122.1(2)
C(6)—N(3)—C(7)	125.2(2)	O(1)—C(3)—C(4)	129.9(2)	C(5)—C(4)—C(3)	105.58(19)

Table 4

Hydrogen bonding distances Å (esd) *and angles* ° (esd)

D—H…A	*d*(D—H)	*d*(H…A)	*d*(D…A)	∠(DHA)
N(3)—H(3N)…O(1)	0.90(2)	1.98(2)	2.732(2)	140(2)
N(3)—H(3N)…N(4)	0.90(2)	2.39(2)	2.763(3)	105.0(18)

found in a similar pyrazolone thiosemicarbazone [20]. The significantly longer N(3)—C(6) bond distance of 1.328 Å indicates a C—N single bond rather than C=N imine form, further this bond distance is comparable to reported C—N bond distances of similar compounds [13]. The double bond character in the C(4)—C(6) bond is indicated by the relatively short 1.400 Å bond distance. The solid state structure of **1a** showed an inter-atomic distance between hydrogen attached to N(3) and O(1) as 1.98 Å, which points towards a strong hydrogen bonding interaction between these atoms. The interatomic distance of pyridine nitrogen [N(4) in Fig. 3] and N(3) hydrogen atom is 2.39 Å (Table 4) also indicates a hydrogen bonding interaction. In addition to this data, the total sum of the bond angles; C(6)—N(3)—C(7) = 125.2°, C(6)—N(3)—H(3N) = 115.4° and C(7)—N(3)—H(3N) = 119.3° is 359.9°, which is practically 360°. These bond angles around N(3) confirms that this nitrogen exists in a planer geometry. The solid state structure determination suggests that a strong hydrogen bonding between N(3)H and O(1) helps to stabilize the amine-one(I) tautameric form of this compound.

4. CONCLUSION

The Schiff bases produced by the reaction between alkyl amines and 4-acetyl-5-methyl-2-phenyl-2,4-dihydro-pyrazol-3-one are shown to exist exclusively in the amine-one(I) tautomeric form in chloroform solutions at room temperature by NMR methods. The crystal structure of 5-methyl-2-phenyl-4-{1-[(pyridin-2-ylmethyl)-amino]-ethylidene}-2,4-dihydro-pyrazol-3-one (**1a)** showed that this 4-acyl-pyrazolone Schiff base exists in the amine-one(I) form in the solid state as well. Furthermore, this solid state structure supports the fact that strong hydrogen bonding between amine hydrogen and the pyrazolone C_3 carbonyl oxygen helps to stabilize the structures of these compounds in the amine-one(I) form.

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REFERENCES

1. *Marchetti F., Pettinari C., Pettinari R.* // Coord. Chem. Rev. – 2005. – **249**. – P. 2909 – 2945.
2. *Kido J., Okamoto Y.* // Chem. Rev. – 2002. – **102**. – P. 2357 – 2368.
3. *Zhou D., Li Q., Huang C. et al.* // Polyhedron. – 1997. – **16**. – P. 1381 – 1389.
4. *Wu X., Sun S., Yang J. et al.* // J. Fluoresc. – 2004. – **14**. – P. 113 – 118.
5. *Jadeja R.N., Shah J.R.* // Polyhedron. – 2007. – **26**. – P. 1677 – 1685.
6. *Jadeja R.N., Shah J.R., Suresh E. et al.* // Ibid. – 2004. – **23**. – P. 2465 – 2474.
7. *Raj D.S., Parmar N.J., Shah J.R.* // Synth. React. Inorg. Metal-Org. Nano-metal Chem. – 2004. – **34**. – P. 697 – 711.
8. *Raj D.S., Shah P.C., Shah J.R.* // Ibid. – 1992. – **22**. – P. 321 – 335.
9. *Maurya R.C., Pandey A., Chaurasia J. et al.* // J. Mol. Struct. – 2006. – **798**. – P. 89 – 101.
10. *Li J., Zhang L., Jia D. et al.* // Inorg. Chim. Acta. – 2007. – **360**. – P. 3504 – 3510.
11. *Xu G.C., Zhang L., Liu L. et al.* // Polyhedron. – 2008. – **27**. – P. 12 – 24.
12. *Yang Y., Zhang L., Liu L. et al.* // Inorg. Chim. Acta. – 2007. – **360**. – P. 2638 – 2646.
13. *Liu L., Jia D.Z., Ji Y.L. et al.* // J. Photochem. Photobio. A: Chem. – 2003. – **154**. – P. 117 – 122.
14. *Peng B.H., Liu G.F., Liu L. et al.* // Photochem. Photobio. A: Chem. – 2005. – **171**. – P. 243 – 249.
15. *Liu L., Jia D.Z., Ji Y.L. et al.* // J. Mol. Struct. – 2003. – **655**. – P. 221 – 227.
16. *Holzer W., Kautsch C., Laggner C. et al.* // Tetrahedron. – 2004. – **60**. – P. 6791 – 6805.
17. *Okafor E.C.* // Polyhedron. – 1983. – **2**. – P. 309 – 316.
18. *Bruker*, SAINTPlus. // Data Reduction and Correction Program v. 6.01, Bruker AXS, Madison, Wisconsin, USA, 1998.
19. *Sheldrick G.M.* SHELXTL v. 5.10 // Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA, 1998.
20. *Peng B.H., Liu G.F., Liu L. et al.* // J. Mol. Struct. – 2004. – **692**. – P. 217 – 222.