Scientific paper

Synthesis, Spectroscopic, Spectrophotometric and Crystallographic Investigations of 4-{[(1*E*)-(3,4-dimethoxyphenyl)methylene]amino}-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one and 4-{[(1*E*)-(2-hydroxy-5-methoxyphenyl)methylene]amino}-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one

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Abstract

Two new Schiff base ligands 4-{[(1*E*)-(3,4-dimethoxyphenyl)methylene]amino}-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (**1**) and 4-{[(1*E*)-(2-hydroxy-5-methoxyphenyl)methylene]amino}-1,5-dimethyl-2-phenyl-1,2-dihydro-3*H*-pyrazol-3-one (**2**) have been prepared and characterized using elemental analysis, UV-vis, FT-IR, ^{1}H and ^{13}C NMR spectroscopy, and X-ray crystallographic technique. Tautomeric equilibria (phenol-imine, O-H···N and keto-amine, O···H-N forms) have been studied by using UV-vis absorption spectra for the compound **2** in some solutions. Crystal structure analyses showed that the title molecules **1** and **2** crystallize in the monoclinic space group $P2_1/c$ and $P2_1$ with the unit cell parameters: a = 12.5665(3) Å and 5.6666(2) Å; b = 10.4791(2) Å and 12.2444(5) Å; c = 14.6240(3) Å and 12.1556(4) Å; V =1820.65(7) Å^3 and 826.84(5) Å^3; D_x = 1.282 g.cm^{-3} and 1.355 g.cm^{-3}; and Z = 4 and 2, respectively.

Keywords: Schiff base, spectroscopic studies, crystal structure, tautomerism, hydrogen bonding

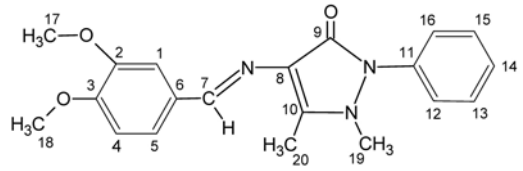
1.Introduction

Schiff base ligands are the basis of an extensive class of transition and main group elements in coordination chemistry.[1–4] The Schiff bases of 4-aminoantipyrine have attracted the attention of the researchers[5,6] because of their biological[7–9] and analytical[10] activities. 4-aminoantipyrine derivatives and their metal complexes have been investigated for bioactivity and analgetic,[11] antimicrobial[12] and anticancer activity.[13] New kinds of chemo-therapeutic antitumor agents containing Schiff bases have increased significant attention among biochemists,[14] and of those aminoantipyrine derivatives are commonly managed intravenously to detect liver disease[15] in clinical treatment.

Both in solution and the solid state, tautomerism in Schiff base derivatives of o-hydroxyaldehydes have been investigated using IR,[16,17] UV,[18–20] ^{1}H NMR,[21,22] and X-ray crystallographic techniques.[23,24] The UV–vis spectra of some Schiff base derivatives of o-hydroxyaldehydes have been studied in both polar and nonpolar solvents.[25] A new band at higher wavelenghts than 400 nm has been observed in polar solvent and in acidic media. However, this band has not been observed in some nonpolar solvents. The results indicate that the absorption band at higher wavelenghts (>400 nm) belongs to the keto-amine form of

the Schiff base. In Schiff bases derived from salicylaldehyde, the keto-amine form was not observed in both polar and non-polar solvents, but it was observed with the acid addition.[26]

In this study, we have synthesized title compounds (Scheme 1) and investigated their molecular structures by using UV-vis, FT-IR, ^{1}H and ^{13}C NMR spectroscopic methods. UV-vis spectra of the compound **2** have been recorded in different solvents, and in basic (NEt_3) and acidic (CF_3COOH) media. Phenol-imine and keto-amine form for compound **2** have been assigned from these spectra. We have also determined crystal structures of **1** and **2** by using X-ray crystallographic technique.



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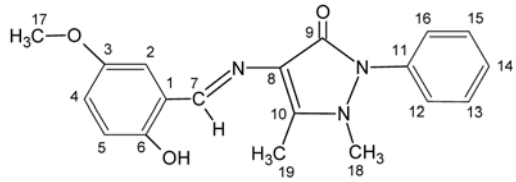

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Scheme 1. Chemical structures of the title compounds **1** and **2**.

2. Experimental

2. 1. Reagents and Techniques

Melting points were measured on a Thomas-Hoover apparatus using a capillary tube. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DPX FT-NMR (400 MHz) spectrometer with $SiMe_4$ as an internal standard. IR spectra were obtained from a PEL-DATA spectrum 100 series spectrometer. Elemental analyses were performed on a LECO CHNS-932 analyzer. 4-aminoantipyrine and 2-hydroxy-5-methoxybenzaldehyde were purchased from Aldrich, and 3,4-dimethoxybenzaldehyde was prepared according to the literature method.[27] UV-vis spectra were obtained using a UNICAM UV2-100 series spectrometer.

2. 2. Synthesis of the Title Compound 1

4-Aminoantipyrine (0.68 g, 3.37 mmol) was dissolved in ethanol (50 mL) and the solution was added dropwise to the solution of 3,4-dimethoxybenzaldehyde (0.56 g, 3.37 mmol) in ethanol (50 mL). The mixture was refluxed for 1h and then allowed to come to ambient temperature. Bright yellow crystals were formed in ethanol and recrystallized in acetone. Fine yellow crystals obtained upon slow evaporation at room temperature were characterized, including single crystal X-ray diffraction. Yield, 0.91 g (77%); mp: 183 C. *Anal. Calc.* for $C_{20}H_{21}N_3O_3$: C, 68.38; H, 5.98; N, 11.97. Found: C, 68.76; H, 6.18; N, 12.23%. IR (ν, cm^{-1}) 1647 (C=O), 1573 (C=N), 1510 (C=C), 1259 (C-O-C). ^{1}H NMR ($CDCl_3$, δ, ppm): 2.39 [$(C\text{-}CH_{3(20)})$, s, 3H], 3.02 [$(N\text{-}CH_{3(19)}$), s, 3H], 3.89 [$(OCH_{3(17)})$, s, 3H], 3.83 [$(OCH_{3(18)})$, s, 3H], 9.66 [$(N{=}CH_{(7)})$, s, 1H], 6.83 [$(H_{(3)})$, d, 1H, *J*=8.15 Hz], 7.22 [$(H_{(14,5)})$, m, 2H], 7.24–7.39 [$(H_{(16,15,13,12)})$, m, 4H], 7.51 [$(H_{(1)})$, s, 1H]. ^{13}C NMR ($CDCl_3$, δ, ppm): 124.19 ($C_{(16,12)}$), 129.08 ($C_{(15,13)}$), 126.70 ($C_{(14)}$), 149.20 ($C_{(11)}$), 131.17 ($C_{(10)}$), 134.85 ($C_{(8)}$), 160.88 ($C_{(9)}$), 156.76 ($C_{(7)}$), 118.71 ($C_{(6)}$), 108.41 ($C_{(1)}$), 151.08 ($C_{(2)}$), 151.57 ($C_{(3)}$), 110.74 ($C_{(4)}$), 122.83 ($C_{(5)}$), 10.09 ($C_{(20)}$), 35.85 ($C_{(19)}$), 55.85 ($C_{(17)}$), 55.80 ($C_{(18)}$).

2. 3. Synthesis of the Title Compound 2

The above synthetic procedure was repeated for **2** by using 2-hydroxy-5-methoxybenzaldehyde. Yield, 0.83 g (74%); mp: 166 C. *Anal. Calc.* for $C_{19}H_{19}N_3O_3$: C, 67.66; H, 5.64; N, 12.46. Found: C, 67.63; H, 5.71; N, 12.59%. IR (ν, cm^{-1}) 1652 (C=O), 1574 (C=N), 1498 (C=C), 1264 (C-O-C). ^{1}H NMR ($CDCl_3$, δ, ppm): 2.37 [$(C\text{-}CH_{3(19)})$, s, 3H], 3.14 [$(N\text{-}CH_{3(18)}$), s, 3H], 3.74 [$(OCH_{3(17)})$, s, 3H], 9.79 [$(N{=}CH_{(7)})$, s, 1H], 6.88 [$(H_{(4)})$, s, 1H], 6.86 [$(H_{(5)})$, s, 1H], 7.28–7.52 [$(H_{(16,15,14,13,12)})$, m, 5H], 7.52 [$(H_{(2)})$, s, 1H], 12.84 [(OH), s, 1H]. ^{1}H NMR ($CDCl_3$+CF_3COOH, δ, ppm): 2.44 [$(C\text{-}CH_{3(19)})$, s, 3H], 3.27 [$(N\text{-}CH_{3(18)}$), s, 3H], 3.78 [$(OCH_{3(17)})$, s, 3H], 9.65 [$(N\text{-}CH_{(7)})$, d, 1H], 9.88 [$(N{=}CH_{(7)})$, s, 1H], 6.89–7.56 [$(H_{(16,15,14,13,12,2,4,5)})$, m, 8H], 12.82 [(OH), bs, 1H], 15.98 [(HN-C), d, 1H]. ^{13}C NMR ($CDCl_3$, δ, ppm): 124.65 ($C_{(16,12)}$), 129.28 ($C_{(15,13)}$), 124.65 ($C_{(14)}$), 134.34 ($C_{(11}$), 119.94 ($C_{(10)}$), 127.30 ($C_{(8)}$), 154.64 ($C_{(9)}$), 160.13 ($C_{(7)}$), 116.17 ($C_{(1)}$), 115.00 ($C_{(2)}$), 149.87 ($C_{(3)}$), 119.12 ($C_{(4)}$), 117.44 ($C_{(5)}$), 152.29 ($C_{(6)}$), 10.18 ($C_{(19)}$), 35.55 ($C_{(18)}$), 55.82 ($C_{(17)}$). ^{13}C NMR ($CDCl_3$+CF_3COOH, δ, ppm): 159.95–112.30 ($C_{(1–5,\ 7–16)}$), 10.01 ($C_{(19)}$), 36.05 ($C_{(18)}$), 57.38 ($C_{(17)}$).

2. 4. The Determination of X-ray Structures

X-ray data were collected on an Oxford Diffraction Xcalibur (TM) Single Crystal X-ray Diffractometer[28] with MoKα radiation using ω/2θ scan mode low-temperature facilities. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. The positions of H atoms were calculated, and were refined. The structures were solved by SHELXS–97[29] and refined with SHELXL–97.[30] The details of the X-ray data collection, structure solution and structure refinements are given in Table 1. Bond distances and angles are listed in Table 2. The molecular structures with the atom-numbering scheme for compound **1** and **2** are shown in Figures 1 and 2,[31]

respectively. Crystallographic data (excluding structure factors) for the structures reported in this present paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 728285 and 728521.[32]

Table 1. Crystal data and structure refinements for the title compounds.

Compound	**1**	**2**
Empirical Formula	$C_{20}H_{21}N_3O_3$	$C_{19}H_{19}N_3O_3$
Formula weight	351.40	337.37
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1$
Crystal size	0.36 × 0.36 × 0.16 mm^3	0.50 × 0.50 × 0.50 mm^3
Unit cell dimensions	a = 12.5665(3) Å b = 10.4791(2)Å, β= 109.018(3)° c = 14.6240(3)	a = 5.6666(2)Å b = 12.2444(5)Å, β=101.376(4)° c = 12.1556(4)
V	1820.65(7) Å^3	826.84(5)Å^3
Z	4	2
D_c	1.282 g cm^{-3}	1.355 g cm^{-3}
μ(MoKα)	0.088 mm^{-1}	0.094 mm^{-1}
F(000)	744	356
$2\theta_{max}$	52.74 °	52.74 °
h, k, l range	$-15 \le h \le 15$ $-12 \le k \le 13$ $-18 \le l \le 18$	$-7 \le h \le 6$ $-15 \le k \le 14$ $-14 \le l \le 15$
Reflections collected	3721	5336
Reflections observed ($I>2\sigma(I)$)	2545	1759
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2545/1/298	1759/1/284
Goodness-of-fit on F^2	1.095	1.113
Final R indices [I>2σ(I)]	R_1 = 0.0368, wR_2 = 0.0916	R_1 = 0.0256, wR_2 = 0.0642
R indices (all data)	R_1 = 0.0643, wR_2 = 0.1192	R_1 = 0.0298, wR_2 = 0.0668
Largest diff. peak and hole	0.241 and –0.250 e.Å^{-3}	0.179 and –0.173 e.Å^{-3}

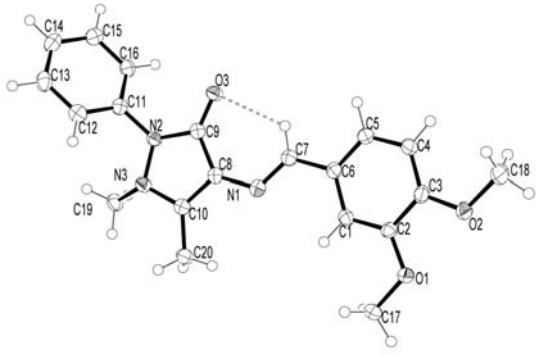


Figure 1. ORTEP-3 drawing[31] of the compound **1** with displacement ellipsoids plotted at 50% probability level; the intramolecular hydrogen bond has been indicated by dashed lines.

Table 2. Some selected bond lengths (Å) and bond angles (°) for the title compounds.

Compound 1			
C(2)-C(3)	1.417(2)	C(3)-O(2)	1.364(2)
C(7)-N(1)	1.288(2)	C(8)-C(10)	1.372(2)
C(8)-N(1)	1.392(2)	C(8)-C(9)	1.449(2)
C(11)-N(2)	1.422(2)	C(12)-C(13)	1.379(2)
C(19)-N(3)	1.467(2)	N(2)-N(3)	1.408(2)
C(7)... O(3)	3.0383		
O(1)-C(2)-C(3)	114.9(1)	C(1)-C(2)-C(3)	120.0(1)
O(3)-C(9)-N(2)	124.0(1)	O(3)-C(9)-C(8)	131.2(1)
N(2)-C(9)-C(8)	104.8(1)	C(8)-C(10)-N(3)	110.3(1)
C(7)-N(1)-C(8)	120.9(1)	C(9)-N(2)-N(3)	110.0(1)
N(2)-N(3)-C(19)	116.1(1)	C(2)-O(1)-C(17)	116.6(1)
Compound 2			
C(6)-O(2)	1.359(2)	C(7)-N(1)	1.288(2)
C(8)-C(10)	1.374(2)	C(8)-N(1)	1.393(3)
C(8)-C(9)	1.445(3)	C(9)-O(3)	1.233(2)
C(10)-C(19)	1.483(2)	C(11)-C(16)	1.382(3)
C(17)-O(1)	1.432(2)	C(18)-N(3)	1.465(3)
O(2)...N(1)	2.6177(2)		
O(1)-C(3)-C(2)	124.3(2)	O(1)-C(3)-C(4)	116.2(2)
C(4)-C(5)-C(6)	120.5(2)	O(2)-C(6)-C(5)	118.8(2)
N(1)-C(7)-C(1)	120.8(2)	C(10)-C(8)-N(1)	122.6(2)
O(3)-C(9)-N(2)	123.3(2)	O(3)-C(9)-C(8)	131.4(2)
N(3)-N(2)-C(11)	115.9(1)	C(9)-N(2)-C(11)	119.6(1)
C(10)-N(3)-N(2)	108.3(1)	C(10)-N(3)-C(18)	123.6(1)

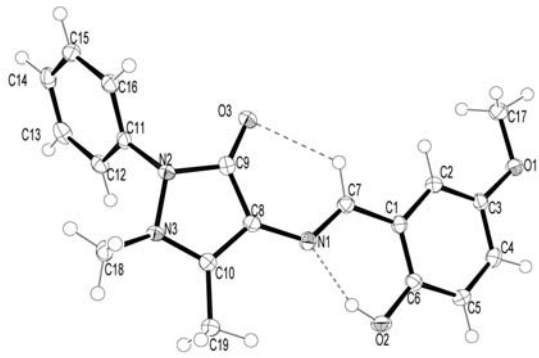


Figure 2. ORTEP-3 drawing[31] of the compound **2** with displacement ellipsoids plotted at 50% probability level; intramolecular hydrogen bonds have been represented by dashed lines.

3. Results and Discussion

3. 1. Spectroscopic Investigation

Direct reaction of one equivalent of 4-aminoantipyrine with one equivalent of appropriate aldehyde in ethanol gives the corresponding Schiff base. Compounds **1** and **2** were isolated as yellow crystalls with 77 and 74% yield, respectively. They were characterized by elemental analysis, UV-vis, IR, ^{1}H and ^{13}C NMR spectroscopic techniques. The characteristic infrared spectra were given in the Experimental section. The IR spectra of **1** and **2** show

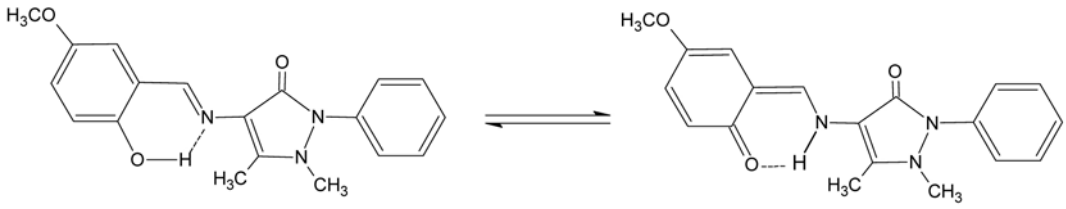
strong bands at 1573 and 1574 cm^{-1}, characteristic for the imine bond and assigned to the azomethine C=N groups. The sharp peaks in the range between 1647 and 1652 cm^{-1} can be attributed to the $\nu_{C=O}$ stretching modes for **1** and **2**, respectively. The phenolic OH stretching band was not observed, indicating the formation of a cyclic intramolecular hydrogen bond.

The ^{1}H NMR spectra of the Schiff bases show characteristic singlets at 9.66 and 9.79 ppm, respectively, corresponding to the azomethine HC=N proton. The aliphatic C-CH_3 and N-CH_3 protons were observed as singlets at 2.39 and 3.02 ppm for compound **1** and at 2.37 and 3.14 ppm for compound **2**. The aromatic protons for compound **1** and **2** appear as multiplets in the range 6.83–7.50 ppm and 6.86–7.52 ppm, respectively. Protons for two methoxy protons in compound **1** were observed at 3.83 and 3.89 ppm, and protons for one methoxy group in compound **2** were detected at 3.74 ppm. The OH proton for compound **2** was observed as a singlet at 12.84 ppm**.**

The UV-vis spectra of Schiff base **1** was measured in DMSO, EtOH and $CHCl_3$. Two absorption bands were observed for compound **1** at 240–280 and at 336–348 nm due to the π–π* transition. UV-vis absorption bands for compounds **1** and **2** in various solvents are presented in Table 3. As one may expect, tautomerism is not possible for compound **1**, thus CF_3COOH and NEt_3 show no effects in UV-vis spectra (Table 3). Figures 3 and 4 show the representative UV-vis spectra of compound **2** in different solvents and in acidic media. The UV-vis spectral behaviour of Schiff bases have been extensively investigated in recent years.[33–35] Tautomerism in Schiff base derivatives of o-hydroxyaldehydes in solution and in solid state have been investigated using mass spectra,[36] NMR,[37] UV-vis[38–42] and X-ray crystallography.[42,43] The plausible existence of tautomerism in solution (phenol-imine and keto-amine forms, O-H···N ⇌ O···H-N), depending on the formation of intramolecular hydrogen bonding is shown in Scheme 2.

Solvent polarity affects the phenol-imine and keto-amine tautomeric equlibria in Schiff bases by stabilizing the more polar keto-amine form, although frequently no clear-cut relation between phenol-imine/keto-amine ratio and solvent polarity could be established.[35] In the spectra of compound **2,** π–π* and intramolecular charge transfer interaction bands[44] are observed at 238–282 and 328–372 nm in DMSO, EtOH, $CHCl_3$ and toluene, respectively. The charge transfer interaction bands originate from 4-aminoantipyrine ring and belongs to the C=N group.[44] The UV-vis spectra for **2** in neutral and basic media (NEt_3) showed that the phenol-imine form is dominant. In basic media, the keto-amine (O...H-N) / phenol-imine (O-H...N) ratios were approximately the same as in the respective pure solvent media of compound **2**. However, in acidic media (CF_3COOH) of $CHCl_3$ and toluene a new bands at 440 nm and 438 nm have been observed, respectively.[26] These bands can be linked with the shift of the tautomeric equilibrium to the keto-amine form. The results in acidic solution indicates that methoxy salicylaldimine **2** gives salt with CF_3COOH.[45] The absence of keto-amine form in the acidic DMSO and EtOH solutions may be explained by the hydrogen bonding to acid (CF_3COOH).[43,46]

After the addition of CF_3COOH in $CDCl_3$ the tautomerism for compound **2** was also studied by ^{1}H and ^{13}C NMR spectroscopy (see Experimental section). The ^{1}H NMR data for compound **2** in $CDCl_3$ showed the existence of only phenol-imine tautomer, while both phenol-imine and keto-amine forms have been observed in acidic $CDCl_3$. In acidic $CDCl_3$ the ^{1}H NMR spectra for compound **2** the OH absorption was observed as a broad singlet at 12.82 ppm, because of CF_3COOH addition. However, in pure $CDCl_3$ as solvent, this absorption was observed as a sharp singlet at 12.84 ppm. N=CH proton was observed as a singlet at 9.88 ppm while N-CH proton was observed as a doublet at 9.65 ppm. The hydroxyl proton (O-H...N) and amine proton (O...H-N) were observed at 12.82 and 15.98 ppm, respectively. The new peaks (for HN-C<u>H</u> and <u>H</u>N-CH) showed that the keto-amine tautomer was present in acidic $CDCl_3$. Because of two tautomeric forms the ^{1}H NMR spectrum of aromatic region became much more complex in acidic medium. The relative ratios of phenol-imine/keto-amine tautomers were estimated to be 49/51% from the spectra of compound **2**. In the ^{13}C NMR spectra of acidic $CDCl_3$ solution of **2** a lot of additional carbon peaks were observed compared to the ^{13}C NMR spectra in pure $CDCl_3$ as solvent. It can be concluded from UV-vis and NMR spectra that the keto-amine/phenol-imine tautomeric forms were present in the acidic solution of compound **2** in $CDCl_3$.



Phenol-imine Keto-amine

Scheme 2. The expected phenol-imine/keto-amine tautomeric equilibria for compound **2.**

Table 3. UV-vis spectral data for **1** and **2.**

Comp.	Solvents	λ, nm (log ε)	Keto-amine isomer (%)[a,b]
1[c,d]	DMSO	280 (4.34); 348 (4.56)	
	DMSO+CF_3COOH	282 (4.23); 344 (4.50)	–
	DMSO+NEt_3	280 (4.12); 348 (4.55)	
	EtOH	240 (4.40); 338 (4.56)	
	EtOH+CF_3COOH	238 (4.39); 336 (4.35)	–
	EtOH+NEt_3	240 (4.28); 336 (4.54)	
	$CHCl_3$	240 (4.36); 340 (4.58)	
	$CHCl_3$+CF_3COOH	242 (4.24); 336 (3.95)	–
	$CHCl_3$+NEt_3	240 (4.28); 336 (4.02)	
2	DMSO	282 (4.31); 338 (4.41); 370 (4.55)	0.0
	DMSO+CF_3COOH	284 (4.19); 340 (4.28); 370 (4.42)	0.0
	DMSO+NEt_3	282 (4.38); 336 (4.41); 370 (4.55)	0.0
	EtOH	238 (4.41); 316 (4.26); 328 (4.26); 368 (4.31)	0.0
	EtOH+CF_3COOH	238 (4.30); 318 (3.72); 328 (4.14); 366 (4.18)	0.0
	EtOH+NEt_3	240 (4.22); 316 (4.28); 328 (4.27); 368 (4.31)	0.0
	$CHCl_3$	244 (4.48); 318 (4.36); 330 (4.36); 368 (4.39)	0.0
	$CHCl_3$+CF_3COOH	244 (4.63); 332 (4.24); 360 (4.31); 440 (4.36)	52.4
	$CHCl_3$+NEt_3	244 (4.44); 316 (4.38); 330 (4.36); 370 (4.39)	0.0
	Toluene	282 (4.36); 320 (4.47); 328 (4.47); 372 (4.49)	0.0
	Toluene+CF_3COOH	284 (4.38); 318 (4.40); 366 (4.44); 438 (4.45)	50.8
	Toluene+NEt_3	284 (4.22); 320 (4.48); 334 (4.47); 376 (4.49)	0.0

[a] A_2/A_1=x(100-x) where A_1= the absorbance of the phenol-imine form; A_2= the absorbance of the keto-amine form; x= the percentage of keto-amine form.
[b] Basic/acidic medium is attained by addition of NEt_3/CF_3COOH (1 mL) to the given solution (ligand concentration: 5×10^{-5} mol dm^{-3}).
[c] Not sufficiently soluble in Toluene.
[d] Tautomerism is impossible for compound **1**, the mark (–) is used.

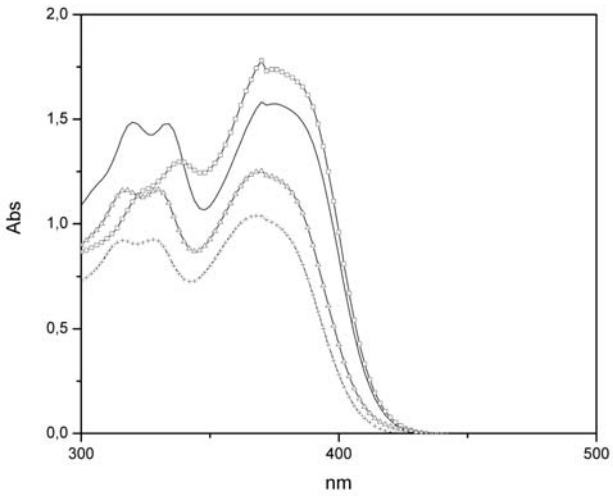


Figure 3. UV-vis spectra showing solvent effect on compound **2** in DMSO (-□-), chloroform (-△-), ethanol (-+-), and toluene (_); concentration 5×10^{-5} mol dm^{-3}.

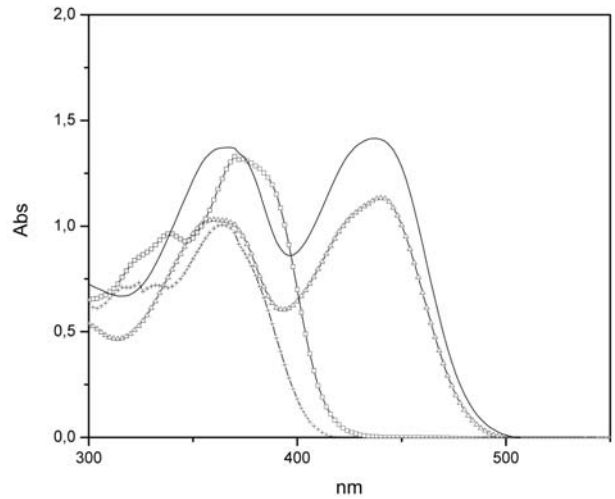


Figure 4. UV-vis spectra showing acidic effect on compound **2** in DMSO (-□-), chloroform (-△-), ethanol (-+-), and toluene (_); concentration 5 x 10^{-5} mol dm^{-3}.

3. 2. Crystallographic Study

Schiff base compounds have a variety of substituents with different electron-donating and electron-withdrawing groups, and therefore may have interesting electro-chemical properties of great interest for molecular electronic devices. They have been under intense investigation in previous years because of their potential applicability in optical communications and many of them have Non Linear Optic (NLO) behavior.[47] Second-order NLO organic materials that contain stable molecules with large

molecular hyperpolarizabilities in noncentrosymmetric packing are of great interest for device applications, but according to a statistical study, an overwhelming majority of a chiral molecules crystallize centrosymmetrically.

Compounds **1** and **2** (see Figures 1 and 2) can be described as comprising of central part of C=N bridging 3,4-dimethoxybenzaldehyde and 2-hydroxy-5-methoxybenzaldehyde and 4-amino-1,2-dihydro-1,5-dimethyl-2-phenyl-3*H*-pyrazole-3-one aniline fragments. Selected bond lengths and angles from the X-ray analysis are presented in Tables 1 and 2, respectively. Determined bond lengths and angles within the aromatic rings are consistent with those expected for sp^2 aromatic carbon atoms. Bond lengths between C6-C7 [1.463(2) Å] in compound **1** and between C1-C7 [1.454(3) Å] in compound **2** are consistent with single bonds between sp^2-hybridized carbon atoms. For the imine nitrogen atoms, N1 and N2, the bond angles C8-N1-C7 [121.0(2)°] for **1** and C8-N1-C7 [121.4(2)°] for **2** confirm their sp^2 character.

In compound **1** are one nonclassical intramolecular hydrogen bond and three intermolecular hydrogen bonds. There are two intramolecular hydrogen bonds and one intermolecular hydrogen bond in compound **2.** The crystal structures are stabilized by intramolecular and intermolecular hydrogen bonding and their geometrical details are listed in Table 4.[48,49]

Weak intramolecular hydrogen bonds occur between C7-H7...O3 [3.0383(3) Å] atoms in compound **1,** and between O2-H2A...N1 [2.6177(2) Å] and C7-H7...O3 [3.0300(2) Å] atoms in compound **2** (see Figures 1 and 2). The sum of the Van der Waals radius of the O and N atoms (3.07 Å) is significantly longer than the intramolecular O...N hydrogen bond length.[50] There are also weak intermolecular hydrogen bonds between C4...O3 [3.4239(2) Å], C13...O3 [3.2787(2) Å], and C20...O3 [3.3080(2) Å] for the compound **1** (see Figure 5) and between C18...O1 [3.3316(1) Å] atoms of neighbouring molecules for the compund **2**.

Table 4. Geometric details of intramolecular and intermolecular hydrogen bonding for the title compounds.[a]

[D – H...A] (Å)	[D – H] (Å)	[H...A] (Å)	[D...A] (Å)	[D – H...A] (°)
Compound 1				
C7-H7... O3	0.98	2.37	3.0383	125
C4-H4... O3^{i}	0.96	2.54	3.4239	154
C13-H13. ..O3^{ii}	1.01	2.44	3.2787	140
C20-H20A...O3^{iii}	1.01	2.55	3.3080	131
Compound 2				
O2-H2A...N1	0.87	1.81	2.6177	154
C7-H7...O3	1.01	2.36	3.0300	123
C18-H18B...O1^{iv}	0.96	2.44	3.3316	154

[a] D: donor, A: acceptor. Symmetry transformation used to generate equivalent atoms:
(i) 1-x, -y, 1-z; (ii) x, 1/2-y, -1/2+z; (iii) 1-x, 1/2+y, 1/2-z; (iv) 1+x, -1+y, z

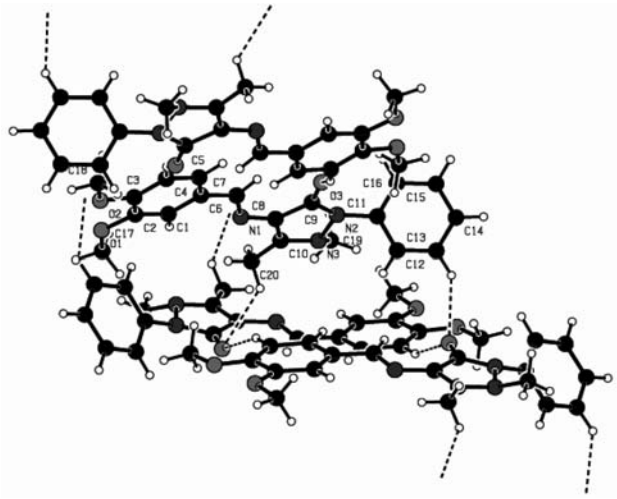


Figure 5. The crystal structure of the compound **1** a perspective view. The intramolecular and intermolecular hydrogen bonds have been indicated by dashed lines.

C-N group in compound **2** seems to have a strong electron withdrawing character. Thus, the C6-O2 bond distance of 1.356(2) Å is also consistent with the C-O single bonding; similarly the C7=N1 distance of 1.288(2) Å is also consistent with the C=N double bonding. The C=O bond distance indicates the presence of the keto form, with a partial double bond character of the CO group (>C=O ↔ C^{+}-O^{-}). The C_{sp3}-O-C_{sp3} bond lengths vary because of the influence of tautomerism. Furthermore, the $\phi_{C=N}$ torsion angles C6–C7–N1–C8 [176.25(13)°] for compound **1** and C1–C7–N1–C8 [–172.49(17)°] for compound **2** show that the configurations around the C7=N1 bond are in accordance with the phenol-imine tautomeric form (Scheme 2).

4. Conclusions

We have prepared a new type of ligands from 4-aminoantipyrine with 3,4-dimethoxybenzaldehyde and 2-hydroxy-5-methoxybenzaldehyde. They were characterized by using elemental analysis, FT-IR, ^{1}H and ^{13}C NMR spectroscopic techniques. The position of the tautomeric equilibrium for compound 2 was investigated by using UV-vis spectrophotometry. In order to determine the tautomeric form and molecular structure of the compound **2** in the solid state**,** we used X-ray crystallographic technique. Based on the crystallographic results, we can conclude that the title compounds were in the phenol-imine tautomeric form.

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Povzetek

Avtorji v prispevku poročajo o pripravi dveh novih Schiffovih baz kot ligandov; 4-{[(1*E*)-(3,4-dimetoksifenil)metilen]amino}-1,5-dimetil-2-fenil-1,2-dihidro-3*H*-pirazol-3-ona (**1**) in 4-{[(1*E*)-(2-hidroksi-5-metoksifenil)metilen]amino}-1,5-dimetil-2-fenil-1,2-dihidro-3*H*-pirazol-3-ona (**2**). Obe spojini sta okarakterizirani z elementno analizo, UV-vis, FT-IR, ^{1}H in ^{13}C NMR spektroskopijami ter z rentgensko kristalografsko analizo. Za nekatere raztopine spojine **2** je bilo s pomočjo UV-vis absorpcijske spektroskopije študirano ravnotežje med fenol-imin (O-H···N) in keto-amin (O···N-H) tavtomerno obliko. Kristalografska analiza je pokazala, da obe spojini (**1** in **2**) kristalizirata v monoklinski prostorski skupini $P2_1/c$ in $P2_1$ s sledečimi parametri celice: a = 12.5665(3) Å in 5.6666(2) Å; b = 10.4791(2) Å in 12.2444(5) Å; c = 14.6240(3) Å in 12.1556(4) Å; V =1820.65(7) Å^3 in 826.84(5) Å^3; D_x = 1.282 g.cm^{-3} in 1.355 g.cm^{-3}; Z = 4 in 2.