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Preference of 4-Aminomethylene-1-methylpyrazolin-5-one tautomer; DFT and AIM calculations

Zaki S. Safi
Department of Chemistry, Faculty of Science, Al-Azhar University of Gaza, Gaza City – **P.O.** 1277, Palestine,
E-mail: z.safi@alazhar-gaza.edu

Abstract: In this study, the gas phase tautomerism of 4-Aminomethylene derivatives of N-methylpyrazolin-5-one is studied using high level density fuctional theory (DFT) calculations. The structures of all possible tautomers and their conformers were optimized at B3LYP6-31+G(d,p) level of theory. Final energies were obtained at B3LYP6-311+G(2df,2p) level. It has been found that the investigated system can exit largely as a unique tautomer, **1a**, which corresponds to the enamine structure stabilized by an intramolecular hydrogen bond. It has been also shown that the topological parameters such as features of bond critical points (bcps) and ring critical points (rcps) may be employed as measures of the H-bond strength.

Key words: 4-aminomethylene-1-methylpyrazolin-5-one, DFT, IHB, RAHB, AIM.

تفضيل متشاكل 4-أمينوميثيلين-N-ميثيل بيرازولين-5-اون: حسابات نظرية دالة الكثافة (DFT) والذرات في الجزيئات(AIM)

ملخص: تناولت هذه الدراسة التشاكل في الطور الغازي لمشتقات 4-أمينوميثيلين-N-ميثيل بيروزالين-5-اون وذلك باستخدام مستوى عالٍ من الحسابات باستخدام نظرية دالة الكثافة. تم ضبط جميع التركيبات لجميع المتشاكلات بصورهم المختلفة عند المستوى النظري B3LYP6-31+G(d,p). تم حساب جميع الطاقات النهائية عند المستوى الأعلى B3LYP6-311+G(2df,2p). بينت هذه الدراسة بأن هذا النظام يمكن أن يتواجد وبصورة كبيرة كمتشاكل وحيد، **1a**، والتى تناظر تركيب الاينامين واعتمدت في ثباتها على وجود روابط هيدروجينية داخلية أيضاً، أظهرت هذه الدراسة بأن المعاملات التوبولوجية، مثل نقاط الرابطة الحرجة ونقاط الحلقة الحرجة، يمكن أن توظف لقياس مدى قوة الرابطة الهيدروجينية.

Introduction:

Quantum mechanical methods have been used to investigate the tautomeric equilibria in heterocyclic systems, which represent a central component of synthetic chemistry and biochemical processes. Also, they have been used to predict the relative energies of tautomerism in both aqueous and gas phases [1-7].

For hundreds of years, 4-Aminomethylene derivatives of pyrazolin-5-ones have been used as ligands of several metal complexes [8-9]. Recently, a new progress was achieved by synthesizing the 4-aminomethylene derivatives of alkylpyrazolones and hence, exploring their tautomeric structures in aqueous media. It was concluded that these derivatives could primarily exist

as a unique tautomer that corresponds to the enamine structure stabilized by an intramolecular hydrogen bond **(IHB)** [10].

Obviously, the importance of the hydrogen bond (HB), and its major role in biological, physical, and chemical applications has attracted a great deal of attention in recent years[11–15]. The possibility of forming a H-bonds in species constituting crystals depends solely on the availability of acidic X-H bonds and Lewis base centers [16,17]. A heteronuclear resonance-assisted hydrogen bonding **(RAHB) is** a special type of intramolecular interaction that was first proposed by Gilli *et al.* [18] in the enol forms of β-diketones[18a] and analogous compounds containing nitrogen[18b,c]. it has been concluded that RAHB enhances the strength of the IMB, which in its turn enhances the stability of the enamine tautomer.

On the other hand, quantum-mechanical principles are applied to the electron density of a molecule in order to gain insight into the molecule's structure and bonding. Between these lines, the Atoms in Molecules (AIM) theory[19] has been employed to reach a better understanding of hydrogen bonding properties [20].

In this paper, the prototropic tautomerisim of the 4-aminomethylene-1-methyl-pyrazolin-5-one **AMMP** and the heteronuclear intramolecular resonance-assisted hydrogen bonds are considered for further computational investigations and analysis. For this purpose, density functional (DFT) calculations have been performed to study the relative stabilities of the different tautomers of the system. The existence of such intramolecular interactions is sought employing AIM analysis, geometry variations, and the hydrogen bond stabilization energies.

Computational Details

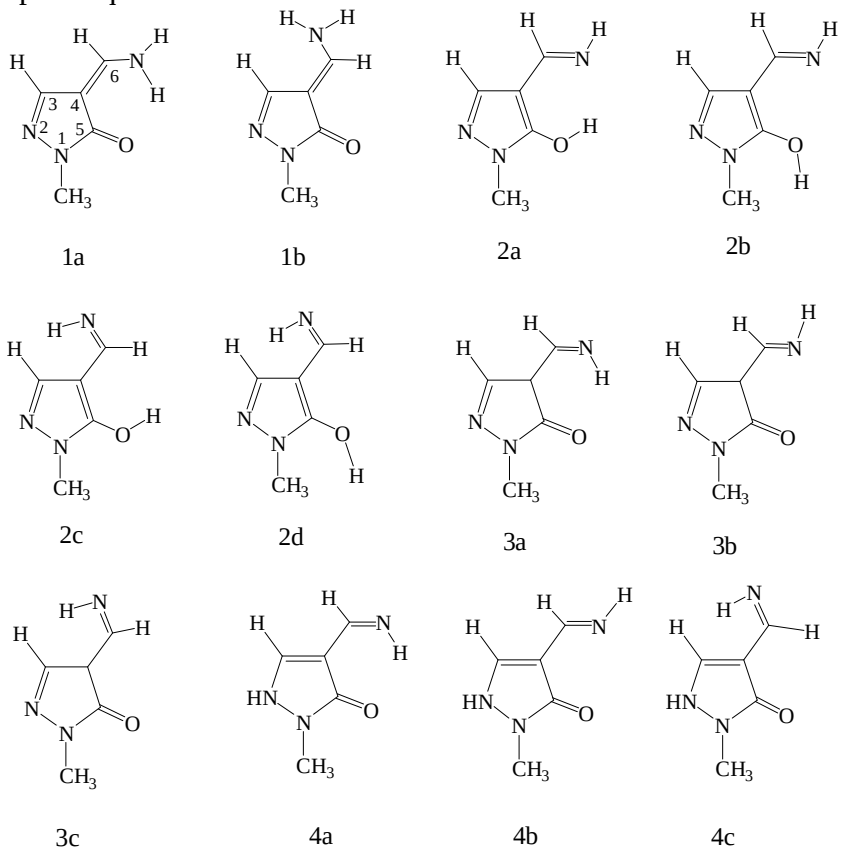
Geometry optimizations were done using the Gaussian 03 package of molecular orbital program.[23] at the hybrid density functional B3LYP approach, which combines Becke's three-parameter nonlocal hybrid exchange potential[21] with the nonlocal correlation of Lee, Yang, and Parr[22]. All the calculations were carried out employing the 6-31+G(d,p) basis set. To enhance the energy calculations, the optimized structures were subjected to a single point investigation at B3LYP/6-311+G(2df,2p) level of theory. Minima were characterized by the absence of imaginary vibrational frequencies. The energy values were corrected for the zero point energy (ZPE) and 298.15 K with frequencies scaled by the empirical factor 0.9806 proposed by Scott and Radom[24]for all vibrational modes.

The bonding characteristics were analyzed by means of the atoms in molecules (AIM) theory[19]. For this purpose we have located the relevant bond critical points and evaluated the charge density for each of them. To

perform the AIM analysis, we have used the AIMPAC series of programs.[26]

Results and discussion

For 4-aminomethylene-1-methyl-pyrazolin-5-one (**AMMP**), four tautomers can be envisaged resulting from an appropriate resonance reaction. Each of these tautomers presents several conformers that lead, in total, to twelve structures schematized in Scheme 1. Hence, in our theoretical survey twelve structures have been optimized. All of them are local minima of the PES with all harmonic frequencies being real. For the most stable conformers of each tautomer, we have carried out a single point calculation at B3LYP/6-311+G(2df,2p) level of theory. The corresponding total, zero point energy (ZPE) correction, and the relative energies are displayed in Table 1. The optimized geometries of these twelve local are available from the author upon request.



Scheme 1: Schematic representation of different tautomers of the AMMP in all possible conformers.

Table1: Relative Energies[a], Enthalpies[a], Entropies[a], and Relative Free Energies[a] of the Different Tautomers and rotatomers of 4-aminomethylen derivatives of 1-methylpyrazolin-5-one. All values are in kJ/mol.

species	ΔE	ΔH	ΔS	ΔG
1a	**0.0**	**0.0**	**0.0**	**0.0**
1b	22.9	24.1	-3.0	21.1
2a	31.4	30.6	0.5	31.2
2b	89.2	90.7	-4.7	86.1
2c	74.6	75.9	-5.1	70.8
2d	74.3	73.4	1.6	75.1
3a	94.9	95.2	-2.1	93.1
3b	92.6	93.4	-4.0	89.3
3c	98.6	99.4	-4.1	95.3
4a	79.3	79.2	0.0	79.2
4b	97.6	97.8	-0.9	96.9
4c	89.4	89.9	-2.0	87.9

[a] Values obtained at B3LYP/6-311+(2df,2p)// B3LYP/6-31+G level of theory.**

As it was mentioned before, **AMMP** presents several tautomers that can be generated through an appropriate resonance structure. So, in order to rationalize their intrinsic reactivity, we have to establish which tautomer is the predominant in the gas phase. One of the most important features of the relative energies, listed in Table 1, that the computed order of stability of tautomers in gas phase was rated as **1a > 2a > 3b > 4a.**

This finding agrees with previous experimental results[10] that also concluded that the keto-amine, enamine, tautomer (**1a**) is the unique tautomer in solution. In fact, it is found that tautomer **1a** is 31.4 $kJmol^{-1}$ more stable than tautomer **2a**. On the other hand, tautomers **3a** and **4a** were found largely less stable than the global minimum, see table 1.

In the upper raw of Figure 1, we present the optimized structures of the most stable tautomers, **1a**, **2a**, **3a** and **4a**, of the considered system, while in the lower one, the molecular graphs of the same species are presented. One of the most important results, deduced from the optimized structures, is that the mentioned tautomers are characterized by the existence of an **IHB**, which leads to form a six-membered ring attached to the pyrazol ring. As is well known that this bond is formed due to the acceptor-donor interaction and their existence can be proved by the location of a bond critical point, bcp,

between the acceptor and the donor atoms. Whereas, the ring-like structure is indicated by finding a ring critical point, rcp, see figure 1.

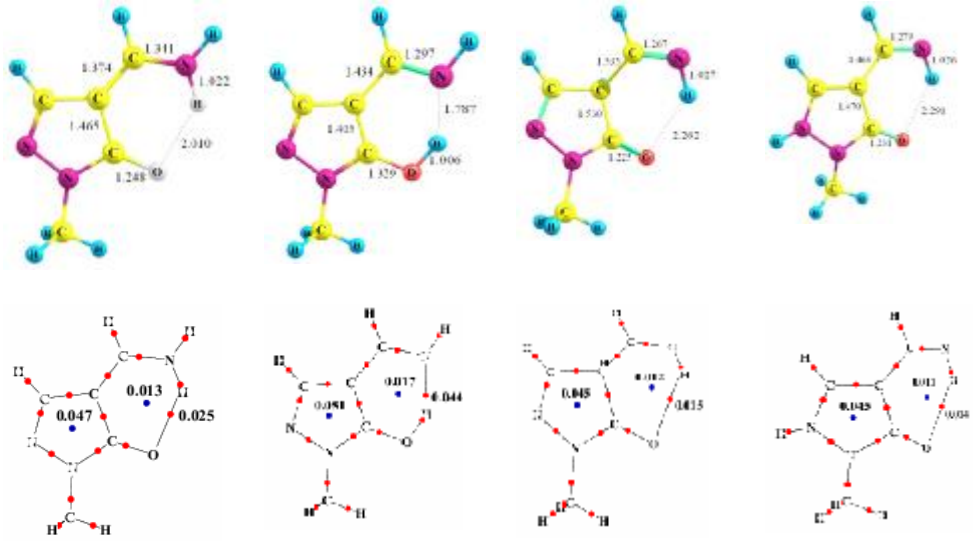


Figure1: Upper raw: B3LYP/6-31+G(d,p) optimized geometries of the most stable tautomers, **1a, 2a, 3a, and 4a**. Bond lengths are in Å. **Lower raw**: Molecular graphs of the most stable tautomers, same as in left column. Red dots and blue dots are bond critical point and ring critical points, respectively. Charge densities are in a.u.

It is worth mentioning that the **IHB** in the **1a**, **3a** and **4a** species is of NH···O type, while the one in the **2a** species is of OH···N type, which can be considered as a heteronuclear intramolecular H-bonds. The **IHB**s of the NH···O are found to be shorter than that of the NH···O type, which is also mirrored in the values of the charge densities calculated at the bond critical points (bcps) of the hydrogen bonds (see Figure 1). It is important to mention that the charge densities at the bcps associated with inter- and intramolecular hydrogen bonds have been shown to accept a direct relationship to the strength of the linkage.[26] Therefore, a comparison of the charge densities of the **IHB** in the different tautomers allowed us to analyze the electronic redistributions associated with these **RAHB**s. In fact, our AIM calculation shows that the charge density at bcps of the NH···O is about twice that in case of N···HO.

As a consequence, for the NH···O bond, the lengthening of the bond distance upon interaction between the two ends (amino hydrogen and oxygen atoms) is more pronounced when the **3a** and **4a** tautomers are considered. (see figure 1 and table **S2**). Also, coherently, the decrease in the

charge density at the bond critical points (bcps) and the ring critical points (rcps) are also greater (see figure 1 and Table **S3**). These findings indicate the weakness of the IHBs that formed in tautomers **3a** and **4a**, which can be used as a good precursor for the destabilization of these tautomers when compared with tautomer **1a**. In fact, one can see that the rcps of the ring-like structures in all cases have the trend of: **2a** (0.17 a.u.) > **1a** (0.13 a.u.) > > **3a** (0.12 a.u.) > **4a** (0.011 a.u.). These simple arguments may led us to conclude that the **IHB** in case of **2a** (NH···O) is the most strongest bond, which are in a good agreement with those reported by Emsley,[27] who suggested that hydrogen bonds can vary in strength from very weak (1-2 kJ mol^{-1}) to extremely strong (>155 kJ mol^{-1}), as in the ion HF_2. However, the trends observed in the relative stabilities of the keto-amine (**1a**), keto-imine (**3a** and **4a**) and enol-imine (**2a**) tautomers do not follow the changes observed in the strength of the **IHB**.

π-Electron delocalisation for Resonance Assisted H-bonds, RAHB

The most immediate evidence of the optimized geometries (Figure 1) of the **1a** tautomer within the tautomerization process is that the C4=C6 and C4-C5 bond lengths approach each other and the C=O bond lengthens, (see Table **S2** of the supporting information for more details). In fact, our results show that the C4=C6 bond length increases while the opposite is true in case of C4-C5. In the tautomer **1a**, in order to form an **IHB** by the interaction between the oxygen atom attached to position 5 within and the amino hydrogen atom, the C=O and N-H bonds lengthen. In case of tautomer **2a** in which the **IHB** is formed by the interaction of the nitrogen atom of the imine group and the hydrogen hydroxyl group attached to position 5, the C=N and O-H bonds lengthen. However, the **IHB** in case of the tautomer **2a** (1.787Å) is smaller than that in the tautomer **1b** (2.001Å), tautomer 1a is found to be more stable than tautomer 1b.

Gilli et al [18b] suggested that, one of the most important features of **RAHB**s is the equalization of the appropriate bonds within the system. That is to say that the changes of the geometry of molecules involved in **RAHB**s are greater than the changes for usual H-bonds since **RAHB**s belong to the strongest H-bonded systems. For the description of this feature the Q-parameter was introduced, $Q=(d_1-d_4)+(d_3-d_2)$, where d_1, d_2, d_3 and d_4 are bond lengths (Scheme 2).

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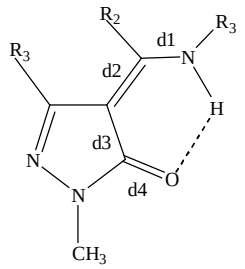

Scheme 2: The derivative of AMMP with the intramolecular resonance assisted hydrogen bond.

Previous studies[18b,28,29] showed that Q-parameter decreases for the **RAHB** systems, the smaller its value the greater the effect of the equalization of bonds and consequently the stronger hydrogen bond.

The resonance effect can be studied by comparing the so-called open configuration, for which IHB exists, and the closed one, for which IHB doesn't exist. Grabowski[28,29] showed that for the closed configuration, the effect is greater than for the open one. In this survey, two configurations: closed configuration (**1a**) and the open configurations (**1b**) will be studied (Scheme 2).

Table 2 shows the Q-parameters for the tautomer 1. We see that the lowest Q-values are observed for the closed ring, **1a**. For the open species, **1b**, the calculated Q-value is found to be higher than that of the closed one. This finding points out that an increase of the delocalization of the π-conjugated system, and hence the decreases of Q-Value of the tautomer **1b**, due to the presence of, may be caused the stabilization of the tautomer **1a** over **1b**. The same results can be obtained for the other tautomers.

Table 2: Q-values for different configurations of **1a**
tautomers considered in this Study.

	C4-C5	C5=O)	C4=C6	C4-C5	Q
1a(C)	1.341	1.248	1.374	1.465	0.185
1b(O)	1.351	1.233	1.364	1.479	0.233

C belongs to the closed structure, ring-like structure.
O belongs to open structure.

Conclusion

In agreement with the experimental results of Belmar *et al* [10] the theoretical results of B3LYP/6-31+G(d,p) calculations on the 4-methylene-1methylpyrazol-5-one, AMMP, show that the keto-amino tautomer is the most stable among all other tautomers. The computed results show that the π-electron delocalisation for the ring-like structure created by the intramolecular H-bond, **IHB**, formation exists. Such delocalisation is greater

for the open configurations than for the closed configurations. The results of this study also show that the topological parameters derived from the theory of Bader[19] may be applied to estimate the H-bond strength. The properties of the rcps and bcps are useful descriptors for the strength of intramolecular H-bonds. The N···H-O intramolecular hydrogen bond is stronger than the N-H···O. The relative stabilities of the different tautomers investigated in this work don't follow the trends in the strength of the intramolecular hydrogen bonds.

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Preference of 4-Aminomethylene-1-methylpyrazolin-5-one

Table **S1**: Total Energies at B3LYP/6-31+G** (E1) and B3LYP/6-311+G(2df,2p)//B3lYP/6-31G* (E2), Zero-Point Energies (ZPE) , Thermal correction of energy and enthalpy and Entropy values of 4-aminomethylene derivatives of 1-methylpyrazolin-5-one.

	E1	E2	ZPE	TCE	TCH	S
1a	-434.229278	-434.350514	0.125947	0.134082	0.135026	88.922
1b	-434.204317	-434.327206	0.124654	0.133657	0.134601	93.096
1c	-434.210628	-434.333024	0.124901	0.133835	0.134779	93.466
1d	-434.210625	-434.333025	0.124805	0.132880	0.133824	88.050
2a	-434.240766	-434.362406	0.125898	0.134314	0.135258	89.356
2b	-434.231259	-434.353036	0.125219	0.134123	0.135067	91.791
3a	-434.204037	-434.324827	0.124445	0.132986	0.133930	91.059
3b	-434.204592	-434.325474	0.124217	0.132924	0.133869	92.601
3c	-434.202042	-434.323224	0.124246	0.132945	0.133889	92.619
4a	-434.209669	-434.332047	0.125739	0.134122	0.135066	89.335
4b	-434.201667	-434.324522	0.125185	0.133670	0.134614	90.074
4c	-434.205176	-434.327767	0.125293	0.133889	0.134833	90.956

All values are in atomic units.
Values of entropy are in Cal.K^{-1}.mol^{-1}

Table S2: Selected bond lengths in **Å**, of all tautomers and rotamers envisaged in the paper.

bonds	**1a**	**2a**		
C4=C6	1.374	1.364		
C4-C5	1.465	1.479		
C5=O	1.248	1.233		
C6-N	1.341	1.351		
N-H	1.022	1.007		
O….H-N	2.010			
	2a	**2b**	**2c**	**2d**
C4-C6	1.434	1.451	1.447	1.447
C4=C5	1.405	1.398	1.398	1.398
C5-O	1.329	1.346	1.354	1.354
C6=N	1.297	1.284	1.284	1.284
O-H	1.006	0.967	0.966	0.966
N….H-O	1.787			
	3a	**3b**	**3c**	
C4-C6	1.535	1.511	1.525	
C4-C5	1.530	1.541	1.543	
C5=O	1.225	1.220	1.220	
C6=N	1.267	1.272	1.271	
N-H	1.027	1.023	1.025	
N-H...O	2.262			
	4a	**4b**	**4c**	
C4-C6	1.463	1.456	1.464	
C4-C5	1.470	1.480	1.473	
C5=O	1.231	1.221	1.227	
C6=N	1.279	1.280	1.282	
N-H	1.026	1.022	1.026	
N-H...O	2.291			

Preference of 4-Aminomethylene-1-methylpyrazolin-5-one

Table **S3:** Selected bond lengths in, charge density, ρ in Atomic units; and energy density, $H(r)$ in atomic units..

Bond	**R(Å)**	**ρ(r)**	**H(r)**
	1a		
C6-N	1.470	0.332	-0.5443
C5=O	1.258	0.384	-0.6549
(C6)N-H	1.000	0.330	-0.4930
O…HN	2.217	0.025	-0.0005
		2a	
C6=N	1.297	0.372	-0.6410
C5-O	1.329	0.318	-0.5092
(C5)O-H	1.006	0.316	-0.5157
N…HO	1.787	0.044	-0.0030
		3a	
C6=N	1.267	0.394	-0.6949
C5=O	1.225	0.402	-0.6917
(C6)N-H	1.027	0.336	-0.4961
O…HN	2.262	0.015	0.0004
		4a	
C6=N	1.279	0.387	-0.6777
C5=O	1.231	0.399	-0.6777
(C6)N-H	1.026	0.337	-0.4981
O…HN	2.291	0.014	0.0002