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Quantum-Chemical Studies of the Structure and Reactivity of Pyrazol-5-ones and Their Thio and Seleno Analogs: V.[1] Effect of Electron Correlation on Tautomerism and Acidity of 1-Methylheteropyrazolones

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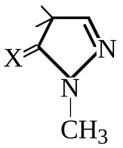
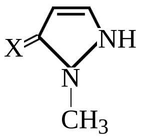
Abstract—The relative stability of tautomeric forms of 1-methyl-substituted heteropyrazolones (O, S, Se) and their gas-phase acidity were estimated by DFT calculations with various basis sets and methods of geometry optimization. The electron correlation effects make an appreciable contribution to the Gibbs free energies of their tautomers and anions, especially those containing the heavy atoms. The qualitative pattern of tautomerism in pyrazolones is essentially similar to that obtained by semiempirical and nonempirical RHF calculations: The most stable is the CH form. For hetero analogs, consideration of electron correlations effects increases the relative stability of SH (SeH) forms. The series of relative acidity of the compounds depending on the heteroatom is preserved (Se ≥ S >> O).

Recently [1–3] we studied the tautomerism and acid–base properties of Δ^2-1-methylpyrazolin-5-one and its thio and seleno analogs at different levels of theory and found that the relative stability of tautomeric forms of these compounds in the gas phase depends on the basis used and the method for geometry optimization.



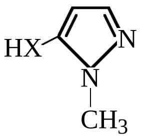
I

CH form



II

NH form



III

XH form

X = O (**Ia**–**IIIa**), S (**Ib**–**IIIb**), Se (**Ic**–**IIIc**).

We found that for unsubstituted pyrazolone the most stable is the CH form **Ia**, irrespective of the calculation method used; the two other forms **IIa** and **IIIa** are considerably less stable. For the thio and seleno analogs, the thermodynamic stability of the CH (**Ib**, **Ic**) and XH (**IIIb**, **IIIc**) forms is close. The relative stability of these forms depends on the calculation method, on the basis used, and on the consideration of the zero vibration energy. The semiempirical PM3 method significantly overestimates the stability of thiol (and probably selenol) form **III** as compared with the other two forms, contrary to nonempirical calculations of any level. However, the effects of electron correlation were not considered in these calculations [4, 5]. At the same time, in analysis of the tautomeric equilibrium of Δ^2-pyrazolin-5-one [6, 7] it was noted that these effects may influence not only the absolute but also the relative stability of the tautomeric forms. It was important to reveal the role of these effects in compounds containing heavy heteroatoms (S, Se) and to evaluate their influence on the acid–base properties of heteropyrazolones.

In this work we calculated the energies of various tautomeric forms of 1-methylheteropyrazolones and their anions by the B3LYP/6–31G*, B3LYP/6–31+G*, and B3LYP/6–31++G** procedures using different methods of geometry optimization (HF/6–31G*, HF/6–31+G*, and B3LYP/6–31G*) within the framework of the GAUSSIAN 94 program [8]. The preferableness of using the B3LYP method as compared to the methods of the Møller–Plesset pertrubation theory (MP2, MP4) for evaluating the effects of electron correlation was noted in [7] as applied to the tautomerism of unsubstituted pyrazol-5-one. The most significant results of calculations are presented in Tables 1–6 and are consecutively considered below.

In Table 1 are listed the total energies and the other contributions to the free energy of heteropyrazolones, calculated on the widely used levels HF/6–31G*//HF/6–31G* and B3LYP/6–31G*//HF/6–31G* and

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[1] For communication IV, see [1].

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Table 1. Energy contributions (E, au) to the Gibbs free energy and relative stability of tautomeric forms of isological 1-methylpyrazolones according to HF/6–31G*//HF/6–31G* and B3LYP/6–31G*//HF/6–31G* calculations

E	Form	$-E_{tot}$	E_{zv}	$\Sigma\Delta_{therm}$ (298 K)	$-E_{ec}$	ΔE_{tot}	ΔG_1[a]	ΔG_2[b]
O	CH	338.69951	0.11104	0.03744	1.90613	0.0	0.0	0.0
	NH	338.68572	0.11234	0.03654	1.90869	36.4	37.2	30.4
	OH	338.68339	0.11145	0.03912	1.91295	42.3	47.3	29.3
S	CH	661.33646	0.10858	0.03902	2.27846	0.0	0.0	0.0
	NH	661.32606	0.10967	0.03820	2.28180	27.2	28.0	19.2
	SH	661.33461	0.10622	0.03930	2.28294	5.0	0.0	–11.8
Se	CH	2661.39736	0.10794	0.04047	3.23856	0.0	0.0	0.0
	NH	2661.38855	0.10914	0.03956	3.24231	23.0	23.9	14.0
	SeH	2661.40097	0.10492	0.04036	3.24224	–9.6	–16.7	–26.4

[a] $\Delta G_1 = \Delta E_{tot} + \Delta E_{zv} + \Sigma\Delta_{therm}$, kJ mol^{-1}. [b] $\Delta G_2 = \Delta G_1 + \Delta E_{ec}$, kJ mol^{-1}.

the corresponding values of the relative stability of these forms. The relative stability of tautomers was evaluated by the equation (the energy of the CH tautomer was taken as zero)

$$\Delta G_{298} = \Delta E_{tot} + \Delta E_{zv} + \Delta(H^0_{298} - H^0_0) - T\Delta S^0_{298}.$$

The following designations are used: E_t, total energy at 0 K including the electron energy and the energy of nucleus–nucleus repulsion [9]; E_{zv}, the energy of zero vibrations; the last two terms are the temperature corrections to the enthalpy and entropy terms, whose algebraic sum is given in the tables as thermal correction [$\Sigma\Delta_{therm}$ (298 K)]. From these quantities we evaluated the Gibbs free energies at 298 K (standard conditions). In the calculations we used the scaling factor of 0.89 accepted in the nonempirical Hartree–Fock calculations and allowing for the anharmonicity of vibrations in real molecules [10]. The energy of electron correlation in DFT calculations was found as the difference between the potential energies of the particles calculated by the B3LYP and HFB methods. In the first method the correction for the electronic correlation was considered using the VWN and LYP functionals [11], whereas in the second method it was absent. The exchange interactions in both methods were taken into account similarly (using the Becke functional [12]).

Our results show that the effects of electron correlation are 20–30 times larger in the absolute value than the corrections for the zero vibration energy, which, in turn, are approximately three times larger than the thermal corrections. The effects of electron correlations regularly increase in going from the oxygen- to selenium-containing compound in all the tautomeric forms. All the corrections are fairly large in the absolute value, but they do not change the principal conclusion about the considerably higher stability of the CH form of pyrazolone as compared to the other two forms. In thio- and selenopyrazolones consideration of the electron correlation effects increases the stability of the SH (SeH) form relative to the CH form. The NH form in all the three compounds remains the least stable as compared to the major tautomer, which agrees with the widespread viewpoint about destabilization in the gas phase of cyclic structures with two neighboring heteroatoms containing lone electron pairs with the same degree of hybridization [6, 13].

It seemed interesting to quantitatively evaluate the effect of electron correlations on the tautomerism of the compounds under study using different bases and the same level of geometry optimization, or, vice versa, the same level of theory and varied methods of geometry optimization.

To this end, we calculated the stability of all the above-mentioned tautomeric forms with the three methods for geometry optimization: HF/6–31G*, HF/6–31+G*, and B3LYP/6–31G*. In each case different levels of energy calculations were used: HF/6–31G*, HF/6–311G*, HF/6–31+G*, HF/6–311+G*, B3LYP/6–31G*, B3LYP/6–31+G*, B3LYP/6–31+G**, and B3LYP/6–31++G*.

Our results showed that the effect of the geometry optimization procedure on the absolute energies of the tautomeric forms of all the compounds is minor, and the relative energies of the tautomeric forms do not change essentially. For example, calculations by the B3LYP/6–31+G* method and the geometry optimization by the HF/6–31G*, HF/6–31+G*, and B3LYP/6–31G* methods gave the relative stability of the most stable SH form in the case of the thio analog of –5.4, –5.0, and –6.3 kJ mol^{-1}, respectively.

The effect of the level of energy calculation at the same geometry on the total energy and relative sta-

Table 2. Total energies (*E*, au) of the neutral forms of heteropyrazolones in the B3LYP/6–31G*-optimized geometry and relative stabilities of tautomers (Δ*E*, kJ mol^{-1})

E	Form	B3LYP/6–31G*//B3LYP/6–31G*		B3LYP/6–31+G*//B3LYP/6–31G*		B3LYP/6–31++G**//B3LYP/6–31G*	
		$-E_{B3LYP}$	Δ*E*	$-E_{B3LYP}$	Δ*E*	$-E_{B3LYP}$	Δ*E*
O	CH	340.73872	0.0	340.75391	0.0	340.76227	0.0
	NH	340.72687	31.0	340.74333	27.6	340.75391	21.8
	OH	340.72619	33.1	340.74293	28.7	340.75605	16.3
S	CH	663.69818	0.0	663.70827	0.0	663.71673	0.0
	NH	663.69026	20.9	663.70099	19.2	663.71174	13.0
	SH	663.69886	–1.7	663.71063	–6.3	663.72117	–11.7
Se	CH	2664.88228	0.0	2664.92397	0.0	2664.93387	0.0
	NH	2664.87576	17.2	2664.91821	15.1	2664.93054	8.8
	SeH	2664.88937	–18.4	2664.92662	–7.1	2664.93915	–13.8

bility of tautomeric forms of isostructural pyrazolones is considerable, as seen from Table 2. The calculations allow the following main conclusions. The CH form of pyrazolone **Ia** (X = O) remains the most stable, irrespective of the basis used as well as of the geometry. At the same time, the relative stability of the two other forms **Ib** and **Ic** changes. The general trend is that the improvement of the basis by including polarization and diffuse functions increases the relative stability of the NH (**Ib**) and OH (**Ic**) forms as compared to the CH form **Ia**. Consideration of the polarization correction for the hydrogen atom significantly decreases the energy of tautomeric forms of all pyrazolones. Additional consideration of diffuse functions on the hydrogen atom practically does not affect the relative stability of tautomers on the HF level of geometry optimization, but considerably increases the relative stability of the NH and OH forms with the B3LYP-optimized geometry (Table 2). In the best bases the OH form is more stable than the NH form. The difference in the relative stability of these forms in the above-mentioned bases reasonably agrees with the experimental data for the structurally related pyrazolones in solutions [7, 14–16]. Noticeable content of OH and NH forms of pyrazolones in polar aprotic and proton-donor solvents may be due to intermolecular H-complex formation [13, 14]. Its efficiency is comparable with the difference in the energy of the tautomers.

Extension of the basis in B3LYP calculations of thio- and selenopyrazoles enhances the stability of the SH (SeH) and NH forms to a still greater extent as compared to simple Hartree–Fock calculations (Table 2). In all the cases when the electron correlation was considered the thiol (selenol) form appeared to be preferable. The preferableness of the XH form was somewhat more pronounced in selenide than in sulfide, especially on the Hartree–Fock levels of geometry optimization. With the B3LYP/6–31++G** basis the relative stability of the thio and seleno tautomeric forms differs to a lesser extent (last column of Table 2).

The results of evaluating the relative stability of tautomers of all 1-methylheteropyrazolones, obtained by us previously by semi- and nonempirical calculations with the same procedures for geometry optimization and energy calculation, are given in Table 3. These data show that the semiempirical calculations are quite sufficient to obtain the qualitative pattern of the tautomerism. In some items they are closer to the results of B3LYP calculations than to the usual HF calculations. The accuracy of quantitative characteristics cannot be judged because of the lack of direct gas-phase experimental data.

In this work we also analyzed the effect of electron correlation on the acidity of heteropyrazolones, which largely determines the practically significant properties of these compounds [17, 18]. Fot this purpose, we have calculated the energy of anions with the same bases and levels of geometry optimization as those used for evaluating the stability of the neutral compounds.

Table 4 shows that the level of geometry optimization at the same level of the energy calculation (e.g., B3LYP/6–31+G*) only slightly effects the energy of the anion. The effect of the basis at the same level of geometry optimization is considerably stronger. Improvement of the basis in the selenopyrazolone anion causes the greater decrease in the energy as compared to the oxygen and sulfur analogs. The effect of polarization functions on the hydrogen atom is considerably larger than the effect of diffuse functions on the same atom. At the same time these two corrections affect the energy of anions to a considerably lesser extent than the diffuse corrections for the heavy atoms.

Table 3. Relative stability of tautomeric forms of isological 1-methylpyrazol-5-ones according to semiempirical and nonempirical calculations (ΔE, kJ mol^{-1}).

E	Form	PM3//PM3	HF/6–31G*// HF/6–31G*	HF/6–31+G*// HF/6–31+G*	B3LYP/6–31G*// B3LYP/6–31G*	B3LYP/6–31++G**// B3LYP/6–31G*
O	CH	0.0	0.0	0.0	0.0	0.0
	NH	20.5	36.4	29.3	31.0	22.0
	OH	26.8 (40.2)[a]	42.3	35.6	33.1	16.3
S	CH	0.0	0.0	0.0	0.0	0.0
	NH	13.8	7.2	36.0	20.8	13.1
	SH	–64.9 (–56.1)[a]	5.0	0.4	–1.8	–11.7
Se	CH	0.0	0.0	0.0	0.0	0.0
	NH	14.2	23.0	28.0	17.2	8.7
	SeH	–24.7 (–16.3)[a]	–9.6	0.8	–18.4	–13.8

[a] The values obtained from semiempirical calculations belong to two conformers differing from each other by the orientation of the EH groups relative to the N^1–CH_3 fragment (S-*trans* and S-*cis* conformers, respectively). In nonempirical calculations only one minimum is localized.

Table 4. Energy of anions (E, au) of 1-methylheteropyrazolones, calculated within the framework of the electron density functional theory

Method (energy//geometry)	X = O	X = S	X = Se
B3LYP/6–31G*//RHF/6–31G*	340.15874	663.15102	2664.33890
B3LYP/6–31+G*//RHF/6–31G*	340.19555	663.17645	2664.39922
B3LYP/6–31+G*//RHF/6–31+G*	340.19586	663.17663	2664.39922
B3LYP/6–31++G*//RHF/6–31+G*	340.20323	663.18400	2664.40683
B3LYP/6–31++G* //RHF/6–31+G*	340.20328	663.18414	2664.40808
B3LYP/6–31G*//B3LYP/6–31G*	340.16236	663.15409	2664.34278
B3LYP/6–31+G*//B3LYP/6–31G*	340.19900	663.17946	2664.40207
B3LYP/6–31++G**//B3LYP/6–31G*	340.20644	663.18692	2664.41096

Table 5. Contributions (E, au) to the Gibbs free energy and to the absolute (PA, kJ mol^{-1}) and relative (ΔPA, kJ mol^{-1}) proton affinities of the anions of 1-methylheteropyrazolones according to the data of nonempirical HF/6–31G*//HF/6–31G* and B3LYP/6–31G*//HF6–31G* calculations

E	$-E_{tot}$	E_{zv}	$\Sigma\Delta_{therm}$ (298 K)	$-E_{ec}$	PA_1[a]	ΔPA_1	PA_2[b]	ΔPA_2	PA_3[c]	ΔPA_3
O	338.11391	0.09711	0.03675	1.91043	1537.6	120.1	1503.3	106.3	1492.0	125.3
S	660.79023	0.09576	0.03876	2.28326	1434.3	16.8	1403.7	6.7	1391.3	24.6
					1429.3	2.6	1403.7	6.2	1372.1	19.3
Se	2660.85749	0.09530	0.03744	3.24405	1417.5	0.0	1397.0	0.0	1366.7	0.0
					1426.7	0.0	1397.5	0.0	1352.8	0.0

[a] First line: $PA_1 = [E_{tot}(\text{anion}) - E_{tot}(\text{CH})]$; second line: $PA_1 = [E_{tot}(\text{anion}) - E_{tot}(\text{EH})]$. [b] $PA_2 = (E_{tot} + \Delta E_{zv} + \Sigma\Delta_{therm})_{anion} - [E_{tot} + (E_{zv} + \Sigma\Delta_{therm})]_{CH\ (EH)}$. [c] $PA_3 = (E_{tot} + \Delta E_{zv} + \Sigma\Delta_{therm} + E_{ec})_{anion} - (E_{tot} + \Delta E_{zv} + \Sigma\Delta_{therm} + E_{ec})_{CH\ (EH)}$.

In Table 5 are given the contributions to the Gibbs free energy of the anions obtained within the framework of the RHF/6–31G*//HF/6–31G* and B3LYP/6–31G*//HF/6–31G* methods. These data show that the electron correlations effects in anions coincide in the order of magnitude with the similar effects in neutral molecules and increase in the absolute value in going from the oxygen- to selenium-containing analog. The absolute CH acidity increases in this order (*PA* of anions decreases); the XH acidity of selenopyrazoles

Table 6. Anion energy (E, au) and absolute (PA, kJ mol^{-1}) and relative (ΔPA, kJ mol^{-1}) proton affinities of anions of isological 1-methylpyrazolones, according to calculations on various levels of theory

E	HF/6–31G*// HF/6–31G*		HF/6–31+G*// HF/6–31+G*		B3LYP/6–31G*// HF/6–31G*		B3LYP/6–31G*// B3LYP/6–31G*	
	$-E_{tot}(B^-)$	PA (ΔPA)	$-E_{tot}(B^-)$	PA (ΔPA)	$-E_{tot}(B^-)$	PA (ΔPA)	$-E_{tot}(B^-)$	PA (ΔPA)
O	338.11391	1537.6	338.13837	1493.3	340.15874 340.03960^a	1513.8 1479.5^a	340.16236	1513.4
		(120.1)		(110.0)		(74.9)		(97.1)
S	660.79023	1434.3 1429.3^a	660.80717	1405.8 1405.0^a	663.15102 663.03130^a	1428.8 1404.6^a	663.15409	1428.4 1430.1^a
		(16.7, 2.5^b)		(22.6, 23.0^b)		(0.0)		(12.1, 0.0^b)
Se	2660.85749	1417.5 1426.7^a	2660.91049	1383.2 1382.0	2664.33890 2664.22076^a	1415.9 1405.4	2664.34278	1416.3 1435.1^a
		(0.0, 0.0^b)		(0.0, 0.0^b)		(0.8)		(0.0, 5.0^b)

[a] With correction for E_{zv} and $\Sigma\Delta_{therm}$(298 K). [b] Figures in parentheses refer to two conformers of the EH forms.

increases the most noticeably with consideration of the electron correlation effect. However, even in the best calculations the absolute values of the deprotonation energies (the proton affinities of anions) remain very high. This fact shows that the experimental values of these energies determined in solutions are largely influenced by the solvation effects [13, 14]. The relative values of acidity are quite reasonable, and any calculations of B3LYP energies reproduce the same order of the increase in acidity ($O \ll S \leq Se$) (Table 6) as established by us previously on the semi- and nonempirical levels [2, 3].

To conclude: Although B3LYP calculations have not brought much new qualitative information, they have indisputably improved the agreement of the calculated structural characteristics and reactivity with the experimental data for related systems. But even these more accurate structural characteristics are correct only for the gas phase predictions. To evaluate the stability of tautomers in condensed media where the effects of intermolecular interactions (self-association, specific solvation, packing effects, etc.) are strong, it is necessary to consider these effects in calculations in the explicit form using DFT methods on the higher levels of theory. The benefit of the calculations of such type was recently demonstrated by the example of studying the tautomerism of structurally related compounds (e.g., of thiol–thione tautomerism [19, 20]).

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