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Quantum-Chemical Study of the Structure and Reactivity of 4,5-Dihydropyrazol-5-ones and Their Thio and Seleno Analogs: VIII.[1] Solvation Effects and Tautomerism of 4,5-Dihydropyrazol-5-ones and Their Thio and Seleno Analogs

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Abstract — The effect of hydration on the stability of tautomeric forms of 1-methyl-4,5-dihydro-1*H*-pyrazol-5-one, 1-methyl-4,5-dihydro-1*H*-pyrazole-5-thione, and 1-methyl-4,5-dihydro-1*H*-pyrazole-5-selone was analyzed by nonempirical quantum-chemical methods at different theory levels. The results of calculations by all these methods, including density functional theory, with two types of models (continuum and discrete) showed stronger stabilization of the NH tautomers of all the examined heteropyrazolones in water, as compared to their CH and XH tautomers. The strongest stabilization effect is reached in the calculation of discrete complexes in terms of the self-consistent reaction field model. The degree of differentiation of the stability of tautomeric forms considerably decreases when electronic correlation is taken into account, whereas the use of polarization functions on hydrogen atoms in addition to polarization functions on heavy atoms almost does not affect the position of the tautomeric equilibrium.
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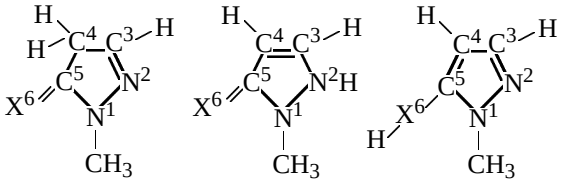
In the preceding studies of this series we analyzed mainly the effect of structural factors (nature of heteroatom, electronic and steric structure of substituents, etc.) on the relative stability of tautomeric forms of chalcogenopyrazolones and their acid–base, redox, and other properties. The relations thus revealed allowed us to characterize the structure and reactivity of pyrazolones in the gas phase and dilute solutions in inert solvents with a sufficient reliability. However, it is known that the structure and properties of pyrazolones essentially change in going to polar and complexing solvents [2, 3]. For example, the simplest pyrazol-5-ones in such solvents exist mainly as NH and OH tautomers **Ib** and **Ic**, respectively, and these tautomers often cannot be distinguished experimentally; in the gas phase and dilute solutions in inert solvents, CH form **Ia** predominates. According to a few available published experimental data [4–6], the solvent nature also affects tautomerism of pyrazolethiones **II** and pyrazoleselones **III**.



Ia–**IIIa** **Ib**–**IIIb** **Ic**–**IIIc**

X = O (**I**), S (**II**), Se (**III**).

Attempts were regularly made to rationalize the effect of solvation on the tautomerism of particular pyrazole derivatives [7–11] in terms of continuum

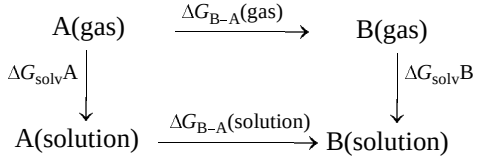
[1] For communication VII, see [1].

models, and Kleinpeter and Koch [11] also tried to estimate the effect of complex formation of substituted 1-phenyl-3-methyl-4-X-pyrazol-5-ones with dimethyl sulfoxide as solvent. However, these studies were performed at different theoretical levels and involved different energy parameters; in some cases, no account was taken of possible variation of geometric parameters of a dissolved substance as a result of solvation, the contribution of electronic effect of substituents was not differentiated, etc. Solvation of pyrazolethiones and pyrazoleselones was not studied at all by theoretical methods, though thione–thiol tautomerism of other heterocycles has attracted strong interest in the recent years [12].

The present work is the first systematic study on the effect of hydration on the tautomeric properties of model (R = CH_3) heteropyrazol-5-ones in the framework of the self-consistent reaction field (SCRF) theory using different approaches and models with variation of basis sets in nonempirical calculations, estimation of the influence of electronic correlation, analysis of the potentialities provided by some discrete solvation models, etc. The study was aimed mainly at comparing trends in variation of the relative stability of tautomers in water and in the gas phase upon variation of the heteroatom X and elucidating the possibility of using different calculation methods to predict on a qualitative level the effect of water as solvent on the state of tautomeric equilibrium of pyrazol-5-ones and their thio and seleno analogs.

The calculations were performed in terms of the restricted Hartree–Fock (RHF) method using 6-31G(*d*), 6-31G(*d,p*), and 6-31++G(*d,p*) basis sets, as well as in terms of the density functional theory [B3LYP/6-31G(*d,p*) and B3LYP/6-31G++(*d,p*)], using Gaussian-98 software package [13]. The geometric parameters were fized and fully optimized without symmetry limitations; second derivative matrix was calculated for all stationary points; and no scaling factors [14] were introduced.

Initially, we calculated the free energy of hydration of possible tautomeric forms of all heteropyrazol-5-ones in terms of the SCRF method using PCM continuum model [15]. In all cases, as starting geometry we used the tautomer structure in the gas phase, which was preliminarily optimized by the corresponding method and additionally optimized in the course of calculations. Table 1 contains the energy parameters of different tautomeric forms in solution, as well as the Gibbs energies of solvation (hydration) and their constituents; the relative energies of tautomers in the gas phase and in water are given in Table 2. The calculations were based on the following thermodynamic cycle [3]:



$$\Delta G_{B-A}(\text{solvent}) = \Delta G_{B-A}(\text{gas}) + \Delta G_{solv}B - \Delta G_{solv}A = \Delta G_{B-A}(\text{gas}) + \Delta\Delta G_{solv}B{-}A$$

Here, A(gas) B(gas) are, respectively, less stable the most stable tautomers in the gas phase; A(solution) and B(solution) are the same tautomers in solution; ΔG_{B-A}(gas) is the Gibbs energy of tautomeric transformation in the gas phase; and ΔG_{B-A}(solution) is the same quantity for solution, which was calculated from the Gibbs energies of solvation (hydration) of both tautomers (ΔG_{solv}A and ΔG_{solv}B, respectively).

The effect of water as solvent on the relative stability of tautomers turned out to be fairly strong (Tables 1, 2). As expected, the more polar and readily polarizable NH forms of all compounds are hydrated most strongly (cf. their dipole moments μ given in Table 2). Both RHF and DFT calculations with all basis sets employed gave qualitatively similar results. As follows from the data in Table 1, the main contribution (stabilizing) to the energy of solvation of all tautomers of compounds **I**–**III** is that produced by electrostatic interactions between the solute and the solvent (G_{el}), while the contribution of nonelectrostatic interactions (Gnonel) is positive and is considerably smaller in absolute value. A slightly higher Gibbs energy of solvation (ΔG_{solv}) obtained by the RHF calculations with the 6-31G(*d,p*) basis set relative that calculated using the 6-31G(*d*) basis set (the results are not given in the present article) originates from electrostatic interactions in keeping with a small increase of the dipole moments μ, whereas the contribution of noneelectrostatic interactions almost does not change. Introduction of diffuse corrections insignificantly changes the Gibbs energy of hydration of sulfur- **IIa**–**IIc** and selenium-containing tautomers (**IIIa**–**IIIc**); by contrast, the stability of pyrazolones **Ia**–**Ic** (especially of the NH tautomer) increases considerably [cf. B3LYP/6-31++G(*d,p*) and B3LYP/6-31G(*d,p*) calculations; Table 1]. Simultaneously, the difference in the stabilities of tautomeric forms somewhat decreases (Table 2). If electronic correlation is taken into account, the Gibbs energy of solvation ΔG_{solv} and the dipole moments μ become smaller [cf. B3LYP/6-31G(*d,p*) and B3LYP/6-31++G(*d,p*) data with RHF/6-31G(*d,p*) and RHF/6-31++G(*d,p*), respectively]; here, the contribution of nonelectrostatic interactions remains almost unchanged, while the

Table 1. Energy parameters of tautomers of compounds **I**–**III** in water, calculated in terms of polarized continuum model (PCM)[a]

Comp. no.	$-E_{tot}$	$-E_0$	$-G_{298}$	$-G_{el}$	G_{nonel}	$-\Delta G_{solv}$
			RHF/6-31G(*d*,*p*)			
Ia	338.727809	338.617564	338.648116	10.84	0.77	10.07
Ib	338.723334	338.611713	338.641709	15.82	1.13	14.69
Ic	338.718236	338.607065	338.637295	12.67	0.58	12.09
IIa	661.365962	661.257258	661.288283	11.40	1.22	10.18
IIb	661.371388	661.261403	661.292478	20.98	1.60	19.37
IIc	661.356317	661.249764	661.281877	7.60	0.84	6.76
IIIa	2661.429715	2661.316381	2661.348777	13.18	4.61	8.58
IIIb	2661.437496	2661.321873	2661.352765	24.56	4.96	19.6
IIIc	2661.425199	2661.313376	2661.345473	6.69	4.79	1.91
			B3LYP/6-31G(*d*,*p*)			
Ia	340.763149	340.660536	340.691143	9.05	0.95	8.10
Ib	340.762553	340.658488	340.688493	15.05	1.35	13.70
Ic	340.758136	340.654667	340.685847	11.87	0.76	11.10
IIa	663.72281	663.621819	663.65334	8.92	1.36	7.56
IIb	663.731106	633.628221	663.659203	18.12	1.77	16.35
IIc	663.719129	663.619631	663.650978	6.82	0.92	5.94
IIIa	2664.90838	2664.802661	2664.835306	9.81	4.72	5.09
IIIb	2664.91836	2664.810467	2664.842754	20.78	5.11	15.67
IIIc	2664.91048	2664.805753	2664.837992	6.60	4.79	1.81
			B3LYP/6-31++G(*d*,*p*)			
Ia	340.780282	340.678224	340.709388	10.71	0.97	9.74
Ib	340.781877	340.678527	340.708919	17.53	1.38	16.15
Ic	340.775389	340.672308	340.703016	12.69	0.79	11.90
IIa	663.733401	663.63270	663.664250	9.24	1.37	7.88
IIb	663.742346	663.641176	663.672439	18.07	1.79	16.28
IIc	663.730092	663.631209	663.662861	8.18	0.86	7.32
IIIa	2664.954038	2664.848048	2664.880087	9.99	4.70	5.28
IIIb	2664.964571	2664.856474	2664.888464	20.53	5.11	15.42
IIIc	2664.952246	2664.848326	2664.880495	7.18	4.84	2.44

[a] Hereinafter, E_{tot} stands for the total energy, E_0 is the total energy with correction for zero-point vibration energy, G_{298} is the Gibbs energy (all in a.u); G_{el} and G_{nonel} are, respectively, electrostatic and nonelectrostatic components of the Gibbs energy of solvation ΔG_{solv} (all in kcal mol^{-1}).

contribution of electrostatic interactions decreases, though not always monotonously.

The calculations with the 6-31G(*d*,*p*) and 6-31++G(*d*,*p*) basis sets give almost the same relative Gibbs energies of tautomers as those obtained previously using the 6-31G(*d*) basis set [16]; the same is valid for the B3LYP/6-31G(*d*,*p*) and B3LYP/6-31++G(*d*,*p*) DFT calculations (Table 2). The most important conclusion drawn from the results of the RHF calculations for the gas phase is the following: the most stable tautomer of pyrazolone **I** (X = O) in the gas phase is CH form Ia (the thermodynamic stabilities of two other tautomers are considerably lower), while the most stable tautomer of thio and seleno analogs is XH form (**IIc** and **IIIc**, respectively). For all compounds, the difference in the energies of tautomers decreases when electronic correlation is taken into account [B3LYP/6-31G(*d*,*p*) and B3LYP/6-31++G(*d*,*p*)].

The most stable tautomer of pyrazolone **I** in water is (as before) **Ia**; only B3LYP/6-31++G(*d*,*p*) calculations predict slightly lower stability of **Ia** relative to **Ib**); the most favorable tautomer of pyrazolethione and pyrazoleselone in water is NH (**IIb** and **IIIb**). Both RHF and DFT calculations give qualitatively similar patterns with respect to all relative energy parameters (ΔE_{tot}, ΔE_0, ΔG_{298}) which are commonly used to characterize tautomeric systems (as an example, Table 2 contains ΔG_{298} values). We can con-

Table 2. Relative Gibbs energies (ΔG_{298}, kcal mol^{-1}) and dipole moments (μ, D) of tautomers of compounds **I**–**III** in the gas phase and in solution and relative Gibbs energies of tautomers of compounds **I**–**III** in water [ΔG_{B-A}(solution), kcal mol^{-1}]

Comp. no.	Gas		Solution		
	ΔG_{298}	μ	ΔG_{298}	μ	ΔG_{B-A}(solution)
	RHF/6-31G(*d*,*p*)				
Ia	0.00	2.56	0.00	3.72	0.00
Ib	8.42	4.87	4.02	7.79	3.80
Ic	6.34	2.83	6.79	3.80	4.32
IIa	1.87	4.04	2.63	6.04	–1.35
IIb	7.91	7.24	0.00	12.07	–4.70
IIc	0.00	1.63	6.65	2.33	0.00
IIIa	6.16	4.26	2.50	6.68	–0.51
IIIb	11.34	7.61	0.00	13.35	–6.35
IIIc	0.00	1.58	4.59	2.16	0.00
	B3LYP/6-31G(*d*,*p*)				
Ia	0.00	2.05	0.00	2.97	0.00
Ib	7.13	4.76	1.66	7.51	1.53
Ic	5.90	2.80	3.32	4.05	2.90
IIa	3.08	3.22	3.68	4.72	1.46
IIb	7.78	6.69	0.00	10.93	–2.63
IIc	0.00	1.61	5.16	2.26	0.00
IIIa	8.61	3.20	4.67	5.43	5.43
IIIb	11.72	6.78	0.00	12.12	–2.14
IIIc	0.00	1.55	2.99	2.27	0.00
	B3LYP/6-31++G(*d*,*p*)				
Ia	0.00	2.32	0.00	3.60	0.00
Ib	6.14	5.20	0.29	8.77	–0.27
Ic	4.80	2.85	4.00	3.89	2.64
IIa	4.31	3.13	5.14	5.06	3.75
IIb	8.40	6.71	0.00	11.60	–1.08
IIc	0.00	1.77	6.01	2.48	0.00
IIIa	4.87	3.24	5.26	5.52	2.03
IIIb	7.85	7.09	0.00	12.82	–5.13
IIIc	0.00	1.61	5.00	1.77	0.00

clude that the contributions of zero-point vibration energy and thermochemical corrections do not change the relative stabilities of heteropyrazolone tautomers in the gas phase and in water to an appreciable extent. On the other hand, it should be noted that pyrazolethiones and pyrazoleselones are characterized by stronger differentiation of the above energy parameters, as compared to their oxygen analog.

We also performed calculations using other continuum models, IPCM and SCIPCM [17], which are based on isodensity surface; these models better simulate the parameters of a dissolved molecule (they

Table 3. Relative total energies (ΔE_{tot}, kcal mol^{-1}) and dipole moments (μ, D) of tautomers of compounds **I**–**III** in water, calculated using the geometric parameters of the isolated molecules in terms of PCM, IPCM, and SCIPCM

Comp. no.	PCM		IPCM		SCIPCM	
	ΔE_{tot}	μ	ΔE_{tot}	μ	ΔE_{tot}	μ
	RHF/6-31G(*d*,*p*)					
Ia	0.00	3.53	0.00	3.63	0.00	3.32
Ib	2.78	6.70	5.40	6.61	6.09	6.05
Ic	3.64	3.88	5.04	4.14	4.99	3.69
IIa	3.14	5.96	0.01	5.69	0.00	5.41
IIb	0.00	10.70	0.00	10.30	0.33	9.84
IIc	5.78	2.38	3.93	2.32	4.80	1.81
IIIa	4.61	6.30	1.92	6.15	0.65	5.79
IIIb	0.00	11.30	0.00	11.10	1.50	9.86
IIIc	4.98	2.19	1.72	2.39	0.00	2.13
	B3LYP/6-31G(*d*,*p*)					
Ia	0.00	3.02	0.00	3.02	0.00	2.71
Ib	3.49	6.64	3.49	6.64	3.43	6.07
Ic	3.18	4.13	3.18	4.13	5.21	3.61
IIa	1.69	4.78	1.69	4.78	1.12	4.67
IIb	0.00	9.85	0.00	9.85	0.00	9.30
IIc	2.55	2.34	2.55	2.34	1.81	2.08
IIIa	5.94	5.04	4.44	4.73	2.32	4.56
IIIb	0.00	10.53	1.12	10.29	1.76	9.64
IIIc	2.28	2.11	0.00	2.41	0.00	2.01

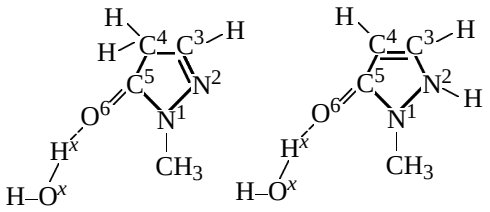
are included in Gaussian-98 [13]). The calculations performed in the frozen framework approximation [the initial geometric parameters were calculated by the HF/6-31G(*d*,*p*)//HF/6-31G(*d*,*p*) and B3LYP/6-31G(*d*,*p*)//B3LYP/6-31G(*d*,*p*) methods, respectively] gave the same order of the relative stabilities of tautomers of the three pyrazole derivatives as that obtained using the simplest polarized continuum model (Table 3). However, the degree of tautomer differentiation by their stability changes: for structures **Ia**–**Ic** it became stronger as in going to more complex model (from PCM to IPCM and then to SCIPCM), while it diminishes for selenoxopyrazoles **IIIa**–**IIIc**; thioxopyrazoles **IIa**–**IIc** occupy an intermediate place. We succeeded in obtaining stable structures only for pyrazolone **I** tautomers by geometry optimization in terms of SCIPCM by the RHF method using 6-31G(*d*) and 6-31G(*d*,*p*) basis sets; despite some geometry variation induced by solvation, the CH tautomer (**Ia**) remained considerably more stable than the two other tautomers (**Ib** and **Ic**).

Insofar as specific solvation is not included into continuum models in the explicit form, while the

Table 4. Principal geometric parameters of tautomers **Ia** and **Ib** and their H-complexes with water **IVa** and **IVb** in the gas phase and in aqueous solution (PCM) according to the RHF/6-31G(*d,p*)//RHF/6-31G(*d,p*) calculations

Parameter	**Ia**		**IVa**		**Ib**		**IVb**	
	gas	solvent	gas	solvent	gas	solvent	gas	solvent
$l(C^5=O^6)$, Å	1.195	1.207	1.201	1.211	1.199	1.219	1.207	1.226
$l(C^-C^5)$, Å	1.520	1.511	1.517	1.512	1.467	1.452	1.463	1.447
$l(C^5–N^1)$, Å	1.359	1.348	1.351	1.343	1.383	1.364	1.371	1.357
$l(N^2–H)$, Å	–	–	–	–	1.002	1.023	1.002	1.023
$l(O^6\cdots H)$, Å	–	–	2.027	1.996	–	–	1.990	1.888
$l(O^6\cdots O^x)$, Å	–	–	2.951	2.943	–	–	2.916	2.840
$\angle O^6\cdots H–O^x$, deg	–	–	164.0	174.7	–	–	164.4	178.0
$\Sigma\angle N^2$, deg	–	–	–	–	330.4	338.7	331.7	339.1

ability of pyrazolones to form H-complexes and self-associates is well known [2, 5, 18], we performed calculations of couples of 1 : 1 and 1 : 2 H-complexes with water at different theory levels with full geometry optimizations. The results of these calculations will be discussed in detail in a special publication; here, we should note that all calculations showed reduction in the energy of all tautomeric forms of compounds **I**–**III** upon formation of H-complexes with water and that (as before) the NH tautomers were stabilized most strongly. As examples, below are given variations in the energy parameters (kcal mol^{-1}) of free tautomers **Ia** and **Ib** and their complexes with water **IVa** and **IVb** in going from the gas phase to solution [RHF/6-31G(*d,p*)/RHF/6-31G(*d,p*) for the gas phase; PCM calculations using the same basis set with full geometry optimization for solution].



IVa **IVb**

	$-\Delta E_{tot}$	$-\Delta E_0$	$-\Delta G_{298}$
Ia	11.56	11.71	11.87
Ib	15.96	16.11	16.27
IVa	14.70	13.03	12.82
IVb	18.80	17.10	16.90

In keeping with modern views on theoretical calculations of the effect of solvation on tautomeric properties of heterocycles [3, 17, 19], the calculation of couples of tautomer complexes, followed by calculations in terms of a continuum model, may be regarded as one of the most promising method ensuring estimation of overall hydration effects (both nonspecific and specific) on tautomeric equilibria.

The procedure implying "immersion into water" of H-complexes gave an additional gain in the stability of tautomers in solution. In this case, decrease in the energy due to complex formation, calculated using both "pure" and "hybrid" continuum models was approximately the same; moreover, it roughly corresponds to the enthalpy of formation of the corresponding hydrogen bond (>C=O···HOH) [20].

It is pertinent to note that the geometric parameters of both tautomers Ia and Ib (except for the carbonyl group ant its nearest environment) almost do not change in going from the gas phase to water in terms of all models, continuum, discrete, and mixed. The parameters of the carbonyl group change uniformly: the C=O bond length increases, and the $C^4–C^5$ and $C^5–N^1$ bonds become shorter, the changes being greater in continuum models than in discrete (Table 4). Additional stabilization of both H complexes in going to continuum model is accompanied by shortening of the distance between the carbonyl oxygen atom and the nearest hydrogen atom of water molecule, as well as of the distance between the two oxygen atoms; the O···H–O angle approaches 180°. In terms of continuum and mixed models, the degree of pyramidality of the N^2 atom in the NH tautomer decreases, while the N^2–H bond extends.

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