4-(1-Alkylbenzimidazol-2-ylazo)-2-pyrazolin-5-ones: specific features of prototropic tautomerism

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Quantum chemical calculations, ^{1}H and ^{13}C NMR, and X-ray studies showed that, in contrast to 4-arylazo-2-pyrazolin-5-ones, 4-(1-alkylbenzimidazol-2-ylazo)-2-pyrazoline-5-ones mainly exist in the condensed phase as unusual ketoazine tautomers of high polarity, while the ketohydrazone tautomer stabilized by intramolecular hydrogen bond apparently predominates in the gas phase. According to calculations, various types of tautomerism are possible for 4-(benzimidazol-2-ylazo)-2-pyrazolin-5-ones, including mono- and bimolecular 1,3-, 1,5-, and 1,7-prototropic migrations proceeding by the single- and double-proton transfer mechanism with low activation energies ($\Delta E^{\neq} \approx 2$—14 kcal mol^{-1}).

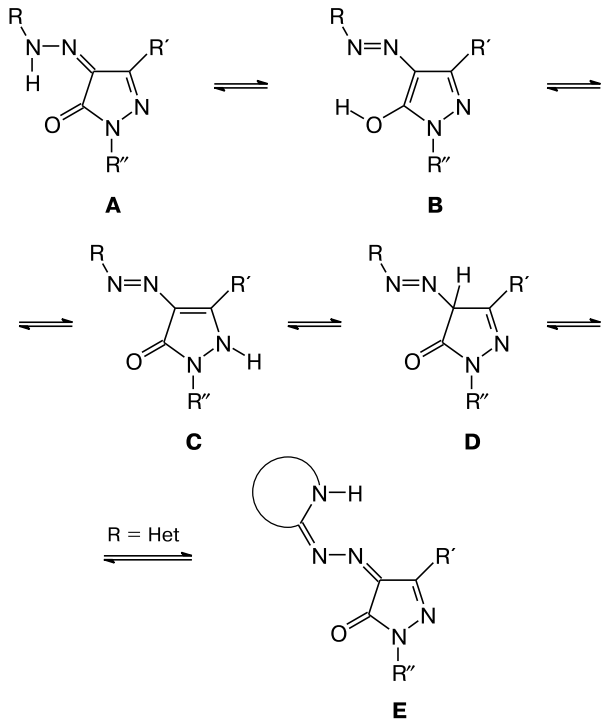
Key words: 4-(alkylbenzimidazol-2-ylazo)-2-pyrazolin-5-ones, 4-(benzimidazol-2-ylazo)-2-pyrazolin-5-one hydrates, NMR spectroscopy, X-ray analysis, hydrogen-bonded dimers, tautomerism, double-proton mechanism of tautomerism, *ab initio* quantum chemical calculations, ^{1}H and ^{13}C chemical shifts, quantum chemical calculations, transition states, transformation of hydrogen-bonded rings.

o-Hydroxyazo derivatives mainly exist as ketohydrazone (**A**) or hydroxyazo (**B**) tautomers.[1a—4] Most often, the former predominates for hydroxyhetarylazo derivatives,[1,2—7] whereas the latter for aromatic azo compounds.[2—4] The ketohydrazone form is also characteristic of compounds formed by azocoupling of aryldiazonium salts with various acyclic CH-acids (see, *e.g.*, Refs 8—11).

4-Arylazo-5-hydroxypyrazoles can exist not only in the forms **A** and **B**, but also **C** and **D**, which correspond to hydroxypyrazole/pyrazolinone tautomerism in the hydroxyazo form **B**. These compounds exist almost exclusively in the tautomeric form **A** both in solutions and in the crystalline state.[4,5,12—23] The same set of tautomers is considered for 4-hetarylazo-5-hydroxypyrazoles.[2] However, there should be an exception, namely, the compounds whose molecules contain the azo group bonded to the C=N group of the hetarene ring. In this case the fifth, ketoazine, tautomeric form **E** corresponding to migration of a hydrogen atom to the nitrogen atom of this cyclic group (Scheme 1) is possible.

The existence of type-**E** tautomeric structures can also be assumed for hetarylazophenols (see, *e.g.*, Ref. 2), but as far as we know information on their formation is unavailable.

Scheme 1



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In the present work we have studied tautomerism of new hetarylazo-2-pyrazolin-5-one derivatives including 4-(1-R-benzimidazol-2-ylazo)-3-methyl-1-phenyl-2-pyrazolin-5-ones (R = Me (**1**), Bu (**2**)) obtained by azo-coupling of the corresponding benzimidazol-2-yldiazonium salts with 3-methyl-1-phenyl-2-pyrazolin-5-one. It was found that the unusual (*cf.* Refs 1, 4, 5) ketoazine tautomeric form **E** is quite important for these bishetarylazo derivatives.

Results and Discussion

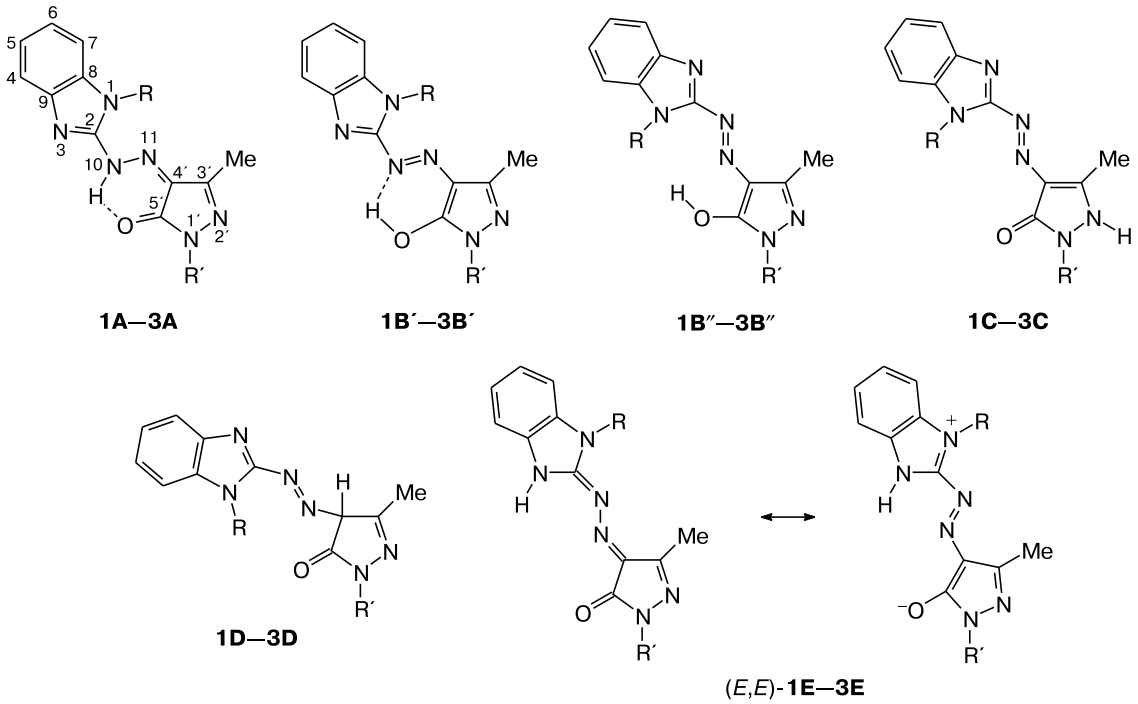
Tautomerism of 4-(benzimidazol-2-ylazo)-2-pyrazolin-5-ones: quantum chemical and X-ray diffraction studies. We have studied pyrazolinone **1** and its structural analog **3** devoid of *N*-phenyl group.

We calculated the geometric parameters and the total energies of the tautomers of compound **1** (Scheme 2, structures **1A—E**), which were chosen to be potentially stabilizable through, *e.g.*, existence of steric prerequisites for the formation of intramolecular hydrogen bond (IHB), planar geometry of the conjugated fragment of the molecule, and the *E*-configuration with respect to the N=N bond. For the hydroxy tautomer **1B** we have studied two conformers, **1B′** and **1B″**, because formally an IHB can be formed in both systems. The *E*,*E*-**1E** isomer relative to the exocyclic double bonds was chosen based on the results of preliminary calculations, which predict much lower stabilities of other geometric isomers of molecule **1E**.

Restricted Hartree—Fock (RHF/6-31G*) calculations revealed planar carbon-heteroatom skeletons (C_s symmetry) for the structures **1B′**, **1B″**, and **1E**. Other structures calculated by this method, which ignores the electron correlation, are nonplanar. Only the tautomer **1A** and conformer **1B′** are stabilized by hydrogen bonds. In the conformer **1B″** and isomer (*E*,*E*)-**1E** the H—O—N(11) and N(3)—H—N(11) angles (Table 1) are inappropriate for the formation of the IHB. According to calculations, the stabilities of structures **1A—E** decrease in the order **1E** ≈ **1A** >> **1B′** ≈ **1D** ≈ **1C** > **1B″**. The relative energies of tautomers **1A—E** are listed in Table 1. Thus, the most stable tautomeric forms are **1E** and **1A**, whereas structures **1B—D** are much less stable and, as in the case of structurally simpler 2-pyrazolin-5-ones (see Ref. 10), have close energies. Most probably, structures **1B—D** do not fall on the conditional thermodynamic scale of tautomerism, according to which the free energy difference between tautomers should be at most 20 kJ mol^{-1} (see Refs 5, 24).

The high stabilities of tautomers **1A** and **1E** seem to be first of all determined by the energetically favorable topology of the bonds at the C(4) and C(5) atoms of the pyrazole ring. Namely, these atoms form exocyclic double bonds, thus, probably, minimizing angular strain, which is usually rather high in five-membered rings.

Scheme 2



R = Me, R′ = Ph (**1**); R = Bu, R′ = Ph (**2**); R = Me, R′ = H (**3**)

Table 1. The total (E_{tot}) and relative (ΔE) energies, dipole moments (μ), and parameters of hydrogen bonds calculated for different forms of compound **1**, monohydrates of compound **3**, dimers **4**—**8**, and transition states of tautomerism[a]

Structure	$-E_{tot}$/au	ΔE^b/kcal mol^{-1}	μ_{calc}/D	R(H...A)[c]/Å	ω(D—H...A)[c]/deg
1A	1092.46334[d]	0	4.8	2.11	127.4
	1098.61894	0	4.6	1.94	133.4
	(1098.55515)[e]	0			
1B′	1092.44464	14.0	2.9	2.00	133.5
1B″	1092.43409	20.6	4.8	2.48	107.8
1C	1092.44070	16.4	4.3	—	—
1D	1092.44265	15.2	3.1	—	—
1E	1092.46689[d]	–2.2	7.8	2.37	92.0
	1098.61594	1.9	8.6	2.36	93.6
	(1098.55760)[e]	(–1.5)[f]			
(*E*,*E*)-**3B**·H_2O	944.13504	—	2.4	1.57 (O...HO)	173.1
				1.94 (N...HO)	170.4
(*E*,*E*)-**3E**·H_2O	944.14404	—	5.5	1.88 (O...HO)	167.0
				1.75 (O...HN)	176.9
(*Z*,*Z*)-**3A**·H_2O	944.13129	—	4.0	2.04 (N...HO)	136.4
				1.84 (O...HN)	150.2
(*Z*,*Z*)-**3E**·H_2O	944.13416	—	5.2	1.96 (O...HO)	156.6
				1.77 (O...HN)	155.9
(*Z*,*Z*)-**3B**·H_2O	944.12790	—	2.8	1.69 (O...HO)	153.3
				1.92 (N...HO)	167.2
TS1[g]	944.12771	13.9	3.4	—	—
TS2	944.11813	8.4	1.8	—	—
TS3	944.11201	10.2	3.6	—	—
TS4	867.71512	8.5	3.5	—	—
(*E*,*Z*)-**3A**	867.72864	—	2.9	1.86	138.7
(*E*,*Z*)-**3B**	867.71838	—	4.0	1.81	142.4
4	1725.08906	0	1.4	—	—
5	1725.07206	10.7	6.8	1.93	138.6
6	1725.07494	8.9	7.6	1.79 (N(3)H...O′)	157.9
				2.06 (N(3′)H...N(10))	159.4
7	1725.05360	22.3	2.6	2.05	149.1
8	1725.06511	15.0	3.7	1.88 (N(3)H...N(3′))	168.2
				2.07 (N(10′)H...N(10))	152.4

[a] Tautomeric forms **1A,E**, monohydrates of pyrazolone **3** and its dimers were calculated by the B3LYP/6-31G*, B3LYP/6-31G**, and RHF/6-31G methods, respectively; structures **1B—D** were calculated by the RHF/6-31G* method.

[b] The energies of the tautomers of compound **1** are given relative to that of the ketohydrazone form **A**, those of the dimeric structures are given relative to that of dimer **4**, and those of transition states are given relative to those of noninteracting reactants.

[c] "D" and "A" denote the hydrogen bond donor and acceptor, respectively.

[d] Obtained from RHF/6-31G* calculations.

[e] The G_{tot} value in MeOH obtained from B3LYP/6-31G* calculations using the PCM model is given in parentheses.

[f] The ΔG° value corresponding to the Gibbs free energy difference between the forms **E** and **A** in MeOH is given in parentheses.

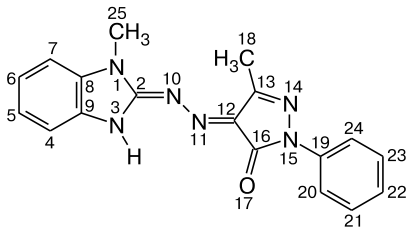
[g] The imaginary vibrational frequencies of **TS1**—**TS4** are 841, 911, 755, and 1127 cm^{-1}, respectively (according to B3LYP/6-31G** calculations).

From this point of view, structures **1B—D** are characterized by less favorable bonding topology; in addition, some of them are destabilized by the absence of IHB (**1B″**, **1C**, **1D**) and (or) by partial or complete violation of the conjugation chain (**1C** and **1D**)*.

Further refinement of the energies of the two lowest-lying tautomers was carried out by the B3LYP/6-31G* method with partial inclusion of the electron correlation energy. It was found that this effect better stabilizes the ketohydrazone tautomer **1A** through its flattening and strengthening of the IHB. As a result, the form **1A** adopts a symmetrical C_s-structure and becomes 1.9 kcal mol^{-1} more stable than (*E*,*E*)-**1E** in the gas phase (see Table 1). Here the crucial role is probably played by the fact that structure **1A** is stabilized by the IHB while the tautomer (*E*,*E*)-**1E** is not. These results show that the 2-benzimidazolylamino group of the ketohydrazone tautomers **A** is prone to quite readily undergo a transition to the imino form.

* The *N*-phenyl group in molecule **1C** is considerably rotated about the C—N bond and deviates from the pyrazole ring plane.

Table 2. Comparison of geometric characteristics (bond lengths (*d*) and bond angles (ω)) of the ketoazine tautomer (*E*,*E*)-**1E** obtained experimentally (X-ray analysis data) and theoretically (from B3LYP/6-31G* calculations)



Bond	*d*/Å		Δ[c]/Å
	Experiment[a]	Calculations[b]	
C(2)—N(10)	1.341	1.327	−0.014
N(3)—H	0.91(3)	1.012	0.108[d]
N(10)—N(11)	1.344	1.352	0.008
N(11)—C(12)	1.312	1.299	−0.013
C(12)—C(13)	1.439	1.459	0.020
C(12)—C(16)	1.456	1.493	0.037
C(13)—N(14)	1.306	1.302	−0.004
N(14)—N(15)	1.417	1.397	−0.020
N(15)—C(16)	1.371	1.399	0.028
C(16)—O(17)	1.242	1.223	−0.019
O(17)—O(H_2O)	2.750	—	—
O(17)...H(H_2O)	1.789	—	—
N(3)—O(H_2O)	2.882	—	—
H(N(3))...O(H_2O)	1.980	—	—

Angle	ω/deg		Δ[c]/deg
	Experiment[a]	Calculations[b]	
N(3)—C(2)—N(10)	129.0	128.5	−0.5
C(2)—N(10)—N(11)	107.2	108.9	1.7
C(12)—C(16)—N(15)	104.1	103.1	−1.0
C(13)—N(14)—N(15)	107.0	109.0	2.0
N(14)—N(15)—C(16)	112.0	112.1	0.1
N(14)—N(15)—C(19)	119.0	118.7	−0.3
C(20)—C(19)—C(24)	120.3	119.8	−0.5
C(19)—C(20)—C(21)	119.4	119.4	0.0
O(17)...H—O(H_2O)	160.7	—	—
N(3)—H...O(H_2O)	174.6	—	—

[a] According to X-ray analysis data for **1** · 1/2H_2O.
[b] Gas-phase data.
[c] Deviation of the calculated value of this parameter for compound **1** from the experimental value obtained for the hemihydrate of this compound.
[d] The lengths of the bonds formed by the hydrogen atom are determined by X-ray analysis with the largest error and reveal systematic underestimation by ~0.1 Å as compared to the results of neutron diffraction and microwave spectroscopy measurements.

From the results obtained for structures **1A—E** it follows that the ketoazine tautomers **E** are highly polar systems (see Table 1, μ_{calc}(**1E**) = 8.6 D)*, which differs them from other tautomers (prototropic isomers). Therefore, in condensed media the ratio of the two main forms of compounds **1—3** should change in favor of the form **E**, which is most efficiently solvated or stabilized by the crystal lattice. With initially small energy difference between the tautomers **A** and **E**, one can expect that the tautomers **E** of pyrazolinones **1—3** will dominate in the condensed phase. Indeed, B3LYP/6-31G* calculations using the PCM model showed that the Gibbs free energy ($G°_{tot}$) of (*E*,*E*)-**1E** in MeOH solution should be 1.5 kcal mol^{-1} lower than that of the tautomer **1A** (see Table 1).

* High polarity of the tautomeric form **E** is due to intramolecular charge transfer from the iminobenzimidazoline fragment to the pyrazolone fragment, as indicated by corresponding spatial orientation of the dipole moment vector in molecule **1E**. In terms of the valence bond method, this effect can be interpreted as a result of a large contribution of the bipolar canonical structure shown in Scheme 2 to the wave function of the form **E**.

The correctness of these conclusions, as applied to the solid phase, was substantiated in our experiments taking a hemihydrate of compound **1** as an example. According to X-ray analysis data, in the crystalline state this compound exists as tautomer **1E** with the *E*,*E*-configuration of substituents at exocyclic double bonds. In this hemihydrate each water molecule is bonded to two neighboring molecules **1E** by four hydrogen bonds in such a manner that two hydrogen-containing ten-membered macrocycles are closed and the entire trimolecular system has a C_2 symmetry (Fig. 1).

The experimental geometric characteristics of the hemihydrate are in reasonable agreement with the results of DFT calculations of structure (*E*,*E*)-**1E** (Table 2).

Molecules **1—3** contain the benzimidazolylazo fragment. As a result, isomerization of these compounds occurs in a much more complex manner than that of the simplest 2-pyrazolin-5-ones. In particular, a quantum chemical study predicts the ability of the forms **A**, **B**, **E** to undergo ready interconversions without both protonating and deprotonating catalytic additives by the inter- or

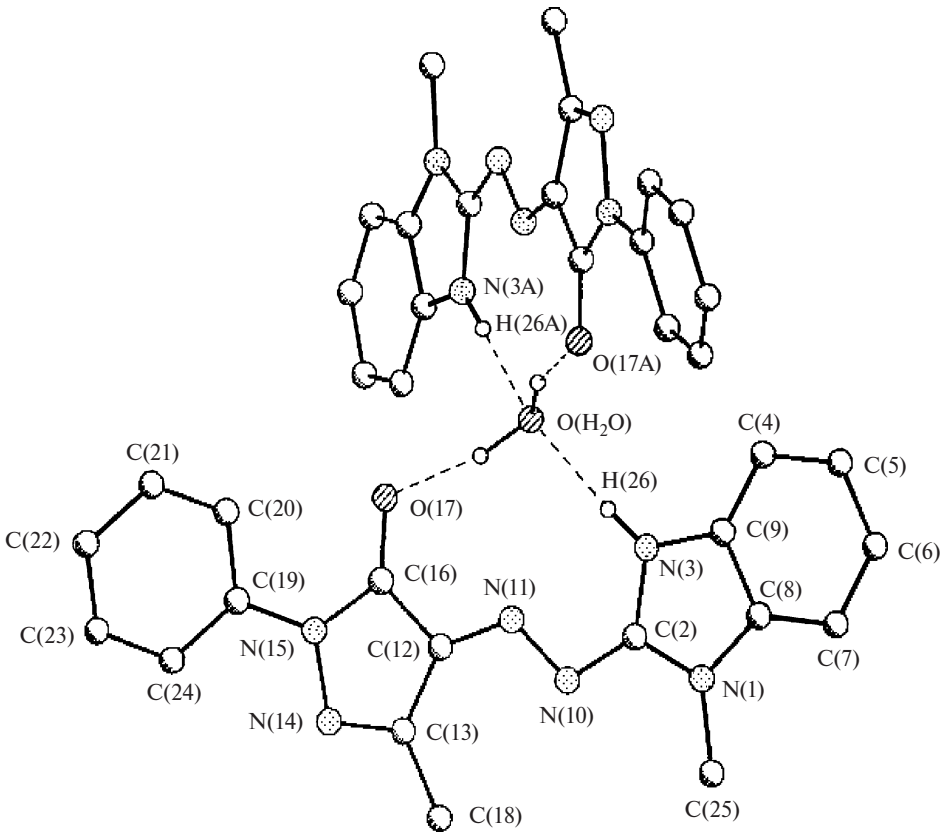


Fig. 1. Molecular structure of a fragment of crystal packing corresponding to hemihydrate **1** · $1/2H_2O$ (according to X-ray analysis data).

intramolecular mechanism, which involves transfer of a proton and transformation of conjugated cyclic system of hydrogen bonds. The most versatile is the intermolecular mechanism of tautomerism (isomerization) with the key step involving double-proton transfer (DPT) in doubly bonded hydrogen associates of benzimidazolylazopyrazolinones. This type of reactions is also often efficient in those cases where monomolecular tautomerism is hampered by high activation barriers.[5]

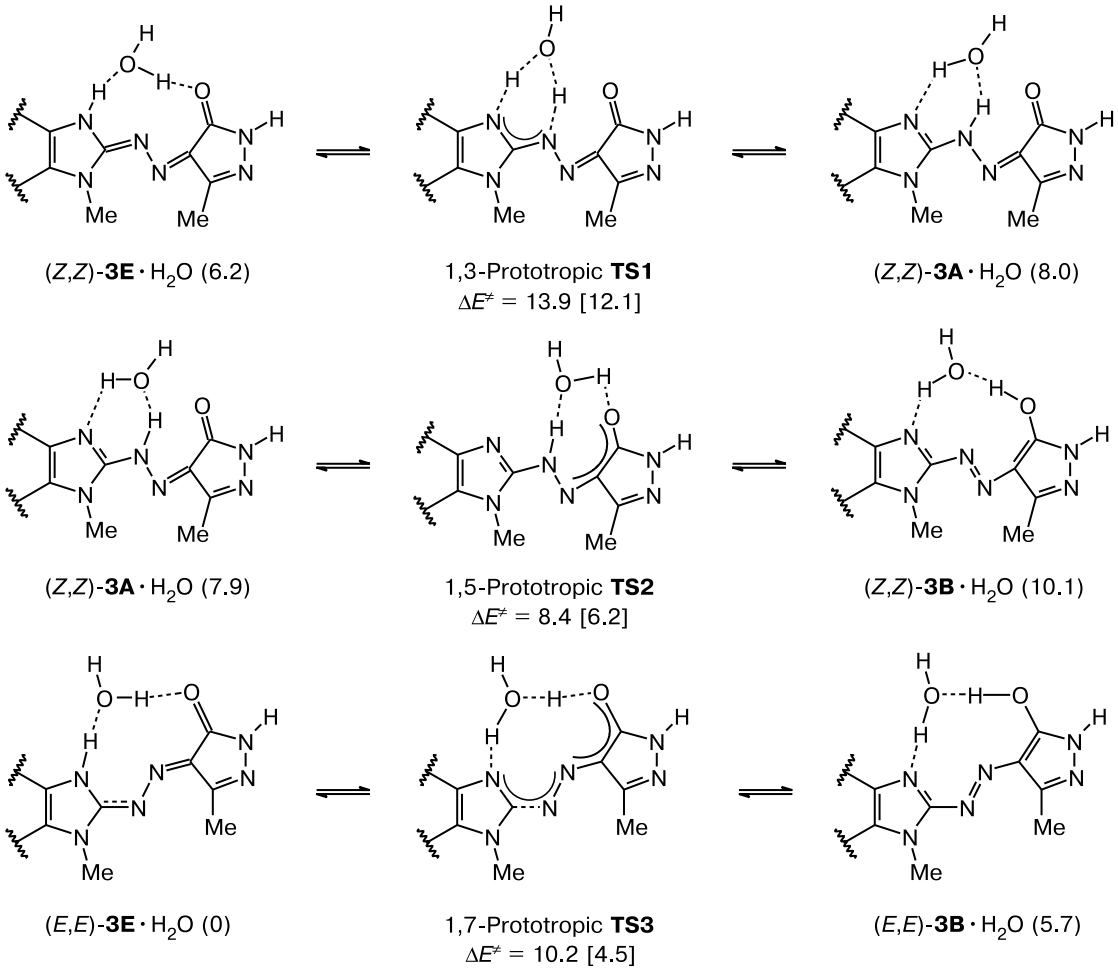
In pyrazolinones **1**—**3**, double-proton transfer provides, in particular, interconversion of the tautomers **A**, **B**, and **E**, which involves intermediate formation and tautomerism of hydrogen-bonded solvates with hydroxyl-containing solvents, which act as catalysts.

The tendency of benzimidazolylazopyrazolinones to formation of this type of solvates is substantiated by not only X-ray analysis data, but also the results of quantum chemical calculations of isomeric monohydrates of compound **3**. The calculations predict the lowest energy for the monohydrate (*E*,*E*)-**3E** · H_2O containing a ten-membered H-bonded macrocycle similar to that of the hemihydrate (*E*,*E*)-**1E** · $1/2H_2O$ (Scheme 3).

An interesting feature of catalytic tautomerism of the forms **3A,B,E** is the variety of possible mechanisms of the process, which include concerted 1,3-, 1,5-, and 1,7-prototropic migration of two protons (NH- or OH-proton of the pyrazolinone and one proton of water molecule) along the perimeter of the six-, eight-, or ten-membered H-bonded ring (see Scheme 3). Both migrating protons move in the ring either clockwise or counterclockwise. These transformations belong to a more general class of double-proton prototropic processes in monosolvates (self-associates), which involve the formation of cyclic transition states (TS). Among them, 1,3-prototropic double-proton tautomerism[5,25—28] has been best studied. It plays an important role in biochemistry, being, in particular, responible for the formation of energetically unfavorable tautomers in hydrogen-bonded pairs of DNA nucleic bases, a key step in the mechanism of DNA point mutation (see, *e.g.*, Ref. 25). The simplest systems appropriate for modeling the key step of this important biochemical reactions are hydrogen-bonded dimers of amides and amidines, free nucleic bases, and their structural heterocyclic analogs.[5,25—28]

Double-proton tautomerism in doubly bonded hydrogen associates usually proceeds in a concerted fashion and readily even in the solid phase at rate constants of up to 10^9—10^{10} s^{-1}.[29—32] Here, the key role may be played by proton tunneling,[33—36] whose contribution rapidly in-

Scheme 3



Note. Numbers in parentheses denote the energies of unsolvated monohydrates (in kcal mol^{-1}) calculated relative to that of the most stable structure (*E*,*E*)-**3E** · H_2O; for transition states shown are the calculated activation energies ($\Delta E^{\neq}$) for the direct and reverse (in brackets) reactions.

creases as the temperature decreases and becomes predominant at low temperatures.[37] Stepwise migration of two protons in symmetrical and many unsymmetrical unsolvated hydrogen associates is unlikely because transfer of the first proton resulting in charge separation is energetically unfavorable. However, in polar media the energy difference between the concerted and non-concerted reaction pathways becomes much smaller.[26,38] For unsymmetrical associates formed by sufficiently strong Brønsted acids and bases, or for substrates characterized by intramolecular DPT and having structure-stabilized zwitterionic intermediates of single-proton transfer (SPT) a two-step DPT mechanism involving two successive SPT acts is possible.[38—42]

According to the results of studies of the transition states **TS1**—**TS3** of compound **3**, located by the B3LYP/6-31G** method, tautomerism of pyrazolinone monohydrates **1**—**3** is of concerted character. Here, the 1,3-, 1,5-, and 1,7-prototropic mechanism of the transformations under study is confirmed by the geometry of these TS (see Fig. 2). The H-bonded rings in which DPT occurs (including the ten-membered ring in **TS3**) are almost planar with small root-mean-square deviation of atoms from the plane (0.035, 0.089, and 0.01 Å for **TS1**, **TS2**, and **TS3**, respectively). Concerted character of DPT in monohydrates of compound **3** follows from the characteristics of transformation of the reacting systems moving along the reaction coordinate. The energies and some other characteristics of **TS1**—**TS3** are summarized in Table 1. Note that the activation energies for reactions ($\Delta E^{\neq}_{calc}$) are low and depend only slightly on the size of the atomic matrix used to describe proton migration

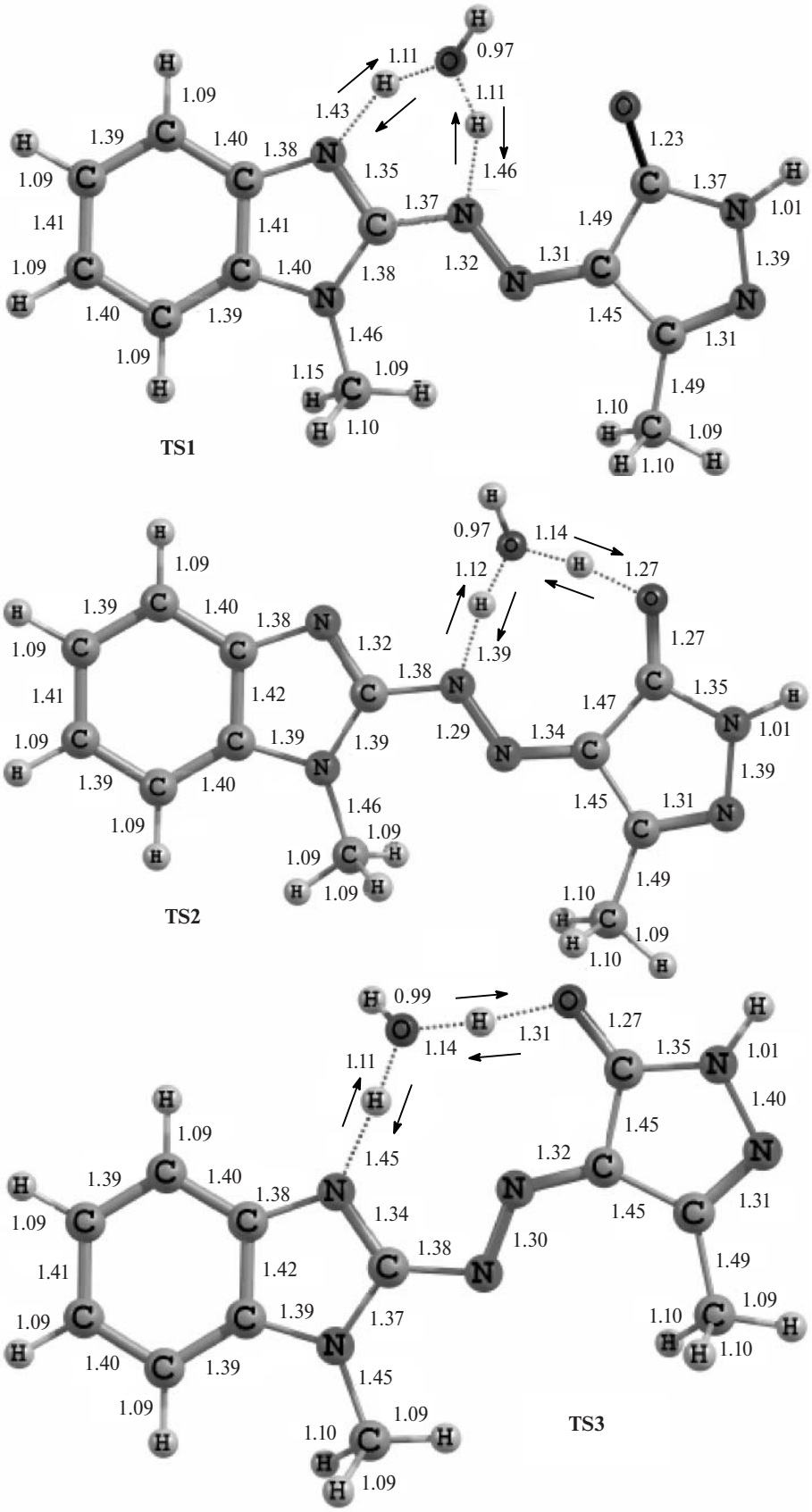


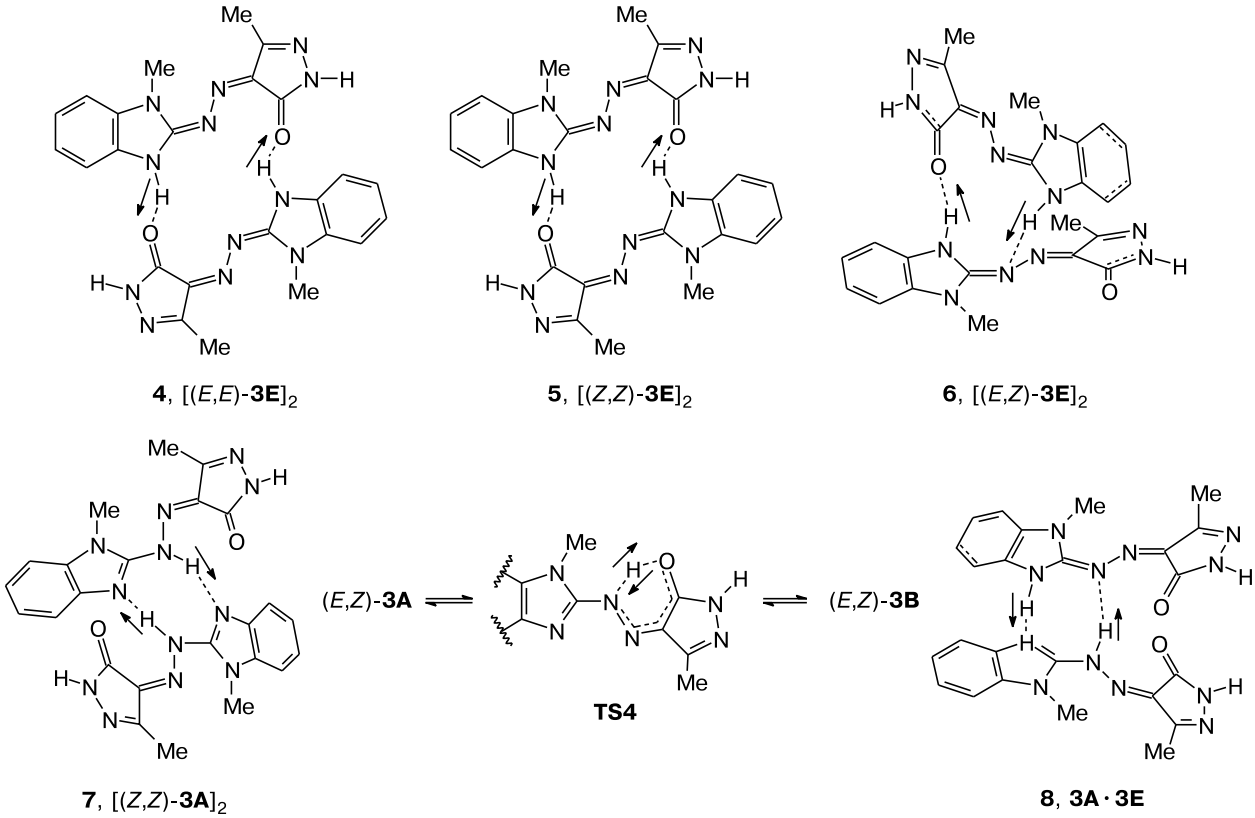
Fig. 2. B3LYP/6-31G** calculated geometries of transition states **TS1**—**TS3**. Arrows show the directions of proton motion for direct and inverse DPT. The bond lengths are given in Å.

between its outermost elements (see Table 1, $\Delta E^{\neq}$ = 8—14 kcal mol^{-1}).

A characteristic feature of tautomerism of the monohydrates of pyrazolinone **3** is that in two of the three cases it involves transformation of H-bonded rings. No transformation occurs only in the third reaction (**TS3**) proceeding with conservation of the ten-membered H-bonded ring on going from the reactant to the TS and then to the reaction product. In the other two reactions the (n+3)-membered H-bonded ring necessary for 1,n-prototropic double-proton tautomerism is formed by narrowing or expanding the H-bonded ring in the initial monohydrate. In particular, in the first reaction 1,3-prototropic tautomerism of monohydrate (Z,Z)-**3E**$\cdot H_2O$ involves transformation of its ten-membered H-bonded macrocycle to the six-membered H-bonded ring **TS1**, which is also included in the reaction product. In the second reaction the eight-membered H-bonded ring **TS2** is formed by transformation of the six-membered H-bonded ring of the initial reactant, monohydrate (Z,Z)-**3A**$\cdot H_2O$, while the formation of the final product, that is, monohydrate (Z,Z)-**3B**$\cdot H_2O$, is accompanied by the formation of ten-membered H-bonded ring. These features differ the solvent-promoted tautomerism of pyrazolinones from degenerate 1,3-prototropic tautomerism of the formic acid[43] and formamidine monosolvates,[34,44—46] which occurs exclusively with conservation of the size and atomic composition of the H-bonded rings. Clearly, the last reaction in Scheme 3, which involves the lowest-lying tautomer (E,E)-**3E**, is the most practically important.

An important role in intermolecular mechanism of tautomerism of pyrazolinones **1**—**3** should also be played by the self-associates of solvates (cyclic hydrogen-bonded dimers). The aptitude of the tautomeric forms **A**, **B**, and **E** for dimerization is confirmed by the results of RHF/6-31G quantum chemical calculations of pyrazolinone **3**, according to which this compound can form dimers **4**—**8** (Scheme 4, Table 1). Dimer **4** (C_2 symmetry) is the most stable, it is formed by the lowest-lying tautomer (E,E)-**3E** and includes a sixteen-membered H-bonded macrocycle. This is due to two intermolecular hydrogen bonds (IMHB) N(3)—H...O=C. Dimers **5** and **6** are respectively formed by the Z,Z- and E,Z-forms of

Scheme 4



Note. Proton migration directions are arrowed.

tautomer **3E**. The former is structurally similar to dimer **4**, whereas the latter (next in stability) is asymmetrical and linked by two IMHBs, N(3)—H...O=C and N(3)—H...N(10). Structures **7** and **8** belong to amidine-type dimers, being formed by the tautomer **3A** and tautomers **3A** and **3B**, respectively. Since dimerization of benzimidazolylazopyrazolinone **3** is sterically hindered, all dimers have essentially nonplanar geometries; dimer **6** (Fig. 3) is characterized by almost perpendicular arrangement of the planes of two monomers relative to each other.

As in the monohydrates of pyrazolinone **3** considered above, DPT should occur in dimers **4**—**8** (see Scheme 4), resulting in tautomeric forms that can act as intermediates of the following transformations:

$$\mathbf{A} \rightleftharpoons \mathbf{E} \rightleftharpoons \mathbf{B},$$

$$2\,\mathbf{E} \rightleftharpoons \mathbf{A} + \mathbf{B},$$

$$\mathbf{A} + \mathbf{B} \rightleftharpoons \mathbf{B} + \mathbf{A}.$$

However, we failed to locate the TS of double proton transfer in the dimers of pyrazolinone **3**, which seems to be due to computational difficulties associated with a large number of atoms in the dimers and with a complex topology of the potential energy surface (PES) in the vicinity of the TS of DPT. In this connection mention may be made that the transition state of concerted DPT could be located in our recent RHF/6-31G study of 1,2,4-triazino-[2,3-*a*]benzimidazol-5(4)*H*-3-one homodimers containing a much smaller number of atoms.[47]

The forms **A** and **B** can also undergo an interconversion with ease due to intramolecular single-proton transfer within the IHB. Unlike the TS of 1,2- and 1,3-prototropism studied earlier,[45,48—51] the cyclic state **TS4** of the reaction (*E*,*Z*)-**3A** $\rightleftharpoons$ (*E*,*Z*)-**3B** located by the B3LYP/6-31G** method (see Scheme 4) is characterized by small strain and low energy. The $\Delta E^{\neq}_{calc}$ values for the direct and reverse reactions (see Table 1, 8.5 and 2.0 kcal mol^{-1}, respectively) point to high rates of the tautomerism proceeding by this mechanism.

NMR study of pyrazolinones 1 and 2. The largest proportion of the ketoazine tautomeric form **E** in the solutions of pyrazolinones **1** and **2** was confirmed in a study of the ^{1}H and ^{13}C NMR spectra of these compounds in $CDCl_3$ (this solvent is characterized by relatively low polarity and weak solvation effect) and in polar DMSO-d_6 (Table 3).

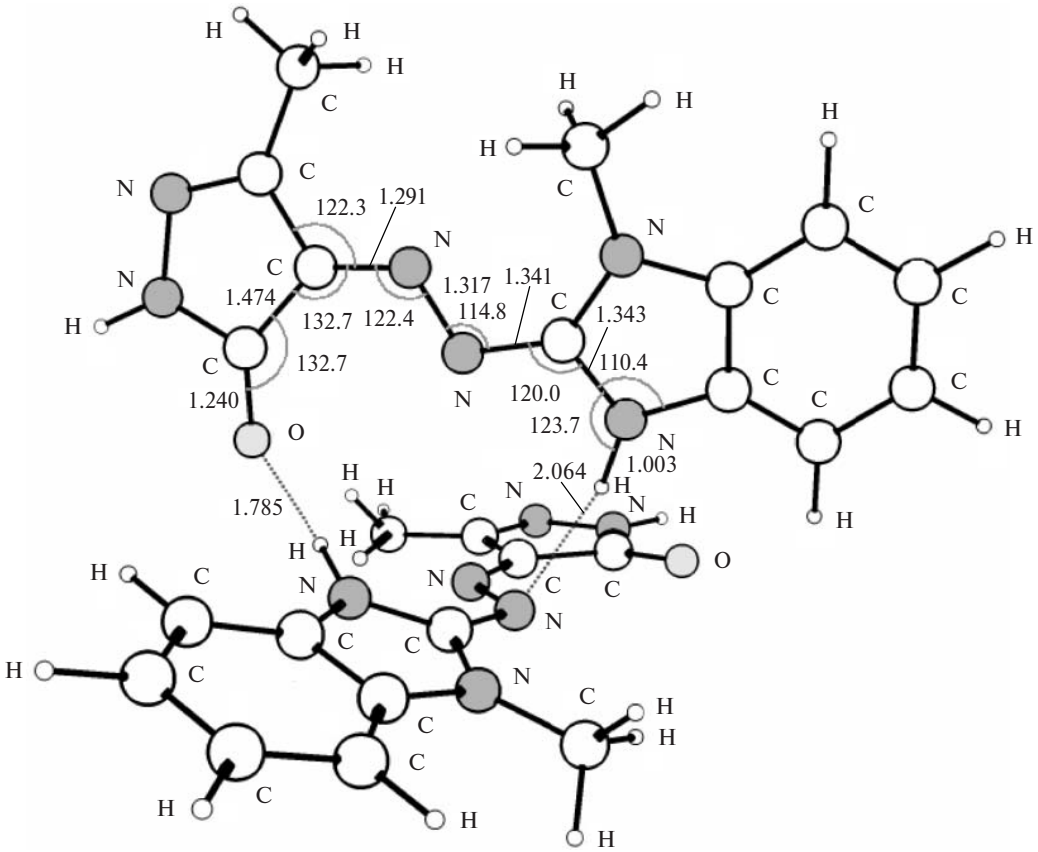


Fig. 3. Molecular structure of asymmetrical homodimer **6** according to RHF/6-31G calculations. Shown are selected bond lengths (in Å) and bond angles (in degrees).

These NMR spectra exhibit conventional patterns (in particular, they show no broadened signals, except for the NH group signal), which suggests a significant shift of the tautomeric equilibrium toward the predominant tautomeric form whose nature could not be determined by analyzing the NMR spectra. To solve this problem, we have carried out additional DFT (PW86/IGLO-II//B3LYP/6-31G*) calculations of the ^{1}H and ^{13}C chemical shifts for the tautomers **1A** and **1E**. They gave quite realistic δ_{calc} values (see Table 3) and showed that the calculated chemical shifts obtained for tautomer **1E** rather than **1A** are much closer to the experimental chemical shifts of pyrazolinone **1**. The root-mean-square deviations (*R*) of the calculated ^{1}H and ^{13}C chemical shifts from the corresponding experimental values were 0.5 and 1.8 ppm (^{1}H) and 1.7 and 6.3 ppm (^{13}C) for **1E** and **1A**, respectively.

Table 3. Calculated (δ_{calc}) and experimental (δ_{exp}) chemical shifts in the ^{1}H and ^{13}C NMR spectra of compounds **1** and **2**

Atom	δ_{calc}[a]		δ_{exp}[b]	
	(*E*,*E*)-**1A**	(*E*,*E*)-**1E**	**1**[c]	**2**
		^{1}H		
C(4)H	7.97	7.54	7.22—7.34[d]	7.22—7.32
C(5)H	7.44	7.56	7.22—7.34	7.22—7.32
C(6)H	7.81	7.56	7.22—7.34	7.22—7.32
C(7)H	7.48	7.51	7.22—7.34	7.22—7.32
NCH_3 (NCH_2)	4.35	3.63	3.80	4.22
C(18)H	2.31	2.19	2.60	2.56
C(20)H	8.92	8.96	7.95	7.95
C(21)H	7.60	7.42	7.38	7.40
C(22)H	7.35	7.18	7.11	7.12
C(23)H	7.53	7.57	7.38	7.40
C(24)H	8.00	7.89	7.95	7.95
NH	13.70	9.20	7.69	7.73
		^{13}C		
C(2)	145.52	155.76	156.34	157.6
C(4)	123.61	111.00	112.00	111.6
C(5)	126.20	126.67	123.61	123.8
C(6)	126.77	125.62	122.83	122.9
C(7)	109.61	109.86	110.17	109.3
C(8)	140.11	135.13	135.26	135.8
C(9)	144.02	131.36	132.21	131.4
C(12)	130.48	143.49	141.77 (128.3)	142.4 (к)
C(13)	147.82	140.32	139.19 (148.3)	129.7
C(16)	157.62	162.02	162.06 (157.6)	163.4
C(18)	14.80	20.66	18.05	17.3
C(19)	142.24	142.79	139.19 (137.9)	138.8
C(20)	118.41	117.15	117.45 (118.3)	118.5
C(21)	130.99	130.39	128.67 (128.8)	128.7
C(22)	127.17	125.25	123.61 (124.9)	124.2
C(23)	131.31	130.57	128.67	128.7
C(24)	118.29	117.65	117.45	118.5
C_{NMe} (C_{NCH_2})	32.51	28.47	28.83	42.6

Note. The root-mean-square deviations (*R*) of the calculated chemical shifts from corresponding experimental values were 0.5 and 1.8 ppm (^{1}H) and 1.7 and 6.3 ppm (^{13}C) for **1E** and **1A**, respectively (averaging was performed over the types of magnetically nonequivalent ^{13}C or ^{1}H nuclei).

[a] Calculated by the PW86/IGLO-II//B3LYP/6-31G* method for the lowest-lying tautomers of compound **1**; the chemical shifts are given relative to Me_4Si.

[b] ^{13}C NMR spectrum of pyrazolinone **1** was recorded in DMSO-d_6, other NMR spectra were recorded in $CDCl_3$.

[c] For comparison, the chemical shifts in the ^{13}C NMR spectra of 3-methyl-1-phenyl-4-phenylazo-2-pyrazolin-5-one[2] are given in parentheses.

[d] The *R* value for the protons of this multiplet was calculated using an average value of 7.28 ppm.

Compounds **1** and **2** are also characterized by close values of the chemical shifts of the *o*-phenylene protons H(4)—H(7), which manifest themselves as a multiplet in the NMR spectra. This is rarely observed for benzimidazole derivatives. This feature of pyrazolinones **1** and **2** also points to their existence in solution in the form **E**, because calculations gave the corresponding result for only one of the two tautomers, namely, **1E** (see Table 3). Thus, 4-(1-alkylbenzimidazol-2-ylazo)-2-pyrazolin-5-ones belong to heteroaromatic *o*-hydroxyazo compounds, which are prone to exist in the ketoazine tautomeric form in the condensed phase.

Summing up, it should be emphasized that the results obtained are of crucial importance for coordination chemistry of azo-ligand systems to which researchers pay incessant interest.[4,5,7,52].

Experimental

IR spectra of compounds **1** and **2** were measured on a Nicolet Impacs-400 instrument (Nujol mull). ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity-300 spectrometer (300 MHz) in $CDCl_3$ and DMSO-d_6 (see Table 3) with internal stabilization the ^{2}H resonance line of the deuterated solvent. The energies of tautomers were calculated using the GAMESS (US) program[53] (PC Gamess version).[54,55] The stationary points on the PES of the molecules and reaction systems under study were identified by calculating the corresponding force constant matrices with the same basis set as that used in the final geometry optimization. The correspondence between a given TS and the particular reaction was substantiated by monitoring the behavior of the reaction system when moving along the reaction coordinate from the transition state toward both reactants and products. The energies of reactants, TS, and products were calculated ignoring the zero-point vibrational energy (ZPE) correction. *Ab initio* calculations of the ^{1}H and ^{13}C chemical shifts (*vs*. Me_4Si) were carried out using the DeMon program.[56]

3-Methyl-4-(1-methylbenzimidazol-2-ylazo)-1-phenyl-2-pyrazolin-5-one (1) hemihydrate. 2-Amino-1-methylbenzimidazole (1.47 g, 10 mmol) was dissolved in 87% phosphoric acid (15 mL) with stirring at 50 °C, the solution was cooled to −10 °C, and finely ground sodium nitrite (0.76 g, 11 mmol) was added in

small portions at such a rate that no reddish brown NO_x vapor was observed. The reaction mixture was kept for 5 min at −5 °C, then the temperature was raised to 15 °C over a period of 30 min and urea (0.2 g) was added. After the gas liberation ceased, the cooled solution of the diazo compound was slowly added at 5—7 °C to a stirred solution of 3-methyl-1-phenyl-2-pyrazolin-5-one (1.8 g, 10 mmol) in an AcOH—EtOH mixture (30 mL, 1 : 1 v/v). Then water (20 mL) was added to the reaction mass in small portions with stirring over a period of 30 min, the temperature was gradually raised to room temperature, and the mixture was left for 6 h at this temperature. The precipitate (bright red protonated form of the azo compound) was filtered off, washed with water, acetone, and thoroughly triturated with 10% NH_4OH to maintain a weakly basic reaction in order to obtain a base. The yield of the hemihydrate of pyrazolinone **1** was 2.8 g (82%), orange crystals, m.p. 262—263 °C (from AcOEt) (with decomp.). Found (%): C, 63.15; H, 4.92; N, 24.44. $2(C_{18}H_{16}N_6O) \cdot H_2O$. Calculated (%): C, 63.33; H, 5.02; N, 24.62. IR, ν/cm^{-1}: 3328 (NH), 1667 (C=O).

4-(1-Butylbenzimidazol-2-ylazo)-3-methyl-1-phenyl-2-pyrazolin-5-one (2) was obtained analogously from 2-amino-1-butylbenzimidazole and 3-methyl-1-phenyl-2-pyrazolin-5-one. Yield 79%, bright red crystals, m.p. 203—205 °C (from AcOEt). Found (%): C, 67.36; H, 5.92; N, 22.45. $C_{21}H_{22}N_6O$. Calculated (%): C, 67.48; H, 6.02; N, 22.35. IR, ν/cm^{-1}: 3433 (NH), 1667 (C=O).

X-ray diffraction study of $[(E,E)\text{-}\mathbf{1}]_2 \cdot H_2O$ ($C_{36}H_{36}N_{12}O_3$) was carried out at 120 K on a Smart 1000 CCD automated three-circle diffractometer (Mo-Kα radiation, graphite monochromator, ω-scan, $2\theta < 54°$). At 120 K crystals are orthorhombic: $a = 14.4304(17)$ Å, $b = 7.4263(9)$ Å, $c = 30.572(4)$ Å, $V = 3276.3(7)$ Å^3, space group *Pbcn*, $Z = 8$, M = 341.38, $d_{calc} = 1.384$ g cm^{-3}, $\mu = 0.94$ cm^{-1}, $F(000) = 1432$. From a total of 20219 measured reflections ($R_{int} = 0.0873$), 3583 independent reflections were used in further calculations and refinement. The structure of $[(E,E)\text{-}\mathbf{1}]_2 \cdot H_2O$ was solved by the direct method and refined by the least squares method in the full-matrix anisotropic approximation. Hydrogen atoms were located from the difference Fourier syntheses of the electron density and refined anisotropically. The final *R*-factors were $R = 0.0528$ over 1691 reflections with $I > 2\sigma(I)$, $wR_2 = 0.1262$, and GOF = 1.002 over all measured reflections. All calculations were carried out using the SHELXTL PLUS 5 program package.

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