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Tautomerism and Acid–Base Properties of Formyl Derivatives of 1-Phenyl-3-methyl-4,5-dihydropyrazol-5-one and Its Thio Analog

A. I. Movchan, A. R. Kurbangalieva, O. N. Kataeva, I. A. Litvinov, and G. A. Chmutova

Kazan State University, Kazan, Tatarstan, Russia

Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center,
Russian Academy of Sciences, Kazan, Tatarstan, Russia

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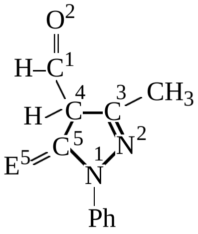
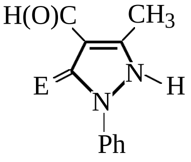
Abstract—A single-crystal X-ray diffraction study showed that 1-phenyl-3-methyl-4-formyl-4,5-dihydropyrazol-5-one occurs in the solid phase as two conformers of the NH tautomer. The acidity and basicity constants of 1-phenyl-3-methyl-4-formyl-4,5-dihydropyrazol-5-one and its analog, -5-thione, in 50% aqueous dioxane were measured. PM3 calculations qualitatively explan the differences in the tautomerism and acid–base properties of 4-formylpyrazolone (-pyrazolethione) and the corresponding compounds without the formyl substituent.

The steady interest in structural studies of pyrazol-5-ones with carbonyl-containing substituents in the 4-position of the ring is due to their wide use as metal extractants, color formation ingredients, drugs, etc., as well as to their tautomerism [1, 2]. It is well known that, in nonpolar and low-polarity solvents, as a rule, the enol forms of N^1-substituted pyrazolones are realized because of their stabilization by fairly strong intramolecular hydrogen bonds with the substituent in the 4-position [1, 3–7], while in polar, proton-donor, and proton-acceptor solvents the forms [mainly NH and/or OH] stabilized by intermolecular hydrogen bonds or dipole–dipole interactions prevail. In the solid phase, two or more molecules of the same pyrazolone occurring in one or other tautomeric form take part in intermolecular interactions, as indicated by recent X-ray diffraction studies of 4-acylpyrazolones [4–6, 8–11]. In some cases, e.g., in 1-phenyl-3-methyl-4-benzoyl- and 1,3-dimethyl-4-cinnamoyl-4,5-dihydropyrazol-5-ones, different tautomeric forms crystallize from different solvents [6, 10]. Thio compounds are poorly studied in this respect [11, 12], mainly because of their low solubility in the majority of common organic solvents.

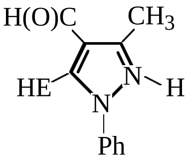
Pyrazol-5-ones with the 4-formyl substituent, in particular, 3-methyl-1-phenyl-4-formyl-4,5-dihydropyrazol-5-one **I** and 3-methyl-1-phenyl-4-formyl-4,5-dihydropyrazole-5-thione **II**, whose structure was discussed in numerous papers [13–18], differ from acyl-substituted derivatives in that the number of possible tautomers in them is larger. To the three common forms, CH (a), NH (b), and OH (c), the hydroxymethylene form (d) is added.



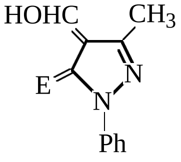
Ia, IIa



Ib, IIb



Ic, IIc



Id, IId

E = O (**I**), S (**II**).

Different authors assigned different structures to **I**: CH (**Ia**) [13, 14], OH (**Ic**) [15], or hydroxymethylene (**Id**) [16, 17]. In the most comprehensive study [17], based on the IR and UV data, as well on analysis of the chemical behavior, it was inferred that compound **I** occurs in the hydroxymethylene form (**Id**). The same authors assigned to the thio analog **II** the thiol form SH (**IIc**) with an intramolecular hydrogen bond [18]. In that study, the IR spectra were recorded for films and solutions in nonpolar or low-polarity sol-

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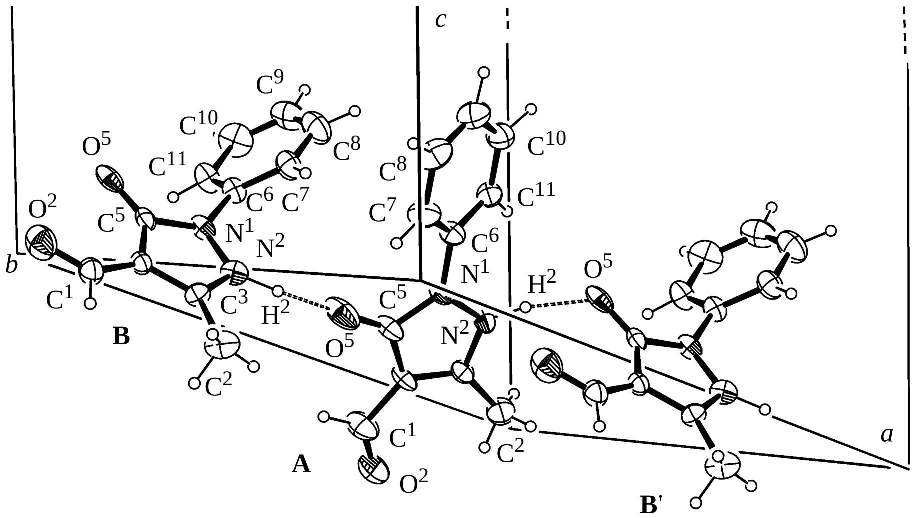


Atom numbering and scheme of hydrogen bonds in compound **I**.

vents (CCl_4, $CHCl_3$, THF), while the UV spectra were taken in cyclohexane and alcohols, i.e., the range of the examined conditions was limited.

Proceeding with the studies of the structure of chalcopyrazolones by various physical and quantum-chemical methods aimed to elucidate and quantitatively characterize the intra- and intermolecular H bonding as factors of stabilization of a given tautomeric form, we examined in detail formyl derivatives **I** and **II** in the solid state. We also wished to obtain new data on the behavior of these compounds in solutions and to evaluate the “intrinsic” stability of different tautomeric forms of formylpyrazolone and its thio analog by quantum-chemical calculations. It was also of interest to compare the structure and properties of **I** and **II** with those of the model compounds, 3-methyl-1-phenyl-4,5-dihydropyrazol-5-one **III** and its thio analog **IV** containing no 4-formyl substituent.

Compound **I** was prepared by the known procedures and had the same constants as those reported in [17]. We studied its crystal and molecular structure by single crystal X-ray diffraction. The figure and the main geometric parameters given in Table 1 show that, in the solid state, compound **I** occurs not in the hydroxymethylene form **Id** as it was suggested in [17], but in the NH form **Ib**.

The asymmetric cell contains two independent molecules occurring in conformations that differ in the orientation of formyl groups relative to the plane of the pyrazolone system; the phenyl ring at the N^1 atom is turned by 20° (see figure). In molecule **A**, the $C^1{=}O^2$ bond is eclipsed with the $C^3{=}C^4$ bond, and in molecule **B** it is eclipsed with the $C^4–C^5$ bond. Molecules **A** and **B** alternate in the crystal to form infinite chains with intermolecular hydrogen bonds N–H···O along the crystallographic directions [1, 1, 0] and [1, –1, 0]. The hydrogen bonds have the following parameters: $N^{2A}–H^{2A}\cdots O^{5B'}$ ($1/2 - x$, $-1/2 + y$, $1/2 - z$), $N^{2A}–H^{2A}$ 0.96(2), $H^{2A}\cdots O^{5B'}$ 1.66(2), $N^{2A}\cdots O^{5B'}$ 2.602(3) Å, $\angle N^{2A}–H^{2A}\cdots O^{5B'}$ 167(2)°; $N^{2B}–H^{2B}\cdots O^{5A''}$ ($-x$, y, $1/2 - z$), $N^{2B}–H^{2B}$ 1.07(4), $H^{2B}\cdots O^{5A''}$ 1.52(4), $N^{2B}\cdots O^{5A''}$ 2.587(3) Å, $\angle N^{2B}–H^{2B}\cdots O^{5A''}$ 176(3)°.

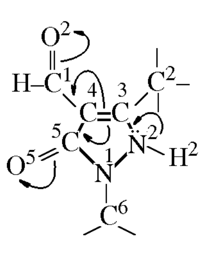
The fact that the formyl substituent does not take part in H bonding is probably due to the packing effects and to the presence of only one hydrogen atom capable of forming a strong hydrogen bond.

The following features of the molecular structure should be noted. The $C^5{=}O^5$ bond in pyrazolone **I**, participating in the intermolecular H bonding, in both conformers is longer than the similar bond in the formyl fragment, $C^1{=}O^2$, but shorter than the corresponding $C^5{=}O^5$ bond of pyrazolone **III** [12]. The endocyclic bond angles in **I** and **III** are virtually the same (the “outer” bond angles are also close to each other), but the $N^2–C^3$ bonds in both conformers of **I** are appreciably shorter, and the $C^3{=}C^4$ bonds, appreciably longer than in **III**. This is probably due to the presence in **I** of two pathways of intramolecular charge transfer, compared to a single pathway in **III**.

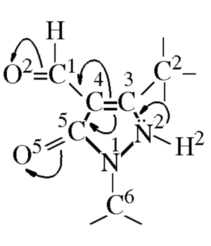
Active participation of the formyl substituent in conjugation is favored by the fact that the deviation of the plane of this substituent from the plane of the pyrazolone ring in both conformers is only slight. This is in agreement with the planar configuration of

Table 1. Main geometric parameters of conformers of the NH forms of **I** and **III**

Parameter	NH form of **I**		NH form of **III** [12]
	conformer **IA**	conformer **IB**	
Bond	*d*, Å		
N^1–N^2	1.386(3)	1.377(3)	1.385(2)
N^1–C^5	1.385(3)	1.375(4)	1.394(3)
N^2–C^3	1.323(4)	1.328(3)	1.352(3)
C^3–C^4	1.373(4)	1.386(4)	1.359(3)
C^4–C^5	1.417(5)	1.428(3)	1.409(3)
C^5–O^5	1.235(4)	1.248(4)	1.260(3)
N^1–C^6	1.414(4)	1.422(3)	1.423(3)
C^3–C^2	1.494(5)	1.478(4)	1.485(3)
C^1–O^2	1.219(5)	1.215(4)	
C^4–C^1	1.438(4)	1.430(4)	
Bond angle	ω, deg		
$N^2N^1C^5$	108.0(2)	109.4(2)	108.4(2)
$N^1N^2C^3$	109.3(2)	109.1(2)	108.0(2)
$N^2C^3C^4$	109.1(3)	108.9(2)	109.3(2)
$C^3C^4C^5$	107.8(2)	107.4(2)	108.5(2)
$C^4C^5N^1$	105.7(3)	105.2(2)	105.5(2)
$C^4C^5O^5$	132.2(3)	132.8(3)	132.8(2)
$N^1C^5O^5$	122.2(3)	122.0(2)	121.7(2)
$N^2N^1C^7$	120.1(2)	120.5(2)	120.5(2)
$C^5N^1C^6$	131.1(3)	128.4(2)	130.0(2)
$N^2C^3C^2$	120.2(2)	118.9(3)	119.4(2)
$C^4C^3C^2$	130.7(3)	132.2(2)	131.3(2)
$C^5C^4C^1$	123.0(3)	128.5(3)	
$C^3C^4C^1$	123.0(3)	123.7(2)	
$C^4C^1O^2$	124.9(3)	124.5(3)	
Torsion angle	τ, deg		
$C^5N^1C^6C^7$	37.94(0.45)	–118.77(0.33)	28.9(2)
$N^2N^1C^6C^{11}$	26.51(0.39)	–138.22(0.28)	
$O^2C^1C^4C^3$	0.79(0.56)	–178.18(0.29)	
$O^2C^1C^4C^5$	–179.78(0.34)	–5.26(0.50)	



A



B

bonds at the N^2 atom in **I** (conformers **A** and **B**), as well as with nearly equal effective negative charges on the O^5 and O^1 atoms and effective positive charge on the N^2 atom in **I**, exceeding that on the N^2 atom in **III**, as follows from the semiempirical calculations of the structure (see below). The angles by which the phenyl substituents at the N^1 atom are turned relative to the plane of the pyrazolone system in **I** are larger than in **III**.

The IR spectrum of **I** in Nujol is rather complex but, in principle, is consistent with the results of the X-ray diffraction analysis. The spectrum contains three separate bands of the carbonyl group [1684, 1668, and 1636 cm^{-1} (s)] corresponding to the hydrogen-bonded and free carbonyl in different conformers, a weak broad band in the region of ~2600 cm^{-1} (ν_{NH}), and medium-intensity bands at 1570 and 1532 cm^{-1} characteristic of the C=C and C=N fragments.

The IR spectra of **I** in different solvents, as well as the ^{1}H NMR spectra, substantially differ from each other, which suggests that different tautomeric forms are realized. The most distinctive features of the spectra are the following. The IR spectra of solutions of **I** in $CHCl_3$, CCl_4, dioxane, and acetonitrile contain a broad band at 3100 cm^{-1} (ν_{OH} associated), and in DMSO and ethanol, a broad band of medium intensity at 2400–2600 cm^{-1} (ν_{NH} associated). The ^{1}H NMR spectrum in deuterochloroform contains a signal of methyl protons at 2.43 ppm, a strongly split multiplet of phenyl protons in the region of 7.2–7.8 ppm, and a signal in the region of 9.53 ppm corresponding to the aldehyde proton.

Judging from the intensities of the characteristic bands in the IR spectra of **I** and related compounds with 4-RCO substituents [3–7], we believe that, in $CHCl_3$ and CCl_4, the OH form with the intramolecular hydrogen bond prevails; in dioxane and acetonitrile, a mixture of the OH and hydroxymethylene forms is present, with the former prevailing in CH_3CN and the latter, in dioxane; in DMSO and ethanol, along with large amounts of the hydroxymethylene form, the NH form hydrogen-bonded with the solvent molecules is also present.

Unfortunately, we failed to prepare a crystalline sample of thiopyrazolone **II**, but our data on the spectral characteristics of this compound in the solid phase (IR spectrum in Nujol) and in solutions fully support the conclusion made in [18] that the thiol (SH) form is realized under any conditions. In addition to the previously studied IR spectra in $CHCl_3$, CCl_4, and THF, we studied the spectra in dioxane, acetonitrile, dimethyl sulfoxide, and ethanol. All the spectra contain the S–H stretching vibration bands at about 2450 cm^{-1} (br, w), whereas the absorption bands of OH, NH, and C=S groups [1, 18, 19] are lacking. Realization of the SH form in the chloroform solution was also supported by the ^{1}H NMR spectrum which contained the signals at 2.50 (3H, CH_3), 7.4–7.7 (5H, C_6H_5), and 9.9 ppm (1H, CHO), with the signals of 2-H and 4-H protons of the pyrazolone ring, which should be observed in the NH and OH forms, respectively [3, 20], being absent.

At the same time, it should be noted that the state of the SH group is different in different solvents, as seen from the shape of the absorption bands of the SH and carbonyl groups in the region of ~1640–1680 cm^{-1}. In the IR spectrum of **II** in $CHCl_3$ and CCl_4, the SH band is broad, smeared, and weak, and the $\nu_{C=O}$ band is relatively short-wave (1644 and 1648 cm^{-1}, respectively). When the solutions are diluted tenfold, the position, shape, and width of the band at 2450 cm^{-1} remain virtually unchanged, suggesting formation in this solvent of a fairly strong intramolecular hydrogen bond.

In dioxane, acetonitrile, and ethanol, the pattern is similar, but on the background of the main strong band $\nu_{C=O}$ a new narrow weak band appears as a shoulder at 1676–1678 cm^{-1}. We assign this band to the free carbonyl group of the formyl substituent, i.e., to the conformer without intramolecular hydrogen band. In DMSO, the intensity of the band at 1678 cm^{-1} increases sharply; in this solvent, the intramolecular hydrogen bond is virtually absent. As judged from the position and shape of the SH and C=O stretching vibration bands, the intramolecular hydrogen bond is absent in solid compound **II** also.

By potentiometric titration, we evaluated the acid–base properties of **I** and **II**, which have a pronounced effect on their properties important for practice, in particular, on their capability for oxidative coupling in the process of color formation [2]. High acidity of **I** in aqueous alcohol (pK_a 2.94) was one of the evidences in favor of the existence of **I** in the hydroxymethylene form [17]. In the titration, 50 vol % aqueous dioxane was used as solvent; this choice was governed by the fairly high solubility in it of the compounds under consideration and their analogs [21, 22]. In this solvent, we previously studied the kinetics of the coupling reactions involving pyrazol-5-ones as color-forming components [21]. The results of the potentiometric titration of formylpyrazolones **I** and **II** and of model compounds **III** and **IV** without the 4-substituent, processed with the CPESSP program [23], are given in Table 2. In the data processing, we considered the possibility of formation of mono-, di-, and other protonated and deprotonated species.

Table 2. Acidity and basicity constants of **I**–**IV**

Comp. no.	pK_a	p$K^{2+}_{BH_2}$	pK_{DH_2}
I	3.56 ± 0.03	4.68 ± 0.02	
II	2.77 ± 0.06	3.61 ± 0.01	
III	8.44 ± 0.03	4.16 ± 0.03	3.70 ± 0.13
IV	5.78 ± 0.06	4.55 ± 0.03	3.42 ± 0.5

The obtained values of pK_a for **I** and **III** are in reasonable agreement with the previous data [18]; the acidity of thio derivatives was measured for the first time. The data presented in Table 2, as expected, show that introduction of the formyl substituent substantially increases the acidity of pyrazolone and its thio analog, with thio derivatives **II** and **IV** being more acidic than the respective oxygen compounds **I** and **III**. Data on the basicity of the compounds characterize their diprotonated forms (p$K^{2+}_{BH_2}$) which are the major species present in the solution under the conditions of the experiment. They are difficult to compare, since any of the tautomeric forms of **I**–**IV** can be protonated at alternative centers. Since we failed to obtain reliable characteristics of the tautomeric equilibria in the systems under discussion in 50% aqueous dioxane, the values of pK_a and pK_b should be considered as apparent.

To gain a deeper insight into the nature of the tautomerism of **I** and **II** and of acid–base properties of **I**–**IV**, we supplemented the experimental studies by PM3 calculations [24]. The method proved to be useful in studying the structure and acid–base properties of the simplest model pyrazolones [25, 26], and, as compared to DFT, gave better results for **III** and **IV** [27].

By PM3 calculations, we obtained the following data on the relative stability of tautomeric forms of **I** and **II** (for the most stable conformers), $\Delta\Delta H_f$, kJ mol^{-1}): 18.9 (**Ia**), 87.1 (**IIa**), 7.9 (**Ib**), 76.5 (**IIb**), 0.0 (**Ic, IIc**), 18.7 (**Id**), and 58.7 (**IId**). Thus, the calculations qualitatively explain the differences in the tautomerism of **I** and **II**. In particular, they suggest slight differences in the stability of varios tautomeric forms of pyrazolone **I** and hence easy transformation of one tautomeric form into another, specifically, under the influence of intermolecular interaction with the solvent. In nonpolar solvents, the most stable OH form of **I** is realized, presumably as conformer **A** stabilized by the intramolecular hydrogen bond similar to that existing in 4-acyl-substituted pyrazolones [3–7]. In the thio analog **II**, the stability of the thiol form is much greater than that of the other forms; only this form was detected under varied experimental conditions.

The calculated energies of deprotonation of various tautomeric forms of **I** and **II**, listed in Table 3, are

Table 3. Enthalpies of formation (ΔH_f^0, kJ mol^{-1}) of anioms of **I**–**IV** and deprotonation energies of of tautomeric forms (E_{deprot}, kJ mol^{-1}), according to PM3 calculations

Comp. no.	ΔH_f^0(anion)[a]	E_{deprot}[b]			
		CH	NH	EH	hydroxy-methylene
I	–266	1247	1258	1267	1247
II	–42.5	1178	1189	1268	1206
III	–59.9	1336	1318	1308	
IV	136	1238	1225	1303	

[a] $\Delta H_f^0(H^+)$ 1480 kJ mol^{-1}. [b] Data given for the most stable conformers of CH, NH, and EH forms and the most stable geometric isomer of the hydroxymethylene form.

also in reasonable agreement with the experiment when compared to those of compounds **III** and **IV** unsubstituted in 4-position.

It should be primarily noted that the calculations adequately reproduce the relative acidities of the compounds under study. Namely, they indicate that introduction of the electron-withdrawing formyl group into 4-position facilitates deprotonation of all the tautomeric forms of **I** and **II** (as compared to **III** and **IV**, respectively) and that the acidity of the thio compounds is higher than that of the oxygen analogs (except the EH forms which have approximately equal acidity). Taking into account that ΔpK_a 1 for normal conditions corresponds to $\Delta\Delta G$ 1.37 kcal mol^{-1} and that the entropy of proton transfer is insignificant [28], it can be concluded that changes in the acidity with introduction of the formyl substituent into both the oxygen- and sulfur-containing compounds are in agreement with the calculated data within the order of magnitude. The absolute values of the calculated energies of deprotonation are considerably overestimated; more consistent results can be obtained taking into account the electron correlation, but the principal improvement, as follows from our model calculations [27], is possible only when solvation effects are taken into account. It should be emphasized that, as follows from the calculations, the tautomeric forms of **I** differ in acidity insignificantly. This result casts some doubt on the possibility of using the experimental pK_a value of **I** as an argument in favor of existence of 3-methyl-1-phenyl-4-formyl-4,5-dihydropyrazol-5-one in solutions in a specific tautomeric form.

Interpretation of the calculation results for the basicity is more complicated as compared to the acidity: the anion is common for all the tautomers, while protonation can lead to the formation of several complexes even from one tautomeric form; in addition, the formyl oxygen atom can also act as a protonation site. The enthalpies of formation of the most probable cations [25–27] and the proton affinities of **I**–**IV** are given in Table 4. These data show that the basicities of all the centers in **I** and **II** are lower than those of the corresponding centers in **III** and **IV** where the electron-withdrawing formyl substituent is absent. The preferable protonation centers in all the com-

Table 4. Enthalpies of formation of protonated complexes of tautomeric forms of **I**–**IV** (ΔH_f^0, kJ mol^{-1}) and the corresponding proton affinities (*PA*, kJ mol^{-1}), according to PM3 calculations

Form, protonation site	**I**		**II**		**III**		**IV**	
	ΔH_f^0	*PA*	ΔH_f^0	*PA*	ΔH_f^0	*PA*	ΔH_f^0	*PA*
CH at N^2	659	785	969	770	771	793	1080	777
CH at E^5	678	766	893	846	780	784	997	860
CH at O^1	788	656	1083	656				
NH at N^2	692	743	996	733	812	770	1110	761
NH at E^5	622	813	843	886	748	834	964	907
NH at O^1	630	805	932	797				
EH at N^2	622	821	843	810	748	844	964	829
EH at E^5	872	571	908	745	990	602	1020	773
EH at O^1	656	787	870	783				
Hydroxymethylene at N^2	618	828	910	801				
Hydroxymethylene at E^5	635	811	852	859				
Hydroxymethylene at O^1	841	605	869	842				

pounds are N^2 (especially in the enol forms) and E^5 (mainly in the keto forms). The formyl oxygen atom, O^1, noticeably competes with the pyrazolone oxygen atom as the protonation center only in the NH form of **I**. In the keto forms of **II**, protonation of the sulfur atom is more probable than that of the N^2 atom; in the respective forms of **I**, except the NH form, the O^5 and N^2 atoms are comparable in activity.

EXPERIMENTAL

The IR spectra were registered on a Specord M-80 instrument in the range 600–4000 cm^{-1} in the solid state (mulls in Vaseline oil) and in solutions (0.1 M, cell thickness d 0.1–0.12 mm). The accuracy was ± 1 cm^{-1}. The ^1H NMR spectra were recorded on a Varian Unity-300 spectrometer (300 MHz) at 25°C. The chemical shifts were determined relative to the residual proton signals of deuterochloroform.

Single crystal X-ray diffraction study of I. Crystals of **I**, $C_{11}H_{10}N_2O_2$, are monoclinic, space group $C2/c$. Unit cell parameters at 20°C: a 17.970(3), b 13.316(2), c 17.740(2) Å; β 108.79(1)°, V 4018.9(2) $Å^3$, Z 16, d_{calc} 1.34 g cm^{-3}. The unit cell parameters and intensities of 5452 reflections, including 2179 reflections with $I \geq 3\sigma$, were measured on an Enraf-Nonius CAD-4 automatic four-circle diffractometer (MoK_α radiation, graphite monochromator, $\omega/2\theta$ scanning, $\theta \leq 26.9°$). No decrease in the intensities of three check reflections during the experiment was observed. No correction for absorption (μMo 8.81 cm^{-1}) was required.

The structure was solved by the direct method using the SIR program [29] and refined first in isotropic and then in the anisotropic approximation. The hydrogen atoms were revealed from the differential electron density series and refined isotropically. The final divergence factors were R 0.040 and R_W 0.042 for 2179 unique reflections with $F^2 \geq 3\sigma$. All the calculations were performed on an Alpha Station 200 computer with the MolEN software [30]. The intermolecular interactions were analyzed using the PLATON program [31]. The principal geometric parameters of the structures are given in Table 1; the molecular geometry and the system of hydrogen bonds in the crystal are shown in the figure.

The semiempirical calculations were performed using the VAMPC software kindly provided by Dr. T. Clarke (Erlangen-Nuremberg University, Germany). The calculations were made with full geometry optimization. In all the cases, the matrix of second derivatives was calculated to characterize the type of the stationary points. Only the points with all positive second derivatives were taken into consideration.

3-Methyl-1-phenyl-4-formylpyrazol-5-one I was prepared by the standard procedure [17]. White crystalline substance, after crystallization from ethyl acetate mp 173–174°C (published data: mp 175°C [17]), R_f 0.28 (acetone–toluene, 1 : 6).

3-Methyl-1-phenyl-4-formylpyrazol-5-one II was prepared by a slightly modified procedure from [18]. The yellowish precipitate was purified by repeated reprecipitation from an alkaline solution; mp 91–93°C (published data: mp 91–92°C [18]), R_f 0.44 (acetone–toluene, 1 : 6).

The protolytic properties of **I**–**IV** were studied in aqueous-dioxane solutions (50 vol % dioxane) by pH-metric titration in an argon flow at 25 ± 0.1°C. A 673M ionometer was used. The glass electrode was calibrated against buffer solutions [32]. Aqueous-dioxane solutions of **I**–**IV** (c 0.01 M) were directly titrated with the solutions of HCl (c 0.01 M) and KOH (c ~0.01 M) containing dioxane in the corresponding concentration. The ionic strengths of the solutions of the titrant and sample being titrated were kept constant and equal to 0.1 (KCl).

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