

X-ray diffraction analysis and spectral studies of new derivatives of pyrazol-5-one

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The molecular and crystal structures of 4-acetamido-2,3-dimethyl-1-phenylpyrazol-5-one (**1**) and 4-maleylamido-2,3-dimethyl-1-phenylpyrazol-5-one (**2**) were studied. The molecular conformations are stabilized via systems of intermolecular hydrogen bonds between the amide groups and the carbonyl oxygen atoms of the pyrazolone rings. The conformation of compound **2** is additionally stabilized via an intramolecular interaction between the carboxyl group and the amide oxygen atom. According to the IR spectral data, protonation of the compounds under study in an acetonitrile solution occurs at the carbonyl oxygen atom of the pyrazolone ring, which is also confirmed by the UV spectral data.

Key words: pyrazol-5-one, derivatives; X-ray diffraction analysis; IR spectroscopy.

Derivatives of pyrazol-5-one are widely used in pharmacology, analytical chemistry,¹ and chemistry of dyes.² These compounds can also serve as useful ligands in complexation with d and f elements, which is of interest in connection with the problem of the preparation of new materials possessing advantageous properties.

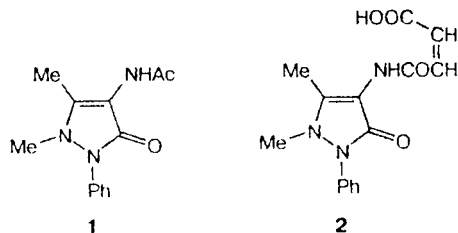
Previously,^{3–7} we have reported the synthesis and the spectral and structural characteristics of complexes of the simplest pyrazol-5-one derivatives, viz., antipyrine, amidopyrine, and ligands of the diantiprylmethane series. The present work is devoted to studies of the structures and spectral properties of 4-acetamido-2,3-dimethyl-1-phenylpyrazol-5-one (**1**) and 4-maleylamido-2,3-dimethyl-1-phenylpyrazol-5-one (**2**) by X-ray diffraction analysis and IR and UV spectroscopy.

These compounds are of interest as potential ligands possessing several possible coordination centers. Therefore, with the aim of modeling processes of complexation, we considered the spectral properties of solutions of protonated forms of the ligands.

Experimental

Single crystals of compounds **1** and **2** were prepared by recrystallization from acetonitrile. The X-ray diffraction data were collected on an automated Enraf-Nonius CAD-4 diffractometer (Mo-K α radiation, $\theta/2\theta$ scanning technique). The principal crystallographic data and the results of the refinement are given in Table 1. Both structures were solved by direct methods. The positions and thermal parameters of the nonhydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were located from difference electron density syntheses and refined isotropically. All calculations were carried out with the use of the SHELXL-93 program package.⁸ The atomic coordinates and equivalent thermal parameters of compounds **1** and **2** are given in Tables 2 and 3, respectively.

The IR spectra were recorded on a Nicolet Magna 750 Fourier IR spectrometer; the resolution was 2 cm⁻¹. The solid samples were prepared as Nujol mulls. The UV spectra were obtained on a Pye Unicam 8800 instrument.



Results and Discussion

The principal interatomic distances and bond angles in molecules **1** and **2** are given in Tables 4–7. The overall views of the molecules and the atomic numbering schemes are shown in Figs. 1 and 2.

The molecular conformations are stabilized *via* intermolecular hydrogen bonds between the carbonyl oxygen atoms of the pyrazolone rings and the hydrogen atoms of the amide groups. The parameters of the N(3)—H...O(1') intermolecular hydrogen bond in the structure of **1** are as follows: N...O, 2.87 Å; N—H, 1.22 Å; H...O, 1.70 Å; the N—H—O angle is 159°; symmetry transformation $1 - x, 1 - y, 1 - z$. The parameters of the N(3)—H(3n)...O(1') intermolecular hydrogen bond in the structure of **2** are as follows: N...O 2.826 Å; N—H 0.89 Å; H...O 1.94 Å; the N—H—O angle is 171°; symmetry transformation $-x, 1 - y, 1 - z$. In addition, the oxygen atom of the amide fragment and the hydrogen atom of the carboxyl group

Table 2. Atomic coordinates ($\times 10^4$) and equivalent thermal parameters ($U_{eq} \cdot 10^3/\text{\AA}^2$) in the structure of **1**

Atom	x	y	z	U_{eq}
O(1)	6112(7)	3804(13)	4741(4)	80(3)
O(2)	3641(7)	3235(14)	3334(5)	97(3)
N(1)	6883(7)	4322(12)	3800(4)	65(3)
N(2)	6618(7)	5072(18)	3249(4)	73(3)
N(3)	4294(7)	4857(15)	4062(5)	69(3)
C(1)	5607(13)	5244(22)	3282(8)	76(5)
C(2)	5262(9)	4777(20)	3828(7)	67(4)
C(3)	6088(12)	4236(17)	4196(7)	63(4)
C(4)	7037(20)	4390(36)	2693(11)	98(8)
C(5)	5042(22)	5985(31)	2764(10)	99(7)
C(6)	7900(12)	4246(19)	3977(8)	63(4)
C(7)	8194(13)	3132(23)	4394(8)	73(5)
C(8)	9171(14)	3010(25)	4575(8)	82(5)
C(9)	9829(15)	4085(25)	4349(11)	87(6)
C(10)	9551(13)	5208(26)	3930(9)	84(6)
C(11)	8594(12)	5318(25)	3757(8)	73(4)
C(12)	3565(12)	4035(21)	3799(8)	79(5)
C(13)	2559(19)	4182(43)	4084(14)	103(8)

Table 1. Principal crystallographic data and results of the refinement for compounds **1** and **2**

Parameter	1	2
Formula	$C_{13}H_{15}N_3O_2$	$C_{15}H_{15}N_3O_4$
Molecular weight	245.28	301.30
Wavelength/Å	0.71073	
Crystal system	Orthorhombic	Triclinic
Space group	<i>Pbca</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	13.562(3)	8.321(2)
<i>b</i> /Å	8.526(2)	9.316(2)
<i>c</i> /Å	21.551(4)	11.023(2)
α /deg	90	70.11(3)
β /deg	90	81.98(3)
γ /deg	90	65.07(3)
<i>V</i> /Å ³	2491.9(9)	728.6(3)
<i>Z</i>	8	2
Number of check reflections	3	3
Interval of their measurements/min	60	60
Stability (%)	0.5	0.2
$\rho_{calc}/g\text{ cm}^{-3}$	1.308	1.373
<i>F</i> (000)	1040	316
$2\theta_{max}$ /deg	45	50
Range of indices	$0 \leq h \leq 13,$ $0 \leq k \leq 8,$ $0 \leq l \leq 22$	$0 \leq h \leq 9,$ $-9 \leq k \leq 10,$ $-12 \leq l \leq 12$
Number of reflections (total)	431	2806
Number of independent reflections	431	1558 ($R_{int} = 0.010$)
Method of refinement	Full-matrix least-squares	
Reflections/Parameters	431/224	1444/260
<i>R_f</i> (based on <i>F</i> ² for reflections with $I \geq 2\sigma(I)$)	0.0297	0.0267
GOOF based on <i>F</i> ²	1.402	1.040
Extinction coefficient	—	0.023(4)

in compound **2** are involved in an intramolecular hydrogen bond to form a seven-membered-ring. The parameters of this O(2)...H(3o)—O(3) bond are as follows: O...O, 2.485 Å; O—H, 1.05 Å; O...H, 1.45 Å; the O—H—O angle is 170°.

The C=O bond lengths in the pyrazolone ring (1.23(2) and 1.239(2) Å) agree well with the corresponding parameters in other derivatives of pyrazol-5-one.^{9,10} The formation of the intramolecular hydrogen bond in the structure of **2** leads to a slight increase in the C=O bond length in the amide group compared to that observed in the structure of **1**, although the bond lengths in compound **1** were determined with a rather low accuracy.

In compound **1**, the N(3)—H bond is twisted by 10° out of the C(2)—N(3)—C(12) plane. In the structure of **2**, the amide fragment is planar; the NH bond is twisted by 1.2° out of the plane. The small values of the torsion angles for the substituents at position 4 of the pyrazolone ring allows one to consider these fragments as virtually planar (the maximum values of the torsion angle are as follows: 10° for C(13)—C(12)—N(3)—H(3n) in the structure of **1** and 6.3° for C(13)—C(14)—C(15)—O(4) in the structure of **2**).

The angle between the C(1)—C(2)—C(3) and C(12)—N(3)—H planes in **1** is 61.8°, which indicates that conjugation between the pyrazolone ring and the amide fragment is virtually absent. The corresponding angle in the structure of **2** is 41.3°.

The angles between the planes of the benzene and pyrazolone rings are 39.9° (**1**) and 34.9° (**2**) (for antipyrine, this parameter is 52.1°),⁹ which hinders the appearance of strong conjugation between these rings. This is also evidenced by the values of the N(1)—C(6) (**1**) and N(1)—C(4) (**2**) bonds (1.43(2) and 1.428(2) Å, respectively), which are close to the standard values for

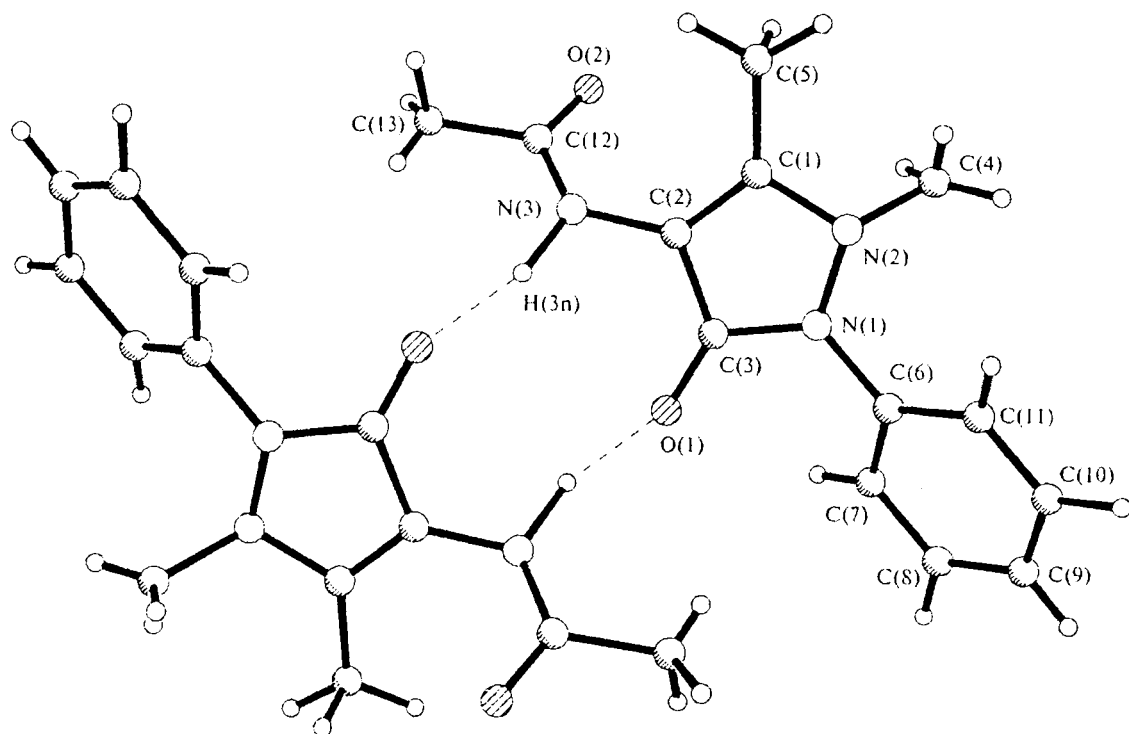


Fig. 1. Structure of compound 1.

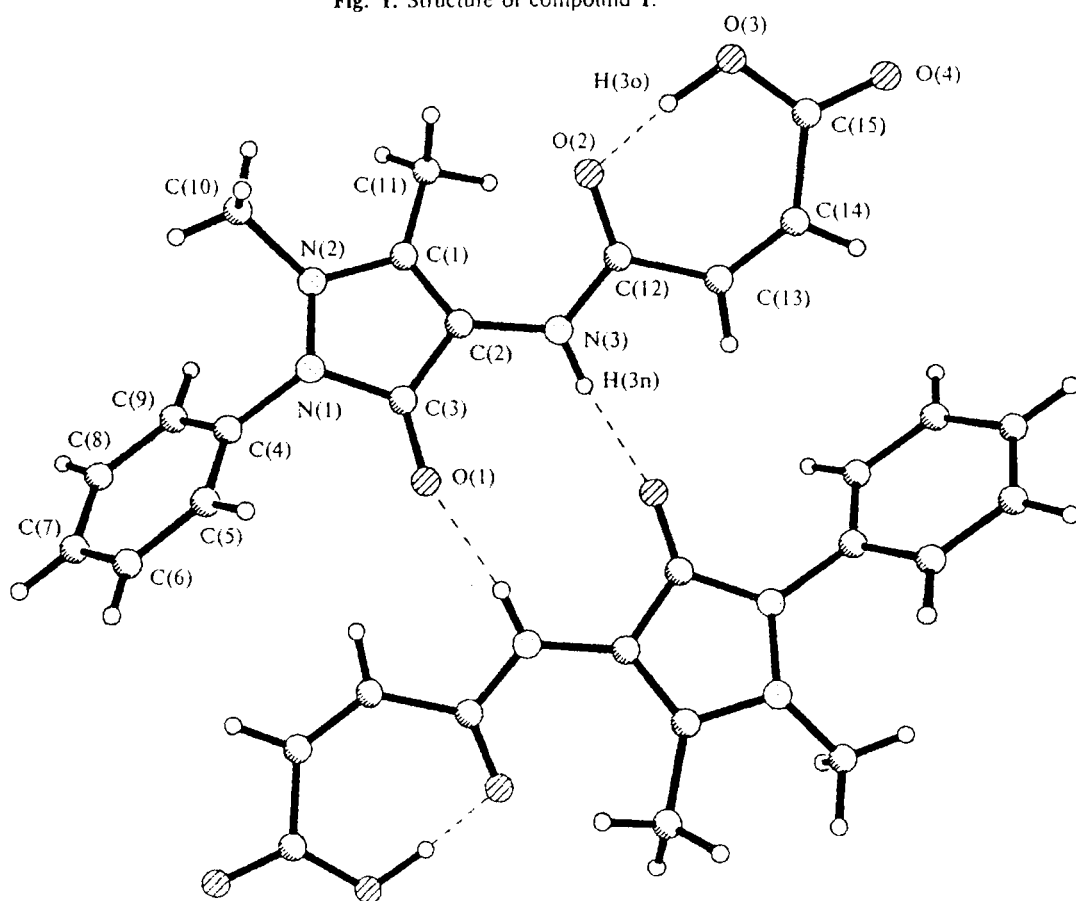


Fig. 2. Structure of compound 2.

C_{Ar}–N_{sp3} bonds (1.42 Å).¹¹ The pyrazolone rings are nearly planar. The torsion angles in these rings are no

Table 3. Atomic coordinates ($\times 10^4$) and equivalent thermal parameters ($U_{eq} \cdot 10^3/\text{\AA}^2$) in the structure of **2**

Atom	x	y	z	U_{eq}
O(1)	1758(2)	5302(2)	5620(1)	56(1)
O(2)	2955(2)	4770(2)	1378(2)	65(1)
O(3)	3348(2)	3339(2)	–244(2)	75(1)
O(4)	1935(2)	2078(2)	–717(2)	75(1)
N(1)	2879(2)	7283(2)	4471(1)	47(1)
N(2)	2921(2)	8189(2)	3167(1)	49(1)
N(3)	1129(2)	5346(2)	3018(2)	46(1)
C(1)	2345(2)	7518(2)	2469(2)	45(1)
C(2)	1884(2)	6299(2)	3290(2)	43(1)
C(3)	2149(2)	6155(2)	4585(2)	44(1)
C(4)	2785(3)	8042(3)	5422(2)	46(1)
C(5)	3312(3)	7040(3)	6674(2)	56(1)
C(6)	3155(3)	7790(4)	7603(2)	66(1)
C(7)	2538(3)	9493(4)	7289(3)	70(1)
C(8)	2066(3)	10464(4)	6036(3)	67(1)
C(9)	2153(3)	9759(3)	5098(2)	55(1)
C(10)	4509(3)	8546(4)	2771(2)	61(1)
C(11)	2228(4)	8227(4)	1041(2)	61(1)
C(12)	1698(3)	4630(2)	2088(2)	46(1)
C(13)	709(3)	3694(2)	1967(2)	49(1)
C(14)	917(3)	2917(3)	1107(2)	52(1)
C(15)	2125(3)	2747(2)	–16(2)	53(1)

Table 4. Bond lengths (d) in the structure of **1**

Bond	$d/\text{\AA}$	Bond	$d/\text{\AA}$
O(1)–C(3)	1.23(2)	C(1)–C(5)	1.49(3)
O(2)–C(12)	1.22(2)	C(2)–C(3)	1.45(2)
N(1)–C(3)	1.38(2)	C(6)–C(7)	1.37(2)
N(1)–N(2)	1.40(1)	C(6)–C(11)	1.39(2)
N(1)–C(6)	1.43(2)	C(7)–C(8)	1.38(3)
N(2)–C(1)	1.38(2)	C(8)–C(9)	1.37(3)
N(2)–C(4)	1.45(2)	C(9)–C(10)	1.37(3)
N(3)–C(12)	1.34(2)	C(10)–C(11)	1.35(2)
N(3)–C(2)	1.41(1)	C(12)–C(13)	1.50(3)
C(1)–C(2)	1.33(2)		

Table 5. Bond angles (ω) in the structure of **1**

Angle	ω/deg	Angle	ω/deg
C(3)–N(1)–N(2)	110.5(8)	O(1)–C(3)–C(2)	130(1)
C(3)–N(1)–C(6)	126(1)	N(1)–C(3)–C(2)	104(1)
N(2)–N(1)–C(6)	119.7(8)	C(7)–C(6)–C(11)	119(2)
C(1)–N(2)–N(1)	105.1(8)	C(7)–C(6)–N(1)	119(2)
C(1)–N(2)–C(4)	118(1)	C(11)–C(6)–N(1)	122(2)
N(1)–N(2)–C(4)	115(1)	C(6)–C(7)–C(8)	121(2)
C(12)–N(3)–C(2)	121(1)	C(7)–C(8)–C(9)	118(2)
C(2)–C(1)–N(2)	111(1)	C(10)–C(9)–C(8)	122(2)
C(2)–C(1)–C(5)	128(2)	C(11)–C(10)–C(9)	120(2)
N(2)–C(1)–C(5)	121(2)	C(10)–C(11)–C(6)	121(2)
C(1)–C(2)–N(3)	129(1)	O(2)–C(12)–N(3)	126(1)
C(1)–C(2)–C(3)	108(1)	O(2)–C(12)–C(13)	117(2)
N(3)–C(2)–C(3)	123(1)	N(3)–C(12)–C(13)	117(2)
O(1)–C(3)–N(1)	126(1)		

greater than 8° and 5° in **1** and **2**, respectively, the maximum deviations from the plane of the ring being observed for the N(1) atom. The carbonyl oxygen atom and the methyl group at position 3 lie nearly in the plane of the pyrazolone ring. On the contrary, the carbon atoms of the methyl groups attached to the N(2) atom deviate from the plane by 0.84–0.85 Å in both structures, which is attributable to steric interactions between the methyl group and the phenyl ring. Therefore, the nitrogen atoms have a pyramidal configuration, the phenyl and methyl substituents being located on opposite sides with respect to the pyrazolone ring. The environment about the N(1) atom is substantially more flattened than that about the N(2) atom. The C(4)–N(2)–N(1)–C(6) and C(10)–N(2)–N(1)–C(4) torsion angles, which characterize the mutual arrangement of the phenyl and methyl substituents in compounds **1** and **2**, are 61.0° and –65.5°, respectively.

The bond lengths in the pyrazolone rings in two structures are in close agreement. Their values are indicative of a certain degree of delocalization of the electron density in the rings. The bond lengths in the

Table 6. Bond lengths (d) in the structure of **2**

Bond	$d/\text{\AA}$	Bond	$d/\text{\AA}$
O(1)–C(3)	1.239(2)	C(1)–C(11)	1.484(3)
O(2)–C(12)	1.241(2)	C(2)–C(3)	1.427(3)
O(3)–C(15)	1.308(3)	C(4)–C(5)	1.383(3)
O(4)–C(15)	1.207(2)	C(4)–C(9)	1.385(3)
N(1)–C(3)	1.384(2)	C(5)–C(6)	1.388(3)
N(1)–N(2)	1.402(2)	C(6)–C(7)	1.374(4)
N(1)–C(4)	1.428(2)	C(7)–C(8)	1.371(4)
N(2)–C(1)	1.378(2)	C(8)–C(9)	1.381(3)
N(2)–C(10)	1.469(3)	C(12)–C(13)	1.473(3)
N(3)–C(12)	1.336(2)	C(13)–C(14)	1.329(3)
N(3)–C(2)	1.406(2)	C(14)–C(15)	1.490(3)
C(1)–C(2)	1.352(3)		

Table 7. Bond angles (ω) in the structure of **2**

Angle	ω/deg	Angle	ω/deg
C(3)–N(1)–N(2)	109.5(1)	C(5)–C(4)–C(9)	120.5(2)
C(3)–N(1)–C(4)	125.4(1)	C(5)–C(4)–N(1)	119.1(2)
N(2)–N(1)–C(4)	118.5(2)	C(9)–C(4)–N(1)	120.3(2)
C(1)–N(2)–N(1)	106.9(1)	C(4)–C(5)–C(6)	118.8(2)
C(1)–N(2)–C(10)	120.5(2)	C(7)–C(6)–C(5)	121.1(2)
N(1)–N(2)–C(10)	115.1(2)	C(8)–C(7)–C(6)	119.3(2)
C(12)–N(3)–C(2)	124.0(2)	C(7)–C(8)–C(9)	121.0(3)
C(2)–C(1)–N(2)	109.2(2)	C(8)–C(9)–C(4)	119.3(2)
C(2)–C(1)–C(11)	131.0(2)	O(2)–C(12)–N(3)	121.8(2)
N(2)–C(1)–C(11)	119.8(2)	O(2)–C(12)–C(13)	123.3(2)
C(1)–C(2)–N(3)	129.2(2)	C(3)–C(12)–C(13)	114.9(2)
C(1)–C(2)–C(3)	109.2(2)	C(14)–C(13)–C(12)	128.6(2)
N(3)–C(2)–C(3)	121.4(2)	C(13)–C(14)–C(15)	132.5(2)
O(1)–C(3)–N(1)	124.9(2)	O(4)–C(15)–O(3)	120.9(2)
O(1)–C(3)–C(2)	130.1(2)	O(4)–C(15)–C(14)	118.8(2)
N(1)–C(3)–C(2)	105.0(2)	O(3)–C(15)–C(14)	120.3(2)

fragment of maleic acid and in the phenyl rings have standard values.

IR spectral studies provided additional data on the structures of the compounds under consideration. In the IR spectra of compounds **1** and **2**, groups of C=O stretching modes in the 1600–1800 cm⁻¹ region and NH and OH stretching modes in the 3100–3600 cm⁻¹ region are most characteristic.

The spectrum of **1** has four intense absorption bands in the former region (Table 8). The assignment of these bands was made taking into account the positions and intensities of analogous bands in the spectra of other derivatives of pyrazol-5-one and aromatic amides.^{3,4} Based on these data, the absorption band at 1653 cm⁻¹ in the spectrum of **1** was assigned to ν C=O of the pyrazolone ring.

Quantum-chemical calculations of normal modes of fragments of the amidopyrine molecule¹² demonstrated that the above-mentioned vibration in derivatives of pyrazol-5-one is not characteristic. The contribution of the C=O bond stretch to this vibration is only ~50%. The C–C and C=C bond stretches of the heterocycle also make substantial contributions to the above-mentioned vibration. Therefore, this frequency in derivatives of pyrazol-5-one corresponds to vibration of the C=C–C=O group, unlike nonaromatic amides in which this frequency corresponds to vibration of the –N–C=O fragment.

The bands at 1614 and 1591 cm⁻¹ are assigned to vibrations of the pyrazolone and phenyl rings, respectively. The band at 1684 cm⁻¹ belongs to ν CO of the amide group (amide I vibration). The higher ν CO fre-

quency of the amide group compared to ν CO of the pyrazolone ring is consistent with the data of X-ray diffraction analysis, according to which the C=O bond in the pyrazolone ring is somewhat longer, which leads to a decrease in its vibration frequency.

The frequency of the band at 1723 cm⁻¹ is too high to be a vibration of the amide group or aromatic rings. Apparently, this band belongs to an overtone of a low-frequency vibration enhanced due to Fermi resonance with the amide I band.

The IR spectrum of compound **1** in the crystalline state has a broad band with the maximum at 3195 cm⁻¹, which is assigned to NH vibrations of the amide group. The low-frequency shift of this band compared to that of the free amino group (about 3500 cm⁻¹) is due to an intermolecular NH...O=C hydrogen bond. The presence of the latter was confirmed by X-ray diffraction analysis.

The IR spectrum of crystalline compound **2** in the ν C=O region is simpler than that of compound **1** in spite of the fact that compound **2** contains an additional carboxyl group. The spectrum of **2** has only two absorption bands (at 1717 and 1645 cm⁻¹, see Table 8), though the latter band is broadened. The band at 1717 cm⁻¹ is assigned to ν C=O of the carboxyl group, whose frequency is somewhat lower due to conjugation with the C=C bond as well as to the involvement of the COOH group in the intramolecular hydrogen bond.

The ν C=O vibrations of the pyrazolone ring and vibrations of the amide group in **2** have, apparently, close frequencies, their absorption bands overlap, and both vibrations contribute to the band observed at 1645 cm⁻¹, as a result of which the latter has a complex contour. The lower value of ν C=O of the pyrazolone ring in **2** compared to that in **1** is due to the involvement of this group in the intramolecular hydrogen bond. The closeness of the frequencies is also consistent with the closeness of the C(3)–O(1) and C(12)–O(2) bond lengths (1.239(2) and 1.241(2) Å, respectively).

The ν NH bands in the spectra of **2** and **1** have close frequencies and are similar in contour, which is indicative of the identical character of the intermolecular hydrogen bonds formed with the participation of the amide groups. The ν OH vibration is observed in the 2800–3100 cm⁻¹ region as a broad band which overlaps with ν CH stretching absorption bands. The low frequency and the large width of the ν OH absorption band are indicative of the presence of a hydrogen bond between the carboxyl group and the carbonyl oxygen atom. Therefore, the spectral and X-ray diffraction data on hydrogen bonding in the crystals of **1** and **2** correlate.

With the aim of modeling the process of complexation, we examined the spectra of **1** and **2** and their protonated forms in acetonitrile solutions. We chose this solvent, which is "inconvenient" for IR spectral studies, because the compounds under consideration are very poorly soluble in aromatic solvents, chloromethanes, and saturated hydrocarbons. The ν C=O region of the IR spectrum of a solution of compound **1** in acetonitrile has

Table 8. Selected vibration frequencies in the IR spectra of compounds **1** and **2**

Assignment	1		2	
	Crystal	Solution	Crystal	Solution
		A B		A B
ν (NH)	3195	3350	3213	
ν (OH) + ν (CH)			2800–3100	
ν (OH) + ν (NH)		3240		3250
?		1755 1755		
?		1725 1725		
ν (CO) _{COOH}			1717	1725 1742
ν (CO) _{amide}	1723	–		
ν (CO) _{amide}	1684	1695		1698
ν (CO) _{pyr} + + ν (CO) _{amide}		1677	1645	1678
ν (CO) _{pyr}	1653	1632		1633
ν (C=C) + + ν (CO) _{pyr}	1614	1624		1610
ν (C=C)	1591		1593	1595

Note. A, in CH₃CN, B, in CH₃CN + HCl.

four absorption bands. Taking into account the spectrum of compound **1** in the solid state, we assigned the bands at 1632 and 1677 cm^{-1} to $\nu\text{C}=\text{O}$ of the pyrazolone ring and to vibrations of the amide group, respectively. The frequencies of the bands at 1725 and 1755 cm^{-1} are too high to be νCO vibrations in amides. Hence, the assignment of these bands presented a serious problem. The elucidation of the nature of these bands calls for special studies. Taking into account their low intensities, it can be suggested that these bands belong to overtones or to combination tones.

The spectrum of a solution of **1** has a νNH broad band with the maximum at 3350 cm^{-1} , which is indicative of hydrogen bonding. The increase in the νNH frequency compared to that observed in the crystalline sample is due to the cleavage of intermolecular hydrogen bonds between the $\text{C}=\text{O}$ groups of the pyrazolone rings and the NH groups and to the formation of intramolecular hydrogen bonds between these groups.

When a solution of **1** was saturated with gaseous HCl , the band at 1677 cm^{-1} disappeared (Fig. 3) and a new band at 1695 cm^{-1} appeared. The band at 1632 cm^{-1} was shifted to 1624 cm^{-1} . The observed changes in the spectrum are consistent with protonation at the carbonyl O atom of the pyrazolone ring. Protonation results in a decrease in the νCO frequency of the pyrazolone ring and

in an increase in the νCO vibration frequency of the nonprotonated amide group. The vibration bands at 1755 and 1725 cm^{-1} remain unchanged upon protonation. This fact confirms the above suggestion that these bands do not belong to vibrations of amide groups.

Protonation leads to a change in the character of hydrogen bonding in the system. This results in a change in the spectrum in the 3000–3400 cm^{-1} region. Thus, the νNH band is shifted from 3350 cm^{-1} to 3240 cm^{-1} , which is accompanied by its substantial broadening. In the protonated form, the COH and NH groups can form bonds with the oxygen atom of the amide fragment of the molecule. In addition, a stretching band of the OH group involved in hydrogen bonding should be observed in this region of the spectrum.

The IR spectrum of an acetonitrile solution of **2**, unlike the spectrum of the crystalline sample, has four absorption bands in the 1600–1800 cm^{-1} region. Two low-frequency bands (1633 and 1610 cm^{-1}) are assigned, by analogy with the spectra of the crystalline sample, to mixed vibrations of the $\text{C}=\text{C}$ and $\text{C}=\text{O}$ bonds of the pyrazolone ring. The bands at 1725 and 1678 cm^{-1} are assigned to the $\nu\text{C}=\text{O}$ vibration of the carboxyl group and to the $\nu\text{C}=\text{O}$ vibration of the amide group, respectively. The frequency of the latter band is higher than that observed in the spectrum in the crystalline state and is associated with cleavage of the hydrogen bonds with the participation of the COOH group.

Noticeable changes are observed in the 1500–1800 cm^{-1} region of the IR spectrum of an acetonitrile solution of compound **2** saturated with gaseous HCl . The intensity of the νCO band of the COOH group is increased substantially and this band is shifted to 1742 cm^{-1} . Two low-frequency bands disappear upon protonation. Taking into account that these bands belong to vibrations with the participation of the $\text{C}=\text{O}$ group of the pyrazolone ring, their disappearance is indicative of protonation at the carbonyl group of the heterocycle. The intensity of the amide band decreases and the band is broadened and shifted to 1698 cm^{-1} .

The electronic absorption spectra of compounds **1** and **2** were measured in aqueous and acetonitrile solutions. The spectra of acetonitrile solutions are similar to those of nonsubstituted and 4-alkyl-substituted anti-pyridines.³ A long-wavelength absorption band for compounds **1** and **2** is observed in the region of 250–280 nm (**1**: 257 nm, $\epsilon = 11000$ in H_2O and 278 nm, $\epsilon = 11100$ in CH_3CN ; **2**: 252 nm, $\epsilon = 11600$ in H_2O and 272 nm, $\epsilon = 11160$ in CH_3CN). When solutions were saturated with gaseous HCl , the intensity of the long-wavelength band decreased and this band disappeared at a concentration of hydrogen ions of $\sim 1 \text{ mol L}^{-1}$ in an aqueous solution and a concentration of $10^{-2} \text{ mol L}^{-1}$ in an acetonitrile solution. Therefore, protonation of the above-mentioned compounds proceeds substantially more readily in nonaqueous than in aqueous solvents.

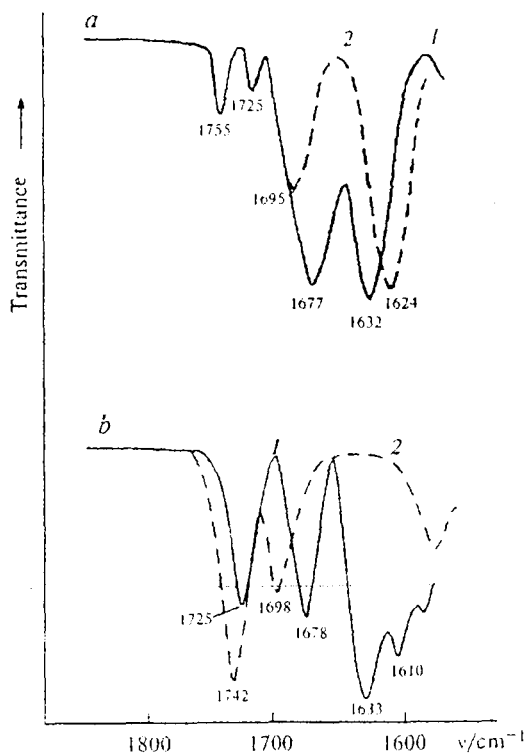


Fig. 3. IR spectra of acetonitrile solutions of compounds **1** (a) and **2** (b) in the absence of HCl (1) and in the presence of HCl (2).

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References

1. *Diantipirilmetan i ego gomologi kak analiticheskie reagenty* [Diantipyrylmethane and Its Homologs as Analytical Reagents], Ed. S. I. Gusev, Izd-vo Permskogo Univ., Perm', 1974 (in Russian).
2. N. V. Trofimov, N. A. Kanayev, and A. I. Busev, *Zh. Obshch. Khim.*, 1975, **45**, 385 [*J. Gen. Chem. USSR*, 1975, **45** (Engl. Transl.)].
3. Yu. N. Medvedev, B. E. Zaitsev, M. L. Kuznetsov, B. V. Lokshin, and F. M. Spiridonov, *Zh. Neorg. Khim.*, 1993, **38**, 1832 [*Russ. J. Inorg. Chem.*, 1993, **38** (Engl. Transl.)].
4. Yu. N. Medvedev, M. L. Kuznetsov, B. E. Zaitsev, B. V. Lokshin, and F. M. Spiridonov, *Zh. Neorg. Khim.*, 1994, **39**, 1505 [*Russ. J. Inorg. Chem.*, 1994, **39** (Engl. Transl.)].
5. M. L. Kuznetsov, Yu. N. Medvedev, B. E. Zaitsev, B. V. Lokshin, and F. M. Spiridonov, *Zh. Neorg. Khim.*, 1995, **40**, 259 [*Russ. J. Inorg. Chem.*, 1995, **40** (Engl. Transl.)].
6. M. L. Kuznetsov, Yu. N. Medvedev, and F. M. Spiridonov, *Koord. Khim.*, 1996, **22**, 225 [*Russ. J. Coord. Chem.*, 1996, **22** (Engl. Transl.)].
7. M. L. Kuznetsov, Yu. N. Medvedev, V. K. Bel'skii, A. I. Dement'ev, and B. E. Zaitsev, *Zh. Neorg. Khim.*, 1997, **42**, 1114 [*Russ. J. Inorg. Chem.*, 1997, **42** (Engl. Transl.)].
8. G. M. Sheldrick, *SHELXL-97, User's Manual*, Göttingen, 1997.
9. T. P. Singh and M. Vijayan, *Acta Cryst.*, 1973, **29B**, 714.
10. T. P. Singh and M. Vijayan, *Acta Cryst.*, 1976, **32B**, 2432.
11. F. H. Allen, O. Kennard, D. G. Watson, C. Bramer, A. G. Orpen, and R. J. Taylor, *Chem. Soc., Perkin Trans. 2*, 1987, S1.
12. M. L. Kuznetsov, A. I. Dement'ev, and S. V. Krasno-shchiokov, *J. Molec. Struct.*, THEOCHEM, 1998, **453**, 17.

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