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Crystal and Molecular Structure of Pyrazol-3-one Derivatives. II.[1] 5-Amino-2,4-dihydro-2-phenyl-3*H*-pyrazol-3-one

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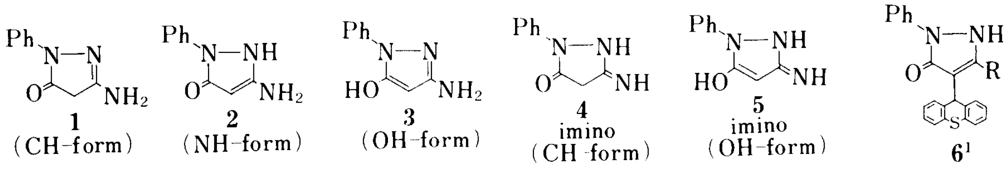
The molecular and crystal structure of 5-amino-2,4-dihydro-2-phenyl-3*H*-pyrazol-3-one was examined by the X-ray diffraction method to establish the predominant tautomeric form (the CH-form) due to the pyrazol-3-one ring. In the crystal, the molecules are linked by the intermolecular hydrogen bond between the NH_2 and $C=O$ groups to form four hydrogen bonds with three adjacent molecules. The title compound, $C_9H_9N_3O$ crystallizes in space group $P2_1/a$ with lattice parameters $a=10.187$ (5), $b=11.481$ (4), $c=7.392$ (4) Å, $\beta=102.43$ (5)°, and $Z=4$.

Keywords——X-ray analysis; crystal structure; tautomerism; MULTAN 78; 5-amino-2,4-dihydro-2-phenyl-3*H*-pyrazol-3-one

Some of the pyrazol-3-ones have important uses in medicine as analgesics and antipyretics and in color photography as magenta dye-formers.[2] The relative abundance of the various tautomeric forms[3-6] of 2,5-disubstituted pyrazol-3-ones has been the subject of much work since Konn's synthesis[8] of the first example of this class. In a course of studying the reactivity[7] of 5-amino- and 5-methyl-2-phenylpyrazol-3-one with various possible tautomeric forms (CH-, OH-, and NH-form), we previously reported that these pyrazol-3-ones underwent dehydration at the 4-position active methylene of the pyrazol-3-one ring with the OH group of xanthen-9-ol or thioxanthen-9-ol to give condensed products (**6**).[1] In the case of 5-amino-2-phenylpyrazol-3-one, the five possible tautomeric forms can be written as shown in Fig. 1; these are the CH-, OH-, NH-, imino CH-, and imino OH-form.

The method nuclear magnetic resonance (NMR) spectroscopy[4] for 5-amino-2-phenylpyrazol-3-one showed that the CH-form (**1**) was predominant in solvents of widely different polarities such as CCl_4, $CDCl_3$, and dimethyl sulfoxiside (DMSO). However, the imino CH-form (**4**) cannot be completely eliminated on NMR evidence alone because the NH signal (intensity 2H) is observed in $CDCl_3$ which could result from exchanging the two sites of NH in the form **4**. In the solid state, additional factors for the tautomeric forms are likely, owing to the possibility of strong hydrogen bonding. The infrared (IR) spectrum[4] of **1** (KBr) is remarkably simple in the 1500—1600 cm^{-1} region, comprising two phenyl ring vibrations. The position of the CO band (1685 cm^{-1}) indicates that it is connected by the hydrogen bond,



1 (CH-form) 2 (NH-form) 3 (OH-form) 4 imino (CH-form) 5 imino (OH-form) 6[1]

Ph = ⌬, R = CH_3, NH_2

Fig. 1

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and the three distinct peaks above 3200 cm^{-1} are assigned in order of decreasing frequency to the asymmetric, symmetric, and hydrogen-bonded NH_2 stretching vibrations.[4] These features of the IR spectrum of **1** seem to rule out the contribution of the imino forms (**4** and **5**) to the tautomeric equilibrium in the solid state. The IR spectrum of **1** is also consistent with polymeric association through the intermolecular hydrogen bonding and is markedly different from those normally observed[3-5] for pyrazol-3-ones in the solid state.

The purpose of the present work was to determine the preferred tautomeric form of 5-amino-2-phenylpyrazol-3-one in the solid state by the X-ray diffraction method, and to compare the result with the structures of the two crystallographically independent molecules of 5-methyl-2-phenyl-pyrazol-3-one that exist in a unit cell in different tautomeric forms (the NH- and OH-form).[9]

Crystal Structure Determination of 1——A crystal of **1**, $C_9H_9N_3O$ (fw 175.21), having dimensions of 0.20 × 0.25 × 0.20 mm was selected for investigation. Systematic absences were unique for the monoclinic space group $P2_1/a$. Crystal data: $a=10.187$ (5), $b=11.481$ (4), $c=7.392$ (4) Å, $\beta=102.43$ (5)°, $Z=4$, volume $=844.3$ $Å^3$, $Dc=1.38$ gcm^{-3}, and $\mu=7.37$ cm^{-1}. Intensity data were collected at room temperature on a Rigaku four-circle diffractometer using Ni-filtered Cu$K\alpha$ radiation by the ω–2θ scan mode. A total of 1529 unique reflections were measured in the range of $2\theta<120°$; 1178 reflections had intensities greater than 3σ (I). Lorentz and polarization corrections were applied, but no absorption corrections were made. The structure was solved by direct methods using MULTAN 78[10] to calculate phase for the $200|E|$ values greater than 1.36. Refinement[11] of nonhydrogen atoms with anisotropic temperature factors and hydrogen atoms with isotropic temperature factors was terminated at a conventional R of 0.066 and a weighted $Rw=0.073$ $(Rw=(\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2)^{1/2})$.

TABLE I. Final Atomic Coordinates and Equivalent Thermal Parameters for Non-H Atoms (× 10^3) and Isotropic Thermal Parameters ($Å^2$) for H Atoms with e.s.d.'s in parentheses

Atom	x	y	z	$B_{eq.}$ or B
N1	1.0343 (3)	0.3095 (3)	0.7100 (5)	4.6
N2	0.9682 (3)	0.4199 (3)	0.7066 (5)	4.2
C3	0.8328 (4)	0.4132 (4)	0.6371 (6)	4.3
C4	0.8063 (4)	0.2878 (4)	0.5793 (6)	4.2
C5	0.9430 (4)	0.2358 (4)	0.6388 (6)	4.7
O6	0.7508 (3)	0.4918 (3)	0.6244 (4)	6.1
N7	0.9668 (3)	0.1213 (3)	0.6232 (4)	7.6
C8	1.0479 (4)	0.5168 (4)	0.7779 (5)	4.0
C9	1.1857 (4)	0.5005 (4)	0.8404 (6)	6.0
C10	1.2657 (5)	0.5943 (5)	0.9150 (7)	6.6
C11	1.2108 (5)	0.7032 (5)	0.9238 (7)	7.2
C12	1.0752 (5)	0.7187 (5)	0.8593 (7)	8.8
C13	0.9916 (5)	0.6265 (4)	0.7853 (7)	6.7
H1C4	0.777 (5)	0.282 (5)	0.428 (7)	3.5
H2C4	0.733 (5)	0.247 (4)	0.657 (7)	2.7
H1N7	0.910 (5)	0.081 (4)	0.561 (7)	3.1
H2N7	1.056 (5)	0.096 (4)	0.638 (7)	3.2
HC9	1.232 (5)	0.419 (4)	0.816 (7)	3.4
HC10	1.375 (5)	0.581 (5)	0.957 (7)	3.5
HC11	1.275 (5)	0.771 (5)	0.976 (8)	5.0
HC12	1.031 (6)	0.798 (5)	0.871 (8)	5.2
HC13	0.883 (5)	0.640 (5)	0.752 (7)	4.1

$B_{eq.}=\frac{1}{6}(B_{11}+B_{22}+B_{33})$

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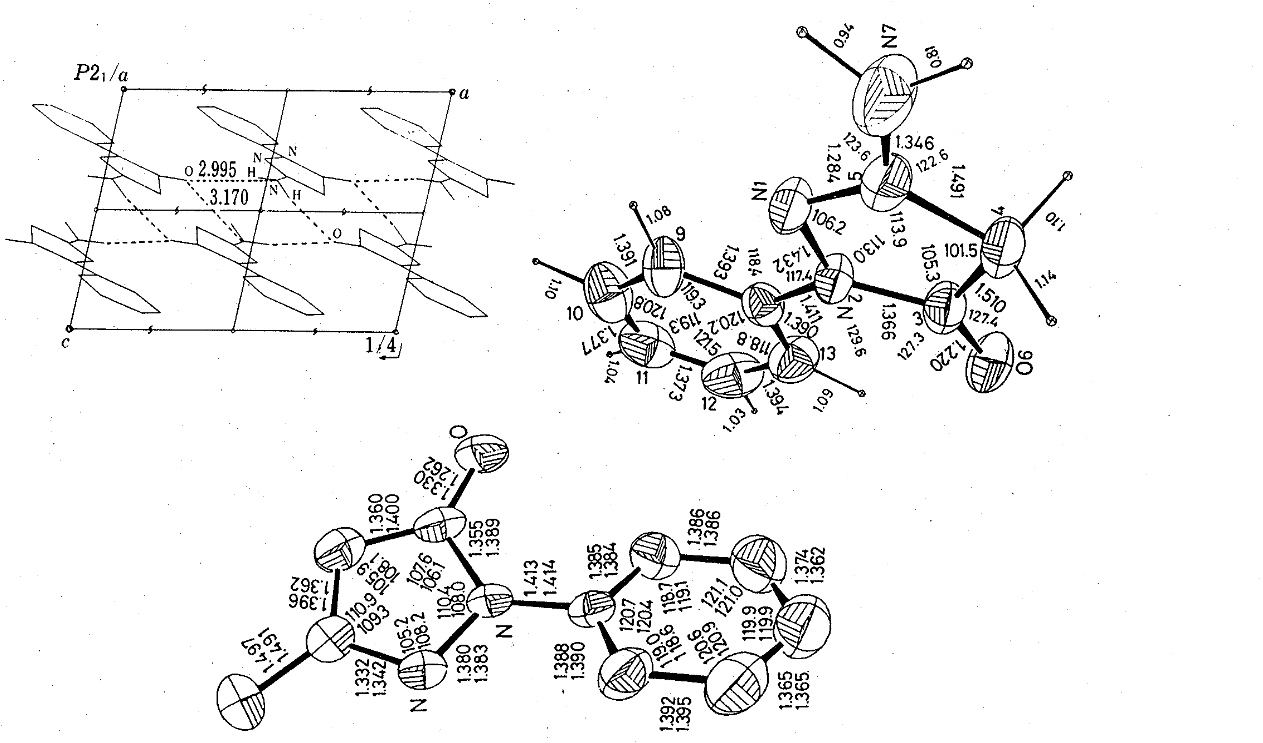

5-methyl-2-phenylpyrazol-3-one ··· $\begin{pmatrix}\text{OH-form}\\ \text{NH-form}\end{pmatrix}^{9}$

Fig. 2. Thermal Ellipsoids are Drawn at the 50% Probability Level

The e.s.d.'s of bond lengths and angles are 0.005—0.008 Å and 0.3—0.5° for **1**, respectively.

The final positional and thermal parameters are given in Table I. The atomic scattering factors for O, N and C were those of Cromer and Waber[12]; for H, the scattering factors of Stewart, Davidson, and Simpson[13] were used.

Results and Discussion

The predominant tautomeric form 5-amino-2-phenylpyrazol-3-one in the solid state now established by the X-ray analysis to exist in the CH-form (**1**). Figure 2 compares some significant bond distances and angles of **1** with those of 5-methyl-2-phenylpyrazol-3-one.[9] These two crystal packing arrangements are quite different, depending upon the intermolecular hydrogen bond due to the different tautomeric forms. In the case of 5-methyl-2-phenylpyrazol-3-one, it has been reported that there are two crystallographically independent forms (the NH- and OH-form) in the unit cells with hydrogen bond characterized by the HO···O (2.48 Å) and HN···N (2.80 Å) lengths. The molecular packing of molecules of **1**, however, are linked together by two kinds of hydrogen bond between the NH_2 and CO groups (2.955 and 3.170 Å) to form a network of hydrogen bonds spread along the ac-plane, as shown in Fig. 2. With regard to the bond lengths of the two compounds, the C–C or C–N bonds of the pyrazol-3-one ring reflect their tautomeric forms and are slightly shortened or elongated from the normal values. They also show the intermediate bond lengths resulting from some electron delocalization: the N–CN and N–CO bond lengths are 1.284 and 1.366 Å, respectively. A final point of particular interest is the dihedral angles between the planes of pyrazol-3-one and the phenyl ring; 1.7 ° for **1** which are compared with 23 and 38 ° for the NH- and OH-form of 5-methyl-2-phenylpyrazol-3-one, respectively.

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