X-RAY DIFFRACTION AND SPECTRAL STUDIES OF 1-PHENYL-3-METHYL-4-(2',4'-DIMETHYLPHENYLAZO)-PYRAZOLONE-5

L. G. Kuz'mina, L. P. Grigor'eva,
Yu. T. Struchkov, Z. I. Ezhkova,
B. E. Zaitsev, V. A. Zaitseva,
and P. P. Pron'kin

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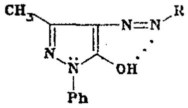
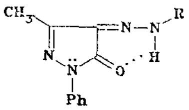
The molecular and crystal structures of 1-phenyl-3-methyl-4-(2',4'-dimethylphenylazo)pyrazolone-5 were determined. In the crystal the molecule exists as the hydrazone tautomer. The pyrazole ring is planar, and the substituents are practically coplanar with it. The molecule contains an intramolecular NH...O hydrogen bond that closes a practically planar six-membered ring (N...O, 2.77 (I), H...O 2.14 Å, angle at $H(N_{(4)})$ hydrogen 131°). The x-ray diffraction data agree with the spectral data and with the CNO calculation.

It should be expected that the characteristic features of the 1-phenyl-3-methyl-4-(2',4'-dimethylphenylazo)pyrazolone-5 molecule (I) would be tautomerism, the formation of intramolecular hydrogen bonds (IMHB), and sensitivity of the π-components of the pyrazolone ring to intra- and intermolecular effects and to the spatial disposition of the phenyl nuclei. Compound I can exist as the tautomers Ia-d; tautomers Ia,b should be stabilized by IMHB.


Ia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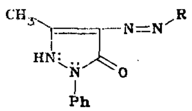
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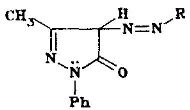
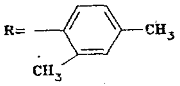

Id



From an analysis of the spectral data for 1-phenyl-3-methyl-4-phenylazopyrazolone-5 (II) [1-5], which is close to I in structure, it was concluded that II exists predominantly as tautomer Ib. The present communication is devoted to establishing the structure of I by x-ray diffraction analysis and to a study of its spectral properties.

IR Absorption Spectra. To determine the type of tautomer, characteristic carbonyl, amino, and hydroxy vibrations were used. The spectra of I in the crystalline state and in solution show the carbonyl valence vibration band, $\nu_{C=O}$, and a diffuse NH bond vibration band, ν_{NH} (Table 1). Assignment of the $\nu_{C=O}$ band to one of the Ia-d tautomers was based on the location of the absorption maximum and the integrated intensity $A_{C=O}$ of this band. In the spectrum of 1-phenyl-3-methyl-4-hydropyrazolone-5 (Table 1), which has a pyrazolone ring structure analogous to tautomer Id, the $\nu_{C=O}$ value is 60 cm^{-1} greater than that in the spectrum of I. Moreover the $A_{C=O}$ values of these compounds differ by 4-5 fold (Table 1). Consequently the observed $\nu_{C=O}$ and $A_{C=O}$ values in the IR spectrum of I in the crystalline state and in solution are evidence that isomer Id is practically absent.

The $\nu_{C=O}$ value in the spectrum of I corresponds to tautomers Ib and Ic. However the $A_{C=O}$ value, 1.0-1.4 units, in I agrees with the presence of Ib but contradicts the presence of Ic. This follows from the fact that for 1-phenyl-2,3-dimethylpyrazolone-5 (III) $A_{C=O}$ is 7.7 units [6], which is 5-7 times larger than in I (Table 1). Ic contains a pyrazolone ring, analogous to III. If we take into account that the substituent at the 4-position of the py-

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Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow 117813. Scientific-Research Institute for Organic Intermediates and Dyes, Moscow 103787. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 816-821, June, 1985. Original article submitted August 8, 1983; revision submitted April 26, 1984.

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TABLE 1. Frequencies and Integrated Intensities of C═O and NH Stretching Vibration Bands

Compound	$\nu_{(N-C=O)}$, cm^{-1}	$A_{(N-C=O)}$, 10^{-4} liter/mole · cm^2	ν_{NH}, cm^{-1}	Solvent
1-Phenyl-3-methyl-4-(2',4'-dimethylphenylazo)pyrazolone)5 (I)	1662	—	2900—3100	cryst.
	1660	0,92	2900—3100	CCl_4
	1655	1,42	2900—3100	$CHCl_3$
1-Phenyl-3-methyl-4-phenylazopyrazolone-5 (II)	1669	2,1	~3100	$CHCl_3$
	1667	1,8	~3100	CCl_4
1-Phenyl-2,3-dimethylpyrazolone-5 (III)	1688	7,7	—	$CHCl_3$
1-Phenyl-3-methyl-4-hydropyrazolone-5	1720	5,0	—	$CHCl_3$

razolone ring has essentially no effect on $A_{C=O}$, then for Ic the $A_{C=O}$ value ought to be close to that for III (Table 1). The assignment of $\nu_{C=O}$ in the I spectrum to the C═O vibrations of Ib also agrees with the presence of the broad NH stretching vibration band that is strongly shifted toward lower frequency. This shift is due to the formation of an IMHB of the NH...O═C type. This follows from the retention of band location and intensity in the IR spectrum of I as the sample is diluted with chloroform or carbon tetrachloride.

Thus from the IR spectra of I it follows that, like II, it exists predominantly as the lactam hydrazone tautomer Ib.

The two methyl groups in the azophenyl fragment of I affect its IR and electron absorption spectra. In the IR spectrum $A_{C=O}$ is 1.5-2 times smaller than in azopyrazolone II; in the electron spectrum λ_{max} of the long-wave band is shifted 11-18 nm toward the long-wave region as compared with λ_{max} of II. These data are evidence of the increase in coplanarity of the rings in going from II to its analog I.

Crystal and Molecular Structure. The structure was solved by the direct method and refined by the least-squares method, first in an isotropic, then in an anisotropic approximation. In a differential synthesis the benzene ring hydrogens and the hydrogen at $N_{(4)}$ were identified; the methyl hydrogens could not be localized. In subsequent calculations we used the phenyl hydrogen coordinates, calculated geometrically. A final refinement was performed by the least-squares method in an anisotropic approximation for nonhydrogen atoms, with fixed positional and temperature parameters for the hydrogen atoms (B_{iso} = 6 $Å^2$), up to R = 0.139 (R_G = 0.075). Table 2 shows the coordinates of the atoms.

Figure 1 shows molecular structure and gives bond lengths and valence angles. In the crystal the molecule exists as the Ib tautomer, as evidenced by both localization of the hydrogen atom at the azo $N_{(4)}$ and the bond lengths found for the pyrazolone fragment. The $N_{(2)}—C_{(3)}$ (1.30(1) Å) and $C_{(2)}—N_{(3)}$ (1.29(1) Å) bonds have increased multiplicity, which is incomplete agreement with the presence of Ib.

Moreover, the bonds under consideration are still longer than the standard C═N bond, which is 1.255 Å [7]. Along with the shortening of the remaining C—N, C—C, and N—N bonds in the azopyrazolone fragment in contrast to the standard values (1.452 [8], 1.50, and 1.46 Å [9], respectively), this indicates substantial delocalization of the π-electron density over the whole azopyrazolone fragment.

The pyrazolone ring is planar within 0.01(1) Å. The substituents are practically coplanar with it; the deviations of $O_{(1)}$, $N_{(3)}$, $N_{(4)}$, C_4 and $C_{(11)}$ from the heterocycle plane are -0.001 (6), 0.025(7), 0.052(8), -0.007(9), and -0.009(9) Å (Table 3).

A similar distribution of bond lengths is found in other molecules that contain a planar iminopyrazolone fragment, specifically 4-(4-N,N-diethylaminophenylimino)-3-methyl-1-phenyl-2-pyrazolin-5-one (IV) and 4-(2,6-dimethyl-4-N,N,diethylaminophenylimino)-3-methyl-1-phenyl-2-pyrazolin-5-one [10].

The $C_{(11)}-C_{(16)}$ and $C_{(21)}-C_{(26)}$ benzene rings are rotated out of the pyrazolone and the $C_{(21)}N_{(4)}N_{(3)}$ planes by 9.4 and 9.2° respectively. Here biphenyl type stresses arise in the molecule between the ortho-substituents (H or CH_3) of the Ph ring and the azopyrazolone part of the molecule; e.g., the intramolecular $H_{(16)}...O_{(1)}$ 2.24 Å, $C_{(16)}...O_{(1)}$ 3.00(1) Å. This is evidence of conjugation of the benzene rings with the central part of the molecule. A similar effect is observed in IV and V, where the rotation of the phenyl ring at $N_{(1)}$ out of the pyrazolone plane is 16 and 3.8°, respectively.

TABLE 2. Coordinates of the Atoms (× 10^4, for H × 10^3)*

Atom	x	y	z	Atom	x	y	z
$N_{(1)}$	10690 (8)	4397(4)	3048(9)	$C_{(22)}$	5774 (10)	5212(5)	−1779(12)
$N_{(2)}$	11217 (7)	5050(4)	3569(9)	$C_{(23)}$	4834 (10)	5592(6)	−2688(11)
$N_{(3)}$	8546 (8)	5602(4)	1158(9)	$C_{(24)}$	4703 (10)	6343(6)	−2507(13)
$N_{(4)}$	7616 (8)	5255(3)	271(9)	$C_{(25)}$	5578 (11)	6683(5)	−1355(13)
$O_{(1)}$	8845 (6)	4046(3)	1398(8)	$C_{(26)}$	6536 (10)	6329(5)	−444(12)
$C_{(1)}$	9590 (10)	4499(4)	2096(13)	$C_{(27)}$	5851 (9)	4448(4)	−2099(12)
$C_{(2)}$	9441 (9)	5250(4)	1972(11)	$C_{(28)}$	3583 (11)	6731(5)	−3609(13)
$C_{(3)}$	10491 (9)	5547(5)	2934(11)	$H_{(4)}$	7585	4812	241
$C_{(4)}$	10765 (9)	6305(4)	3221(12)	$H_{(12)}$	12685	4318	5478
$C_{(11)}$	11354 (10)	3763(5)	3642(13)	$H_{(13)}$	13806	3211	6319
$C_{(12)}$	12377 (11)	3800(5)	4877(13)	$H_{(14)}$	13010	2075	5169
$C_{(13)}$	12945 (10)	3194(6)	5334(14)	$H_{(15)}$	11187	2017	2942
$C_{(14)}$	12520 (13)	2565(6)	4708(15)	$H_{(16)}$	10035	3108	1911
$C_{(15)}$	11491 (12)	2534(5)	3461(14)	$H_{(23)}$	4133	5313	−3616
$C_{(16)}$	10879 (9)	3121(5)	2898(14)	$H_{(25)}$	5526	7251	−1121
$C_{(21)}$	6624 (10)	5600(5)	−632(13)	$H_{(26)}$	7264	6615	467

*The table of temperature parameters can be obtained from the authors.

TABLE 3. Equations of Planes Ax + By + Cz − D = 0, of Fragments of Molecules, Deviations of Atoms from Plane, and Interplanar Angles

Plane	Atom	Deviation of atom from plane, Å	Atom	Deviation of atom from plane, Å
1	$0{,}5407x+0{,}0152y+(-0{,}8411)z-4{,}5511=0$			
	$C_{(1)}$	−0,0097 (102)	* deviation for atoms	
	$C_{(2)}$	0,0062 (92)	$N_{(3)}$	0,025 (7)
	$C_{(3)}$	0,000 (9)	$N_{(4)}$	0,052 (8)
			$O_{(1)}$	−0,001 (6)
	$N_{(2)}$	−0,0055 (72)	$C_{(4)}$	−0,007 (9)
	$N_{(1)}$	0,0096 (76)	$C_{(11)}$	−0,009 (9)
2	$0{,}5576x+0{,}0204y+(-0{,}8299)z-4{,}8026=0$			
	$C_{(2)}$	0	$C_{(1)}$	0,02 (1)
	$N_{(3)}$	0	* $C_{(3)}$	0,022 (9)
	$N_{(4)}$	0	$C_{(21)}$	0,000 (9)
3	$0{,}5576x+0{,}0205y+(-0{,}8299)z-4{,}8029=0$			
	$N_{(3)}$	0	* $C_{(2)}$	−0,000 (9)
	$N_{(4)}$	0		
	$C_{(21)}$	0		
4	$0{,}6359x+0{,}1417y+(-0{,}7587)z-6{,}6683=0$			
	$C_{(21)}$	−0,007 (10)		
	$C_{(22)}$	0,0006 (96)		
	$C_{(23)}$	0,0031 (99)		
	$C_{(24)}$	−0,0002 (105)		
	$C_{(25)}$	−0,006 (11)		
	$C_{(26)}$	0,0099 (96)		
5	$0{,}6553x+0{,}0900y+(-0{,}7500)z-6{,}7482=0$			
	$C_{(11)}$	0,0006 (100)		
	$C_{(12)}$	−0,0112 (106)		
	$C_{(13)}$	0,0178 (107)		
	$C_{(14)}$	−0,0130 (127)		
	$C_{(15)}$	0,0021 (117)		
	$C_{(16)}$	0,0036 (99)		

TABLE 3 (continued)

Planes	Interplanar angle, deg	Planes	Interplanar angle, deg	Planes	Interplanar angle, deg
1—2	1,20	2—3	0,03	3—4	9,23
1—4	10,24	2—4	9,23	3—5	8,27
1—5	9,43	2—5	8,27	4—5	3,20

TABLE 4. Energy Parameters (eV) of Tautomers Ia-c*.

Compound	E_π	E_σ	E_B	ΔH	M
Ia	40,75	76,20	116,95	196,49	2,76
Ib	40,37	76,25	116,62	195,92	4,04
Ic	39,87	76,21	116,08	195,38	3,64

*E_π, π-bonding energy; E_σ, σ-bonding energy; E_B, total bonding energy; H, atomization energy; M, solvation coefficient.

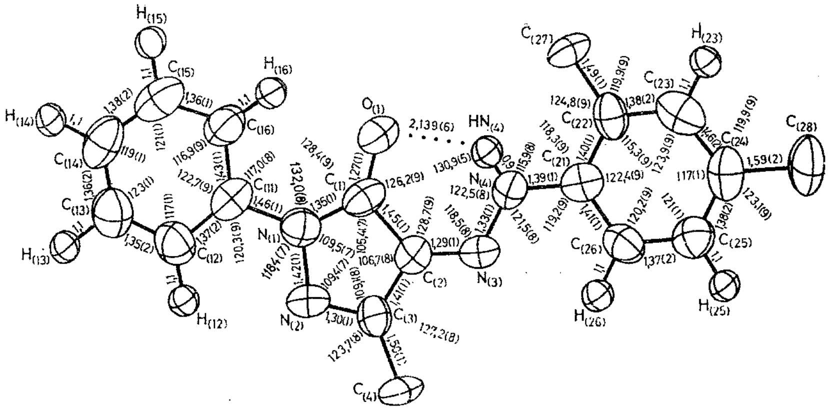

Fig. 1. Molecular Structure, bond lengths, and valence angles.

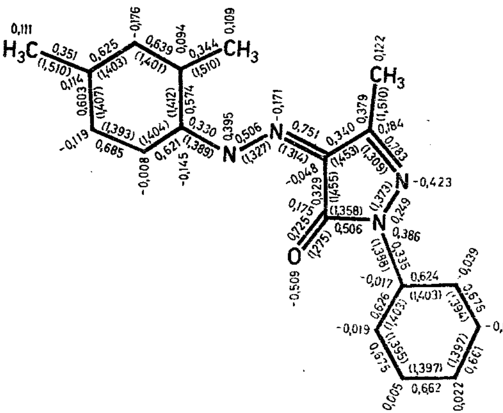

Fig. 2. Calculated bond lengths and π-charges on atoms in tautomer Ib.

There exists in the molecule a N–H...O IMHB that closes a practically planar six-membered ring. The N...O distance is 2.77(1) Å, the H...O is 2.14 Å, and the angle at the $H(N_{(4)})$ hydrogen is 131°.

Quantum Chemical Calculation. From the Pariser–Parr–Pople calculation for tautomer Ib with optimization of interatomic distances from the minimum of the heat of atomization [11], it follows that the bond lengths for I agree satisfactorily with the x-ray diffraction data. The largest deviation of calculated from experimental data for bond lengths in the pyrazolone ring and the azo group was obtained for the cyclic $N_{(1)}$-$N_{(2)}$ bond (0.005 Å). From the satisfactory agreement of bond lengths it may be presumed that the calculated bond orders and π-charges on the atoms in theory describe the π-electron structure of the molecule correctly.

From the heats of atomization, ΔH, it follows that in the gas state the most stable of tautomers Ia-Ic is Ia (Table 4). But in going from gas to condensed state and solutions, tautomer Ib ought to be the more stable, according to its solvation coefficient M. The distribution of π-charges over the atoms is shown in Fig. 2. Here the largest negative charge is centered on the carbonyl oxygen (-0.554), and the largest positive charge on $N_{(1)}$ (+0.506). As a result the molecule of compound I has a large π-dipole moment (μ_π = 7.2 D).

EXPERIMENTAL

The x-ray experiment was carried out on an automatic Hilger Watts diffractometer (1781 independent reflections with F^2 σ, λ_{Cu-K_α}, graphite monochromator, ω-scanning, θ_{max} 57°). Monoclinic crystals: a = 11.254(2), b = 19.199(2), c = 7.4762(5) Å, β = 98.21(1)°; V = 1598.9(6) Å^3, Z = 4, $C_{18}H_{18}N_4O$. Space group $P2_1/n$.

Calculations were carried out on an Eclipse 200/S computer by a modified EXTL program.* IR absorption spectra were recorded on a UR-20 spectrometer. Integrated intensities of absorption bands were measured by the Ramsey method [12].

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*Modifications by A. I. Yanovski and R. G. Gerr at the Institute of Heteroorganic Compounds, Academy of Sciences of the USSR.

STRUCTURE AND COLOR OF PROTONATED BENZIMIDAZOLYL FORMAZANS

A. I. Yalandina, E. G. Kovalev,
G. N. Lipunova, N. P. Bednyagina,
L. G. Egorova, and L. L. Popova

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Benzimidazolyl formazans were titrated spectrophotometrically and their base constants were determined. On the basis of quantum mechanical calculations of electron spectra a hypothesis concerning the chelate structure of the unsymmetrical benzimidazolyl formazans is proposed.

In a study of the photolysis of both sym- and unsym-benzimidazolyl formazans in the presence of tetrahalomethanes, the formation of intensely colored salts was observed [1]. Contrary to expectation, the unsymmetrical formazan hydrohalides obtained either photochemically or chemically are significantly more intensely colored (by 50-100 nm) in nonpolar solvents than the sym-formazan salts. The exceptions are the ortho-phenyl-substituted formazans (IIf, etc.), protonation of which is accompanied by a hypsochromic shift of the long-wave absorption band.

In order to determine the structure and interpret the chromaticity of the protonated forms, we studied the behavior of the sym- (Ia-d) and the unsym- (IIa-f) benzimidazolyl formazans in acid media. In solution the formazans exist as the open imino tautomers I and II [2].

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