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Synthesis, Structure, and Properties of a New Phosphorus-Containing Schiff's Base, a Derivative of Pyrazole-5-one

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Abstract—A new Schiff's base and its salt have been prepared from 2-aminophenyl(triphenyl)phosphonium chloride and 5-hydroxy-3-methyl-1-phenyl-4-formylpyrazole. The products structures have been proved by IR, ^{1}H NMR, and UV spectroscopy, mass spectrometry, X-ray diffraction analysis, and quantum-chemical modeling. Possible tautomerism and some properties of the products have been studied.

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Schiff's bases (also known as azomethines) have been subjects of intensive studies due to diverse biological activity [1] and high complex formation ability [2–7]. Numerous phosphorus-containing azomethines were described, for example, aminophosphines derivatives [8–17]. Azomethines based on pyrazole-5-one are also of interest [18–23], since pyrazolone fragment is a part of many drugs structures [24].

This work is aimed at the synthesis and the study of a new azomethine, product of 2-aminophenyl(triphenyl)phosphonium chloride and 5-hydroxy-3-methyl-1-phenyl-4-formylpyrazole condensation. Recently we have reported on preparation and study of azomethines based on the same amine and substituted salicylic aldehydes [25].

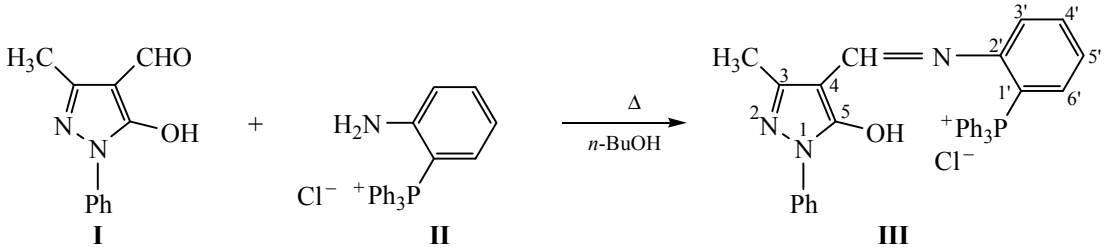
The Schiff's base was prepared according to Scheme 1.

It is known that azomethines based on pyrazole-5-one may exist in different tautomeric forms [18, 19]. Scheme 2 illustrates the most probable tautomeric forms of **III**.

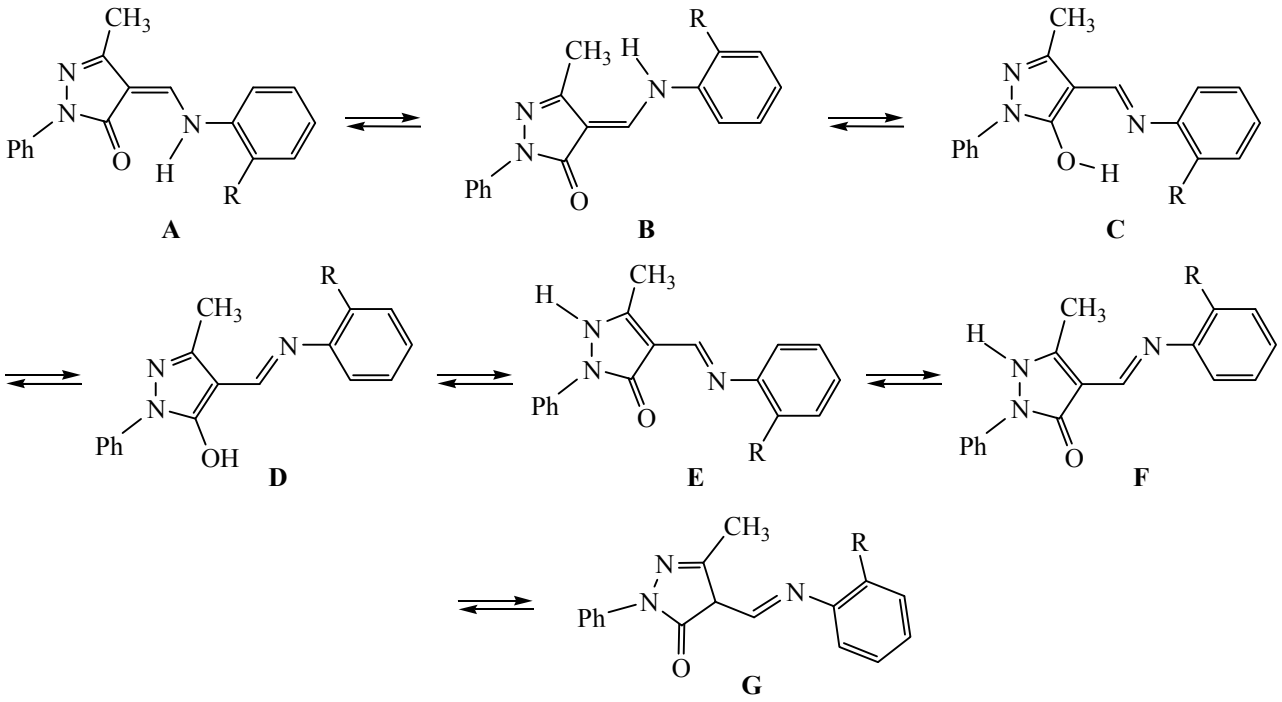
A-G Forms are in dynamic equilibrium, and its state is likely to be appreciably dependent on the nature of the R group containing positively charged phosphonium fragment.

To estimate the relative stability of the tautomers, we performed the quantum-chemical computation of the **III** isomers in the isolated ion approximation. The density functional approximation (DFT) was used, with the B3LYP functional in the 6-311G(d,p) basic

Scheme 1.



Scheme 2.



R = $P^+Ph_3Cl^-$.

set. Table 1 lists the model forms and the calculated total energies of their most stable conformations, as well as the relative stability (ΔE) in the gaseous phase and for the most stable isomers **A, C, E**, and **F** in dimethylsulfoxide DMSO medium.

According to the quantum-chemical simulation results, the most probable form of the prepared Schiff's base in the gaseous phase was its pyrazolone form (**A**), with the intramolecular hydrogen bond between the NH group proton and pyrazolone oxygen atom. In addition, the 5-hydroxypyrazole form **C**, also containing the intramolecular bond of the OH···N type, was relatively stable. When accounting for the medium influence, significant stabilization of **F** isomer and destabilization of B isomer were observed, the most stable isomer being still **A**.

In the ^{1}H NMR (DMSO-d_6) spectrum of **III** the aromatic protons signals were observed at 7.1–8.1 ppm, they were somehow broadened, possibly due to dynamic effects. The 4'-PhN proton signal was observed at 7.10 ppm as a triplet. The 3'-PhN and 5'-PhN protons were also observed as triplets at 7.34 ppm (J_{HH} 7.85 Hz). The signal of benzene ring $H^{5'}$ connected with the P^+Ph_3 group appeared as a doublet at 7.22 ppm (J_{HP} 15.20 Hz, J_{HH} 7.74 Hz). The assignment of the other aromatic protons signals was complicated due to mutual overlapping and broadening. Methyl group signal was observed at 1.96 ppm, azomethine group proton signal appeared at 8.31 ppm, and the acidic proton signal has a shape of very broad singlet at 10.75 ppm, disappearing upon deuteration. The significant broadening of the NH proton signal was likely due to its participation in the strong intramolecular hydrogen bonding, or because of the tautomerism **A↔C**, the latter also causing the absence of the spin-

Table 1. Total energy (E, a. u.) and relative stability (ΔE, kcal mol^{-1}) of the isomers of **III** in the gaseous phase and in DMSO solution, according to B3LYP/6-311G(d,p) computation

Isomer	Gas phase		DMSO	
	E	ΔE	E	ΔE
IIIA	–1932.224049	0.0	–1932.296705	0.0
IIIB	–1932.205659	11.6	–	–
IIIC	–1932.221377	1.7	–1932.289896	4.3
IIID	–1932.202832	13.4	–	–
IIIE	–1932.212802	7.1	–1932.291988	3.1
IIIF	–1932.211091	8.2	–1932.290277	4.0
IIIG	–1932.199938	15.2	–	–

Table 2. Main crystallographic parameters and details of structure refinement for substance **IV**

Parameter	Value
Empirical composition	$C_{36}H_{33}N_3O_{2.50}P$
Crystal system	Triclinic
Space group	*P*-1
Unit cell parameters:	
a, Å	10.2505(7)
b, Å	12.9253(9)
c, Å	13.5489(9)
α, deg	116.2160(10)
β, deg	106.8270(10)
γ, deg	96.6690(10)
Volume, Å ^{3}	1477.95(17)
Z	2
M	578.62
d_{calc}, g cm^{-3}	1.300
Extinction coefficient, mm^{-1}	0.133
F(000)	610
θ range, deg	2.16 < θ < 30.21
Indices range	$-14 \le h \le 14$, $-18 \le k \le 18$, $-19 \le l \le 19$
Reflections total/unique	17513 / 8653 [*R*(int) 0.0312]
Complement to θ = 27.00	98.4%
Refinement method	Full-matrix PLS by F^2
R-indices values [$I>2\sigma(I)$]	R_1 0.0560, wR_2 0.1553
R-indices (all data)	R_1 0.0779, wR_2 0.1729
Precision by F^2	0.999

spin splitting of the azomethine proton signal. This fact also gave a reason for the choice of the keto-imine **A** structure as the most stable, supporting the quantum-chemical computation results on the relative stability.

In order to study the complex formation ability of **III**, we attempted to prepare its chelates with Hg(II), Zn(II), Cd(II), Be(II), and Pb(II) acetates. However, in all the reactions the only product was the same substance containing no metal.

The structure of the prepared substance was determined by X-ray diffraction analysis. Crystallographic data of **IV** and details of the X-ray diffraction experiment are collected in Table 2, and selected geometry parameters (bond lengths and bond angles) are given in Table 3.

Table 3. Principal interatomic distances, bond, and dihedral angles in the **IV** structure

Bond	*d*, Å	Angle	ω, deg
O^1–C^{10}	1.257(3)	$N^1C^7C^8$	124.0(2)
N^3–C^{10}	1.393(3)	$C^6N^1C^7$	119.08(18)
N^2–N^3	1.400(3)	$N^1C^7C^8C^{10}$	–177.4(2)
N^2–C^9	1.312(2)	$C^6N^1C^7C^8$	178.61(19)
C^8–C^9	1.421(3)	$C^5C^6N^1C^7$	–23.2(3)
C^7–C^8	1.410(3)	$C^{10}N^3C^{12}C^{13}$	171.1(2)
N^1–C^7	1.310(3)		

According to the X-ray diffraction data, compound **IV** was of zwitter-ionic nature, being a product of azomethine **III** dehydrohalogenation. In addition to **IV** molecules, ethanol and water molecules were present in the crystal, in the ratio of 1:0.5:1, respectively. Ethanol molecule position was disordered between the two crystallographic positions of equal population. Spatial structure and atom numbering of **IV** are presented in Fig. 1.

All bond lengths and bond angles in the molecule were of ordinary values for the corresponding atoms [18, 26]. The most polar form of the zwitter-ion was observed in the crystal, likely stabilized by polar molecules of water and alcohol.

Pairs of **IV** molecules were bound in the dimers due to the formation of the four hydrogen bonds $O^1\cdots H^{1WA}$ и $H^{1WB}\cdots O^1$. The centrally symmetrical eight-membered cycle was thus formed (Fig. 2). The parameters of the hydrogen bonds are given below, with the symmetry code (i): –*x*,–*y* – 1, –*z*.

D–H	*d*(D–H), Å	*d*(H···A), Å	<DHA, deg	*d*(D···), Å	A
O^{1W}–H^{1WA}	0.842	1.892	175.72	2.731	O^1
O^{1W}–H^{1WB}	0.840	2.123	156.79	2.913	O^{1i}

The formation of such strong hydrogen bonds indirectly proved the high electron density at the O^1 oxygen atom of **IV**.

Thus, upon addition of the phosphonium salt **III** to metal acetates, deprotonation by the acetate anion occurred instead of the complex formation. This was confirmed by the identity of the ^{1}H NMR and IR spectra of the compounds produced upon boiling methanol solutions of **III** with lead, zinc, cadmium, or beryllium acetates. In the ^{1}H NMR (DMSO-d_6) spectra

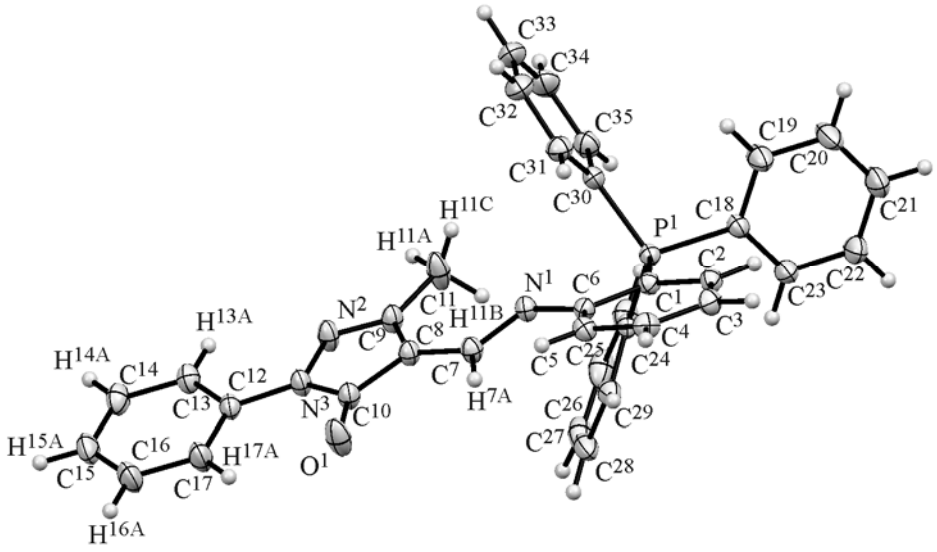


Fig. 1. Spatial structure of the **IV** molecules (ellipsoids of thermal vibrations are shown for the 50% probability).

of the compounds thus prepared, the acidic proton signal was absent, as compared with the spectrum of the compound **III**. The shift to the strong field was characteristic of many of the aromatic protons signals. For instance, the signal of benzene ring $H^{5'}$ proton (bound to the PPh_3^+ group) was observed at 6.79 ppm (δ = 7.21 ppm in **III**), that of the PhN fragment proton $H^{4'}$ was shifted to 6.90 ppm (δ = 7.10 ppm in **III**), and the $H^{3',5'}$ signals were observed at 7.21 ppm (δ = 7.34 ppm in **III**). This could result from the increased electron density of aromatic rings due to the appearance of the negative charge. The most significant shift to the strong field was observed in the case of the methyl group signal; it was registered at δ = 1.02 ppm (δ = 1.96 ppm in **III**). This was likely due to the fact that the pyrazole ring CH_3 protons were located in the anisotropy focus of the two phenyl rings of the PPh_3^+ group that were oriented perpendicular to the molecule plane. This was the evidence of the rigid spatial location of the groups, and thus confirmed that the structure similar to that established from the X-ray diffraction analysis existed in the solution as well.

Thus, basing on the experimental data it could be stated that in the reaction of the above mentioned metal acetates with **III**, a compound **IV** was formed, with the azanide structure. The azanide thus produced could exist in the form of a pair of *Z*,*E* isomers with respect to the C=C bond (**A** and **B**, Scheme 3).

According to the quantum-chemical simulation of **IV** isomers, in the gaseous phase the A form was relatively less stable than **B**, by 2.4 kcal mol^{-1}.

Structure	Gas phase		DMSO	
	E, au	Δ*E*	*E*, au	Δ*E*
IVA	–1931.787708	2.4	–1931.830937	0.0
IVB	–1931.791454	0.0	–1931.822667	5.2

However, the collected spectral and X-ray diffraction data evidenced that the more polar **A** form was more favorable. Indeed, when the solvent effect

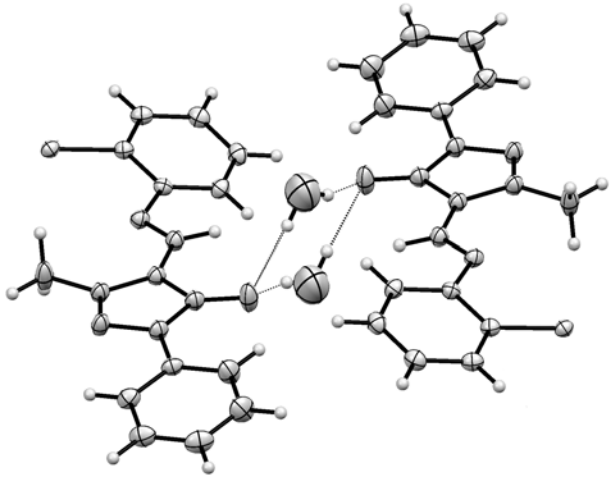
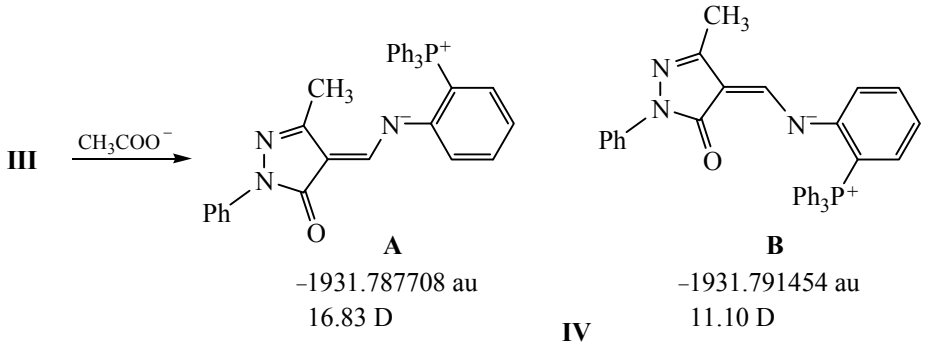


Fig. 2. Hydrogen-bonded dimers in the crystal of **IV**.

Scheme 3.



was taken into account in computations (in the frame of polarized continuum model PCM), in the DMSO medium the relative stability of the isomers was inverted, and the **B** isomer was more stable than **A** (by 5.2 kcal mol^{-1}), which was consistent with the experimental data.

In the IR spectra of the products of interaction of **III** with metal acetates, the absorption band at 3378 cm^{-1} disappeared, as compared with the initial reagent spectrum; this band corresponded to either OH or NH group. In addition, the C=N group band shifted to lower wavenumber (from 1650 to 1591 cm^{-1}) thus also indicating significant structural changes. In keeping with those data, acetates of the above-mentioned metals acted as bases, eliminating the HCl molecule from **III**.

Significant changes in the structure of **III** upon interaction with bases were also clearly revealed in the electronic spectra. The long-wave absorption band observed at λ_{max} = 339 nm (log ε_{max} = 4.82) in the spectrum of **III,** was subjected to strong red shift upon addition of triethylamine (λ_{max} = 388 nm, log ε_{max} = 4.97), whereas addition of HCl excess did not influence much the spectrum shape (λ_{max} = 326 nm, log ε_{max} = 4.80). It should be noted that the spectrum of **IV** in methanol solution was identical to that of **III** with addition of triethylamine, which confirmed easy elimination of HCl from the phosphonium salt molecule.

EXPERIMENTAL

IR spectra were registered in the mineral oil suspension using the Varian Scimitar 1000 FT-IR spectrophotometer (400–4000 cm^{-1}). ^1H NMR spectra were registered using Bruker AM-300 instrument with TMS as the internal reference. Electron absorption spectra were registered using Cary 5000 spectrophotometer, in methanol solution, in the 200–800 nm range, with the optical path length of 1 cm. Mass spectra were registered using the chromato-mass spectrometer Agilent 6410 equipped with triplex quadrupole tandem detector and electrospray ionization source; acetonitrile with 0.1% of acetic acid was used as eluent.

Quantum-chemical computations. Electronic and spatial structures of the studied compounds were obtained in the frame of non-empirical approximation of the density functional theory. The B3LYP hybrid exchange-correlation potential [27] with the exchange part introduced by Becke [28] and the Lee-Yang-Parr correlation part [29] was used. The standard valence-splitted extended Gaussian basic set 6-311G(d,p) was used for computations. Molecules geometry was preliminary optimized along all natural variables without symmetry restrictions. For each of the studied structures, the minimum at the potential energy surface was identified by calculation of the force coefficients matrix and the normal vibrations frequencies. All computations were performed by using GAUSSIAN'03 software [30].

(*E*)-{2-([(5-hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)methylene]amino)phenyl}triphenylphosphonium chloride (III). The solution of 0.4 g (0.002 mol) of 5-hydroxy-3-methyl-1-phenyl-4-formylpyrazole (**I**) [31] in 5 ml of butanol-1 was added to the solution of 0.76 g (0.002 mol) of 2-aminophenyl(triphenyl)phosphonium chloride (**II**) [32] in 5 ml of butanol-1. The resulting solution was boiled for 4 hours and then left overnight. The separated precipitate was filtered off and twice washed with cold butanol-1. The product was then recrystallized from the chloroform–ethyl acetate (1:3) mixture. Yield 58%, yellow needle-shaped crystals, mp > 260°C. IR spectrum, ν, cm^{-1}: 3378 (OH), 1650 (C=N), 1438 ($^+PPh_4$). ^1H NMR

spectrum (DMSO-d_6), δ, ppm (J, Hz): 10.75 br.s (1H, OH), 8.31 s (1H, CH=N), 7.57–8.13 m (5H, ArH and 15H, PPh_3), 7.34 t [2H, $NPh_{H^{3'},H^{5'}}$, $J_{3'(5'),2'(6')} = J_{3'(5'),4'}$ 7.85], 7.21 d.d (1H, H^{5}_{Ar}, $J_{5',4'} = J_{5',6'}$ 7.74, $J_{H^{5'}P}$ 15.20), 7.10 t (1H, $NPh_{H^{4'}}$, $J_{4',3'} = J_{4',5'}$ 7.32), 1.96 s (3H, Me). Mass spectrum, m/z: 538.2 $[M - Cl]^+$, 1075.4 $[M - Cl + M — Cl - H]^+$. Found, %: C 73.48; H 5.02; N 6.84; P 5.29. $C_{35}H_{29}ClN_3OP$. Calculated, %: C 73.23; H 5.06; N 7.32; P 5.41.

(*E*)-[(3-methyl-5-oxo-1-phenyl-1,5-dihydro-4*H*-pyrazol-4-ylidene)methyl)(2-(triphenylphosphonio)-phenyl]amide (IV). The solution of 0.027 g (0.0018 mol) of $Hg(CH_3COO)_2$ in methanol was added to the boiling solution of 0.10 g (0.0009 mol) of **III** in 5 ml of methanol, and the resulting solution was boiled for 5 h. After cooling the mixture, the yellow precipitate was formed. It was filtered off, washed with methanol, and recrystallized from ethanol. Yield 82%, mp > 260°C. IR spectrum, ν, cm^{-1}: 1591 (C=N), 1434 ($^+PPh_4$). ^1H NMR spectrum (DMSO-d_6), δ, ppm (J, Hz): 8.05 s (1H, CH=N), 7.91 d [2H, $NPh_{H^{2'},H^{6'}}$, $J_{2'(6'),3'(5')}$ 8.00], 7.60–7.87 m (1H, H_{Ar}, 15H, PPh_3), 7.51 t (1H, H^{4}_{Ar}, $J_{4',3'} = J_{4',5'}$ 7.00), 7.21 t [2H, $NPh_{H^{3'},H^{5'}}$, $J_{3'(5'),2'(6')} = J_{3'(5'),4'}$ 7.90], 7.10–7.20 m (1H, Ar^{6}_{Ar}, partially overlapping with $NPh_{H^{3'},H^{5'}}$), 6.90 t (1H, $NPh_{H^{4'}}$, $J_{4',3'} = J_{4',5'}$ 7.16), 6.79 d.d (1H, H^{5}_{Ar}, $J_{5',4'} = J_{5',6'}$ 7.78, $J_{H^{5'},P}$ 14.45), 1.02 s (3H, Me). Mass spectrum, m/z: 538.2 $[M + H]^+$, 1075.4 $[M + H + M - H]^+$. Found, %: C 78.63; H 5.17; N 7.64; P 5.49. $C_{35}H_{28}N_3OP$. Calculated, %: C 78.21; H 5.21; N 7.82; P 5.77.

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