Formation of substituted pyrazolines in the reaction of *C,N*-diphenylnitrilimine with a zwitterion derived from triisopropylphosphine and ethyl 2-cyanoacrylate

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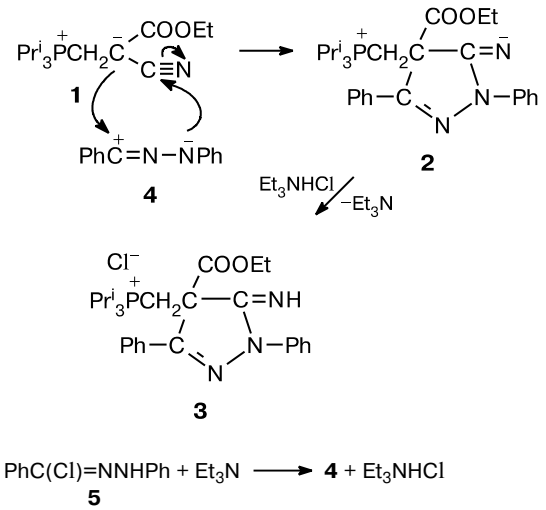
The reaction of *C,N*-diphenylnitrilimine with a P-zwitterion derived from Pr^i_3P and $H_2C{=}C(CN)CO_2Et$ afforded the first representative of 2-pyrazolines containing the phosphonium group and products of the addition of nitrilimine to Pr^i_3P and $H_2C{=}C(CN)CO_2Et$. The reaction of the P-zwitterion with *C*-4-nitrophenyl-*N*-phenylnitrilimine gave rise to a condensation product of one Pr^i_3P molecule and two nitrilimine molecules. The three-dimensional structures of the compounds synthesized were established by X-ray diffraction analysis.

Key words: phosphorus-containing zwitterion, nitrilimines, 2-pyrazolines.

Being carbanions, phosphorus-containing zwitterions of the $R_3P^+CH_2C^-(X)Y$ type (R = Alk or Et_2N; X = CO_2Alk or C(O)Me; Y = CN, CO_2Alk, or C(O)Me)[1] exhibit specific reactivity with respect to electrophilic compounds.[2,3]

We expected that the reactions of zwitterion **1** derived from Pr^i_3P and $CH_2{=}C(CN)CO_2Et$ with 1,3-dipolar compounds (for example, with nitrilimines) would afford cyclic five-membered nonstrained highly basic adduct **2** through the attack of the negatively charged N atom on the cyano group (Scheme 1). Stabilization of anion **2** due to its protonation could give rise to a new type of phosphorylated pyrazolines **3**. To examine this approach, we performed the reaction of zwitterion **1** with diphenylnitrilimine **4** generated by the reaction of the corresponding chloride **5** with Et_3N.

Scheme 1



Actually, the reaction of zwitterion **1** with nitrilimine **4** in MeCN gave rise to the first representative of pyrazolines containing the phosphonium group (**3**) as one of products. The composition and structure of phosphonium salt **3** were confirmed by elemental analysis and ^1H and ^{31}P NMR spectroscopy. The three-dimensional structure of pyrazoline **3** (Fig. 1) was established by X-ray diffraction analysis.

The crystal of compound **3** contains the phosphonium cations, the chloride anions, and the water and THF solvate molecules. In molecule **3**, the C(7)—C(12) (Ph(1)) and C(13)—C(18) (Ph(2)) benzene rings and the heterocycle involving the N(1), N(2), C(1), C(2), and C(3) atoms (Het) form a strongly flattened tricyclic system. The dihedral angles between the Het/Ph(1) and Het/Ph(2) planes are 8.1(3) and 14.1(2)°, respectively. The COOEt and $Pr^i_3P^+CH_2$ substituents are orthogonal to this system. The dihedral angles between the Het/C(4)O(1)O(2) and Het/C(3)C(19)P(1) planes are 87.0(1) and 84.0(2)°, respectively. The chloride ion, the water molecule, and the imino group are linked *via* a hydrogen bond network. The THF solvate molecule is not involved in hydrogen bonding.

The yield of phosphorus-containing pyrazoline **3** was ~10% (according to ^{31}P NMR spectroscopic data for the reaction mixture). Such a low yield is attributable to the

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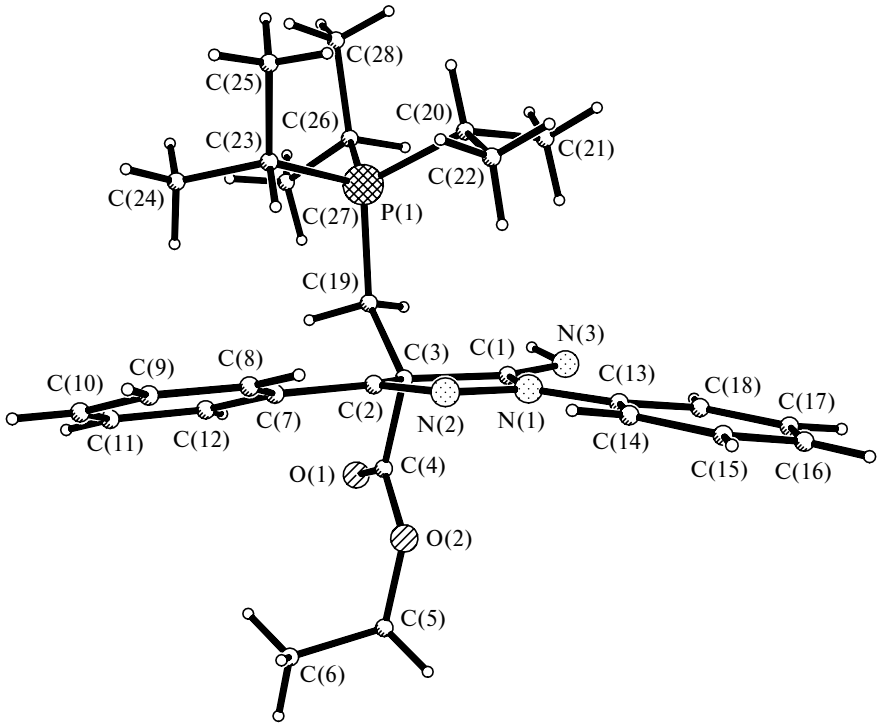


Fig. 1. Molecular structure of phosphorus-containing pyrazoline **3**.

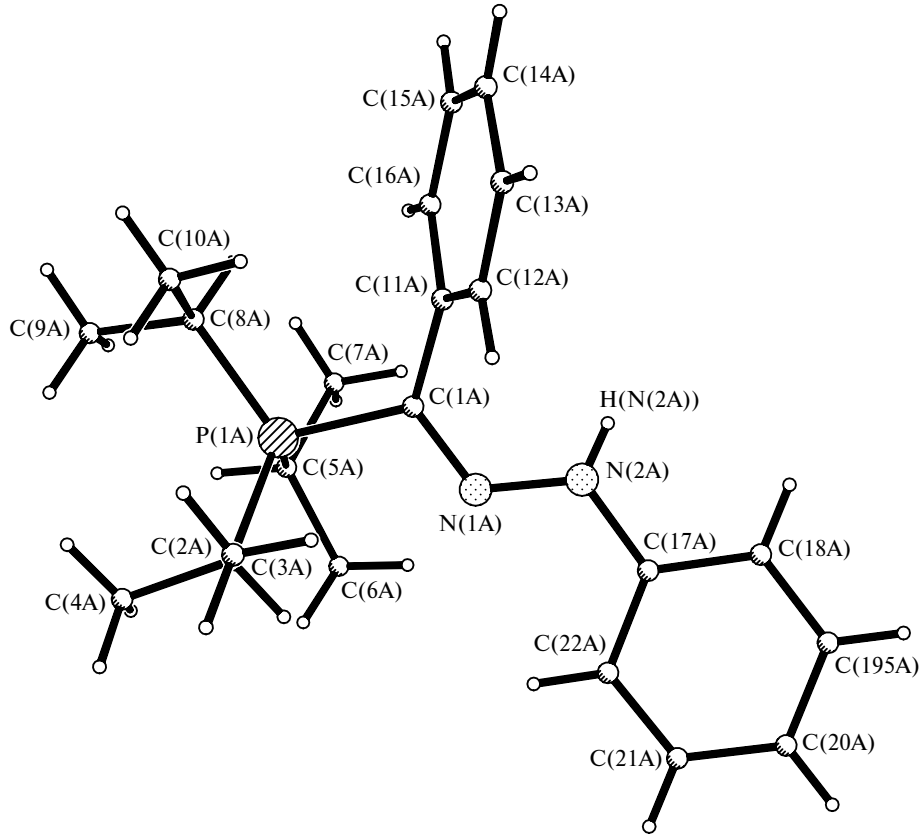
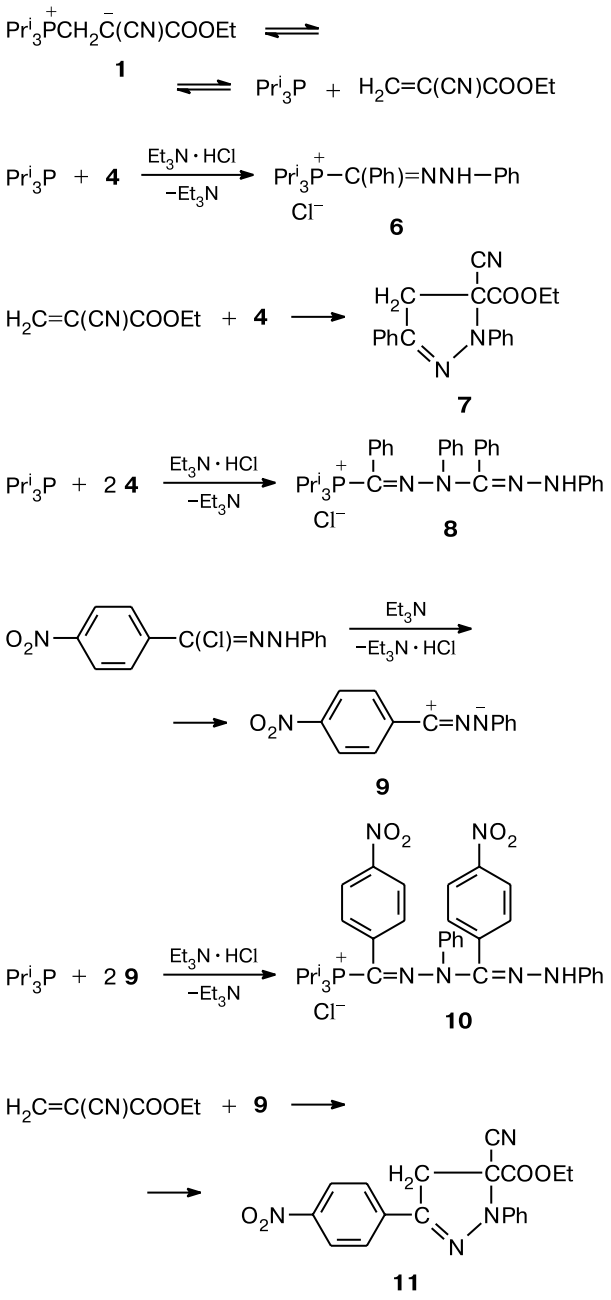


Fig. 2. Molecular structure of one of the rotamers of phosphonium salt **6**.

fact that the starting zwitterion **1** dissociates in a solution into Pr^i_3P and 2-cyanoacrylate.[3] The latter compounds, in turn, actively react with nitrilimine **4** to give phosphonium salt **6** and previously unknown pyrazoline **7** (Scheme 2).

Scheme 2



The reaction also afforded salt **8**, which is the adduct of Pr^i_3P with two molecules of nitrilimine **4**, in low yield. The ^{31}P NMR spectrum of compound **8** has one signal (δ 39.48). In the ^1H NMR spectrum, the ratio between the signals of the aromatic protons and the protons of the isopropyl groups is 20 : 21. It should be noted that the formation of both 1 : 1 and 1 : 2 adducts of triarylphosphines with nitrilimines was described in the literature.[4]

The formation of 4-unsubstituted pyrazoline **7** in the reaction according to Scheme 2 was unexpected. It is known that ethyl 2-cyanoacrylate, serving as the major component of cold-setting adhesives,[5] instantly polymerizes under the action of bases. However, in spite of the presence of Et_3N and Pr^i_3P in the reaction mixture (see Scheme 2), ethyl 2-cyanoacrylate reacts with nitrilimine **4** to give pyrazoline **7**. Apparently, the rate of formation of pyrazoline **7** is higher than the polymerization rate of acrylate formed in the reaction mixture. Alternative pathways giving pyrazolines **7** and **11** in the reactions under consideration will be considered elsewhere.

According to the X-ray diffraction data, salt **6** (Fig. 2) contains two crystallographically independent cations, the chloride anions, and benzene solvate molecules. The cations differ in the orientation of both the benzene rings and isopropyl fragments in the Pr^i_3P moiety and are rotamers. In both cations, the Ph(1)—N—NH—Ph(2) fragment is nonplanar. In two cations, the dihedral angles between the central C(1)—N(1)—N(2)—C(Ph(2))(Het) fragment and the planes of two benzene rings, *viz.*, C(11)—C(16) (Ph(1)) and C(17)—C(22) (Ph(2)), are as follows: Ph(1)/Het, 63.6(2) and 109.1(2)°; Ph(2)/Het, 11.5(3) and 6.5(3)°.

X-ray diffraction study of pyrazoline **7** (Fig. 3) demonstrated that the Ph(1) (C(8)—C(13)) and Ph(2) (C(14)—C(19)) rings and the pyrazoline ring including the N(1), N(2), C(1), C(2), and C(3) atoms (Het), like those in pyrazoline **3**, form a strongly flattened tricyclic system. The dihedral angles between the Het/Ph(1) and Het/Ph(2) planes are 6.6(1) and 11.9(1)°, respectively. The substituents are orthogonal to the heterocycle. The dihedral angles between the Het/C(3)C(5)O(1)O(2) and Het/C(3)C(4)N(3) planes are 81.28(9) and 75.0(2)°, respectively. The selected geometric parameters of molecules **3**, **6**, and **7** are given in Table 1.

The pyrazoline rings in molecules **3** and **7** bear different substituents at the C(1) and C(2) atoms. Both molecules contain the nearly flattened Ph(1)—C(2)=N(2)—N(1)—Ph(2) fragment possessing identical geometric parameters. The average bond lengths (N(1)—N(2), N(2)=C(2), and C(2)—Ph(1) are 1.393, 1.283, and 1.462 Å, respectively) are consistent with the standard values for the N—N (1.401 Å, a planar configuration of the N atoms), C_{sp^2}=N (1.279 Å), and C_{sp^2}—C_{Ar} (1.483 Å) bond lengths. The N(1)—Ph(2) bond (1.408 Å) is longer than the C_{Ar}—NH_2 bond (1.355 Å).

Several structures containing molecules with the pyrazoline ring are available in the Cambridge Structural Database (CSD) [release 5.1 (November 2002)]. Com-

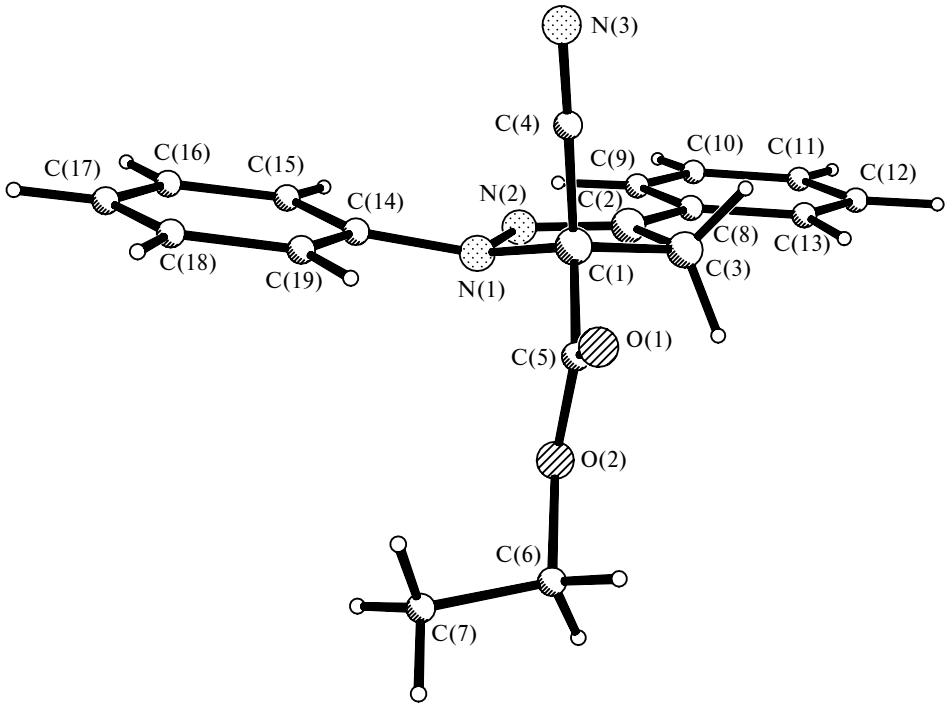
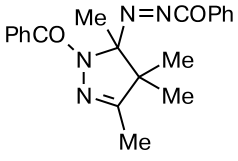
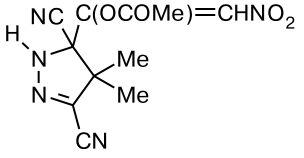


Fig. 3. Molecular structure of pyrazoline **7**.

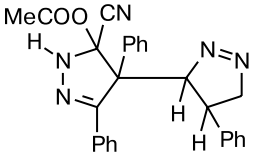
pounds, which are most structurally similar to pyrazoline **7**, (CSD refcodes DEPRUL, CNOXPB, and MPZPZN) are shown below.



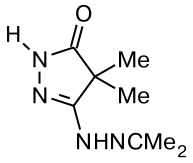
DEPRUL



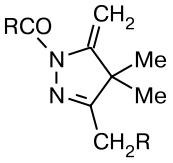
CNOXPB



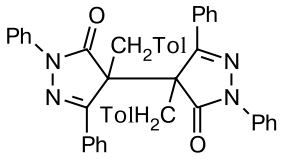
MPZPZN



TEJROP



TAFHEN



TICNAU

In these heterocycles, the endocyclic N—N, C=N, C—C(=), C—N, and C—C bond lengths (1.392—1.415, 1.260—1.268, 1.510—1.514, 1.462—1.470, and 1.550—1.603 Å, respectively) are identical to those in pyrazoline **7** regardless of the nature of substituents.

The compounds presented below are structurally similar to phosphorus-containing pyrazoline **3**.

The main differences between these molecules and compound **3** is the nature of the exocyclic C=X groups (C=N, C=O, or C=C) and the substituents at the nitrogen atom (H, Ph, or RCO). However, these differences have only a slight effect on the endocyclic N—N, C=N, and C—C(=X) bond lengths (1.393—1.417, 1.275—1.293, and 1.517—1.540 Å, respectively; the maximum difference is ~0.02 Å). For the C—C(=N) and (X=)C—N bonds, the observed differences are substantially larger (C—C(=N), 1.513, 1.501, 1.536, and 1.511 Å; (X=)C—N, 1.334, 1.438, 1.360, and 1.400 Å in TEJROP, TAFHEN, TICNAU, and **7**, respectively).

Nitrilimine **9**, which is generated from the corresponding chloride and contains the nitrophenyl group, reacts with zwitterion **1** in dry MeCN or acetone to give an orange crystalline precipitate of phosphonium salt **10** (see Scheme 2). The solubility of the latter compound appeared to be much lower than that of structurally similar compound **8** due to which adduct **10** (23% yield) precipitated from the reaction mixture already within a few min-

Table 1. Selected bond lengths (*d*) and bond angles (ω) in molecules **3**, **6**, and **7**

Parameter	**3**	**6***	**7**
Bond		*d*/Å	
N(1)—N(2)	1.396(4)	1.340(3), 1.330(3)	1.391(2)
N(1)—C(1)	1.400(5)	—	1.467(2)
N(2)—C(2)	1.283(5)	—	1.283(3)
C(2)—C(3)	1.511(5)	—	1.505(3)
C(1)—C(3)	1.524(5)	—	1.545(3)
C(2)—C(Ph(1))	1.466(5)	—	1.457(3)
N(1)—C(Ph(2))	1.416(5)	1.394(4), 1.405(3)	1.400(3)
N(2)—C(1)	—	1.302(3), 1.300(3)	—
C(3)—C(19)	1.540(5)	—	—
C(3)—C(4)	1.536(5)	—	—
C(1)—C(5)	—	—	1.533(2)
C(1)—C(4)	—	—	1.480(3)
C(1)—N(3)	1.262(5)	—	—
C(1)—C(Ph)	—	1.482(4), 1.492(4)	—
C(1)—P(1)	—	1.811(3), 1.792(3)	—
C(1)—N(2)	—	1.302(3), 1.300(3)	—
Angle		ω/deg	
N(2)—N(1)—C(1)	111.7(3)	—	111.3(1)
N(1)—N(2)—C(2)	109.6(3)	—	109.1(2)
N(2)—C(2)—C(3)	112.3(4)	—	113.4(2)
N(1)—C(1)—C(3)	105.1(3)	—	101.8(1)
C(1)—C(3)—C(2)	101.0(3)	—	101.6(2)
N(2)—N(1)—C(Ph(2))	118.6(3)	119.0(3), 118.3(2)	118.3(2)
N(2)—N(1)—C(1)	111.7(3)	—	111.3(2)
N(2)—C(1)—C(Ph)	—	126.4(2), 126.8(3)	—
C(1)—N(1)—C(Ph(2))	129.7(3)	—	123.9(2)
C(2)—C(3)—C(19)	119.87(3)	—	—
C(2)—C(3)—C(4)	108.7(3)	—	—
C(1)—C(3)—C(19)	111.9(3)	—	—
C(1)—C(3)—C(4)	105.5(3)	—	—
C(19)—C(3)—C(4)	108.9(3)	—	—
N(1)—C(1)—C(5)	—	—	113.9(2)
N(1)—C(1)—C(4)	—	—	110.5(2)
C(3)—C(1)—C(5)	—	—	111.1(2)
C(3)—C(1)—C(4)	—	—	110.6(2)
C(5)—C(1)—C(4)	—	—	108.9(2)
N(1)—C(1)—N(3)	124.4(4)	—	—
C(3)—C(1)—N(3)	130.5(4)	—	—
N(2)—C(1)—P(1)	—	111.0(2), 111.6(2)	—
P(1)—C(1)—C(Ph)	—	122.4(2), 121.1(2)	—
C(1)—N(2)—N(1)	—	118.8(2), 120.0(2)	—

* Two independent cations.

utes after mixing of the reagents. In addition, according to the ^{1}H NMR spectroscopic data, the reaction afforded also pyrazoline **11**, which we failed to isolate. The presence of this compound in the reaction mixture is evidenced by the fact that the ^{1}H NMR spectrum has a quadruplet of the methylene protons of the pyrazoline ring characteristic of the spin AB system with $^2J_{H,H}$ = 17.2 Hz (*cf.* lit. data[6]).

The three-dimensional structure of phosphonium salt **10** was established by X-ray diffraction analysis. The crystal structure consists of the cations, Cl^- anions, and EtOH solvate molecules. The Cl^- anions form isolated cation-anion solvated pairs (cation-anion—EtOH) through the N(4)—H...Cl (H...Cl, 2.49 Å; N...Cl, 3.206 Å) and Cl...H—OEt (Cl...H, 2.39 Å; O...Cl, 3.150 Å) hydrogen bonds. The structure of the cation is shown in Fig. 4. The selected geometric parameters are given in Table 2.

Table 2. Selected bond lengths (*d*) and bond angles (ω) in molecule **10**

Bond	*d*/Å	Bond angle	ω/deg
P(1)—C(Et)	1.813(5), 1.816(6), 1.816(5)	C(Et)—P—C(Et)	108.5(3), 115.7(3), 106.8(3)
P(1)—C(1)	1.829(5)	P(1)—C(1)—N(1)	107.8(3)
C(1)—N(1)	1.301(5)	P(1)—C(1)—C(2)	123.0(3)
C(1)—C(2) (C_6H_3—NO_2)	1.481(6)	C(1)—N(1)—N(2)	123.3(4)
		C(2)—C(1)—N(1)	129.1(4)
N(1)—N(2)	1.358(5)	N(1)—N(2)—C(14)	123.6(3)
N(2)—C(14)	1.445(6)	N(1)—N(2)—C(8)	112.7(3)
N(2)—C(8)(Ph)	1.425(6)	C(8)—N(2)—C(14)	119.1(4)
C(14)—N(3)	1.280(6)	N(2)—C(14)—N(3)	122.0(4)
C(14)—C(15) (C_6H_3—NO_2)	1.461(7)	N(2)—C(14)—C(15)	117.5(5)
		N(3)—N(4)—C(21)	119.2(5)
N(3)—N(4)(H)	1.331(6)	N(3)—C(14)—C(15)	119.1(4)
N(4)—C(21)	1.385(6)		

The central acyclic C(1)=N(1)—N(2)—C(14)=N(3)—N(4) fragment is nonplanar. The C(1)—N(1)—N(2)—C(14), N(1)—N(2)—C(14)—N(3), and N(2)—C(14)—N(3)—N(4) torsion angles are 25.3(6), 127.9(5), and 7.0(7)°, respectively. The fragment is twisted primarily about the N(2)—C(14) bond, which can reasonably be accounted for by steric hindrance between the benzene rings C(8)—C(13) and C(15)—C(20) (the dihedral angle is 84.9(2)°).

Therefore, zwitterion **1** serves not only as "latent" triisopropylphosphine[3] but also as "latent" ethyl 2-cyanoacrylate, due to which it can be used in the synthesis of various heterocycles, in particular, of previously unknown pyrazoline **7**. The use of esters of 3-unsubstituted 2-cyanoacrylic acid for such syntheses was not described in the literature. Evidently, this is associated with the fact that nitrilimines **4** and **9** are generally prepared in Et_3N, which is incompatible with 2-cyanoacrylic esters (unlike 2-cyanoacrylic esters containing a substituent at the double bond at position 3[7]) due to their very rapid polymerization.

Experimental

The ^{1}H and ^{31}P NMR spectra were measured on a Bruker AMX-400 spectrometer (400.13 MHz for ^{1}H and 161.98 MHz for ^{31}P) in $CDCl_3$ using Me_4Si as the internal standard and 85% H_3PO_4 as the external standard. The reactions were carried out under dry nitrogen. The solvents were used after purification and dehydration.

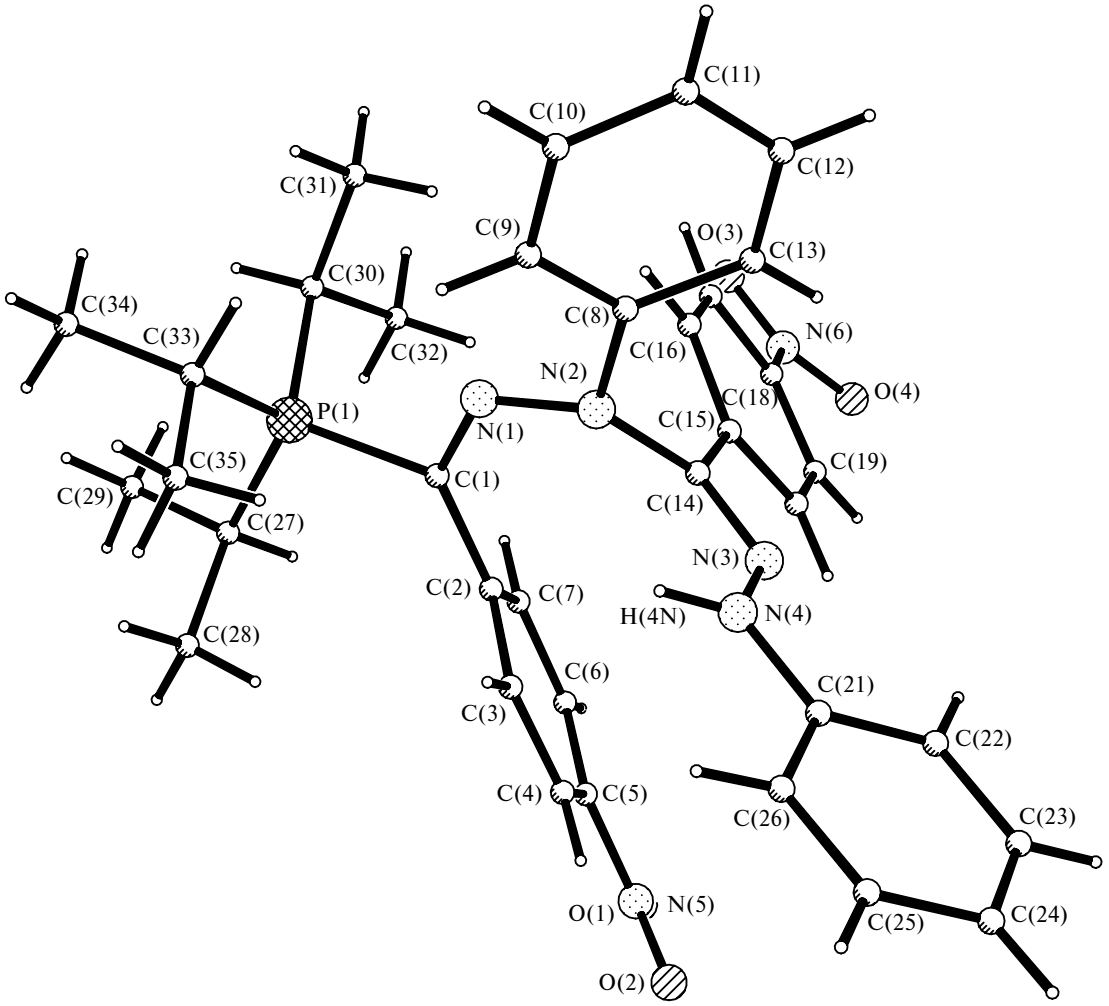


Fig. 4. Molecular structure of phosphonium salt **10**.

Reaction of zwitterion 1 with *N*-phenylbenzhydrazonoyl chloride in the presence of triethylamine. Triethylamine (1.2 mL, 8.7 mmol) was added to a mixture of zwitterion **1** [1] (1.42 g, 5 mmol) and *N*-phenylbenzhydrazonoyl chloride[8] (1.26 g, 5 mmol) in MeCN (50 mL). After 20 h, an additional amount of *N*-phenylbenzhydrazonoyl chloride (0.63 g, 2.7 mmol) was added. After 3 days, the solvent was distilled off *in vacuo*. Fractional crystallization of the residue (from THF, benzene, Me_2CO, and Et_2O) afforded pyrazoline **7**, m.p. 121—122 °C (from Et_2O), in a yield of 0.34 g (21.3%), phosphorus-containing pyrazoline **3**, m.p. 134—135 °C (from a benzene—Me_2CO mixture), in a yield of 0.17 g (6.6%), and phosphonium salt **6**, m.p. 169.5—171.5 °C (from a THF—benzene mixture), in a yield of 0.26 g (13.3%).

Triisopropyl-[(4-ethoxycarbonyl-5-imino-1,3-diphenyl-4,5-dihydro-1*H*-pyrazol-4-yl)methyl]phosphonium chloride (3). Found (%): Cl, 6.64. $C_{28}H_{39}ClN_3O_2P$. Calculated (%): Cl, 6.89. ^{31}P NMR, δ: 46.29. ^{1}H NMR, δ: 1.08 (t, 3 H, $C\underline{H}_3CH_2$, $^3J_{H,H}$ = 7.2 Hz); 1.20 (dd, 9 H, $(C\underline{H}_3)_2CH$, $^3J_{H,H}$ = 7.2 Hz, $^3J_{H,P}$ = 16.4 Hz); 1.31 (dd, 9 H, $(C\underline{H}_3)_2CH$, $^3J_{H,H}$ = 7.2 Hz, $^3J_{H,P}$ = 16.4 Hz); 2.80—3.20 (m, 5 H, CH_2P + $(CH_3)_2C\underline{H}$); 4.10 (br.s, 1 H, NH); 4.19 (dq, 1 H, $^2J_{H,H}$ = 10.5 Hz, $^3J_{H,H}$ = 7.2 Hz); 4.21 (dq, 1 H, $CH_3C\underline{H}_2$, $^2J_{H,H}$ = 10.5 Hz, $^3J_{H,H}$ = 7.2 Hz); 7.19—7.64 (m, 10 H, 2 Ph).

Triisopropyl[phenyl(phenylhydrazono)methyl]phosphonium chloride (6). Found (%): Cl, 9.09. $C_{22}H_{32}ClN_2P$. Calculated (%): Cl, 9.00. ^{31}P NMR, δ: 38.8. ^{1}H NMR, δ: 1.18 (t, 3 H, $C\underline{H}_3CH_2$, $^3J_{HH}$ = 7.2 Hz); 1.37 (dd, 18 H, $(C\underline{H}_3)_2CH$, $^3J_{H,H}$ = 6.8 Hz, $^3J_{H,P}$ = 16.0 Hz); 3.11 (d.sept, 3 H, $(C\underline{H}_3)_2C\underline{H}$, $^3J_{H,H}$ = 6.8 Hz, $^3J_{H,P}$ = 12.8 Hz); 4.29 (dd, 1 H, $^2J_{H,H}$ = 9.8 Hz, $^3J_{H,H}$ = 6.8 Hz); 4.32 (dd, 1 H, $CH_3C\underline{H}_2$, $^2J_{H,H}$ = 9.8 Hz, $^3J_{H,H}$ = 6.8 Hz); 7.27—7.77 (m, 10 H, 2 Ph); 9.53 (s, 1 H, NH).

Ethyl 5-cyano-1,3-diphenyl-4,5-dihydro-1*H*-pyrazole-5-carboxylate (7). Found (%): C, 71.49; H, 5.40; N, 13.09. $C_{19}H_{17}N_3O_2$. Calculated (%): C, 71.47; H, 5.39; N, 13.17. ^{1}H NMR, δ: 1.24 (t, 3 H, $C\underline{H}_3CH_2$, $^3J_{H,H}$ = 7.2 Hz); 4.00 (d, 1 H, $^2J_{H,H}$ = 17.2 Hz); 4.02 (d, 1 H, CCH_2C, $^2J_{H,H}$ = 17.2 Hz); 4.31 (dq, 1 H, $^2J_{H,H}$ = 11.6 Hz, $^3J_{H,H}$ = 7.2 Hz); 4.33 (dq, 1 H, $CH_3C\underline{H}_2$, $^2J_{H,H}$ = 11.6 Hz, $^3J_{H,H}$ = 7.2 Hz); 7.01—7.70 (m, 10 H, 2 Ph).

After separation of compounds **3**, **6**, and **7**, the solutions were combined and the solvents were removed *in vacuo*. The residue was washed many times with an Et_2O—MeCN mixture and then extracted with hot EtOH. The solution was cooled and

Et_2O was added until the reaction mixture turned opaque. Then the mixture was cooled to 0 °C, after which crystals of compound **8** (35 mg) precipitated, m.p. 225 °C. ^{31}P NMR, δ: 39.48. ^1H NMR, δ: 1.34—1.40 (m, 18 H, $(C\underline{H}_3)_2CH$); 3.08—3.12 (m, 3 H, $(CH_3)_2C\underline{H}$); 7.25—7.80 (m, 21 H, Ar); 9.70 (s, 1 H, NH).

Triisopropyl-[(4-nitrophenyl){[(4-nitrophenyl)(phenylhydrazono)methyl]phenylhydrazono}methyl]phosphonium chloride (10). Triethylamine (0.3 mL, 2.1 mmol) was added with stirring to a solution of zwitterion **1** (0.5 g, 1.75 mmol) and *N*-phenyl-*p*-nitrobenzhydrazonoyl chloride[8] (0.58 g, 2.1 mmol) in acetone (25 mL), an orange precipitate being gradually formed (0.54 g). After crystallization of the precipitate from 95% EtOH and separation of Et_3NHCl (0.2 g), orange salt **10** was obtained in a yield of 0.25 g, m.p. 225—225.5 °C. Found (%): C, 61.69; H, 6.34; N, 11.76. $C_{37}H_{46}ClN_6O_5P$. Calculated (%): C, 61.62; H, 6.38; N, 11.66. ^{31}P NMR, δ: 44.51. ^1H NMR, δ: 1.37 (dd, 18 H, $(C\underline{H}_3)_2CH$, $^3J_{H,H}$ = 6.8 Hz, $^3J_{H,P}$ = 16.0 Hz); 3.11 (d.sept, 3 H, $(CH_3)_2C\underline{H}$, $^3J_{H,H}$ = 6.8 Hz, $^3J_{H,P}$ = 12.8 Hz); 6.70—8.25 (m, 18 H, Ar); 11.05 (1 H, NH). The solvent was removed *in vacuo*, the precipitate was extracted with hot benzene, and the benzene extract was diluted with light petroleum. Crystals were obtained in a yield of 100 mg (m.p. 180—185 °C). According to the ^1H NMR spectroscopic data, these crystals consisted primarily of pyrazoline **11**. The ^1H NMR spectrum has signals characteristic of the protons of the CH_2 group in the pyrazoline ring, δ_H: 4.00 and 4.02 (both d, 1 H each, $^2J_{H,H}$ = 17.2 Hz). The residue of the benzene extract contains a phosphorus-containing compound, whose chemical shift (δ_P 46.98; the only signal) corre-

Table 3. Crystallographic data and details of structure refinement for **3**, **6**, **7**, and **10**

Compound	**3**	**6**	**7**	**10**
Molecular formula	$[C_{28}H_{39}N_3O_2P]^+Cl^-\cdot 0.25C_4H_8O\cdot H_2O$	$[C_{22}H_{32}N_2P]^+Cl^-\cdot 0.375C_6H_6$	$C_{19}H_{17}N_3O_2$	$[C_{35}H_{40}N_6O_4P]^+Cl^-\cdot 0.5C_2H_7O$
M	552.08	420.21	319.36	698.18
Space group	$C2/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a/Å	32.085(7)	9.677(3)	15.657(3)	10.601(6)
b/Å	9.289(2)	14.917(5)	13.918(3)	10.735(6)
c/Å	21.343(5)	18.453(6)	7.683(2)	18.923(11)
α/deg	90	108.938(7)	90	97.31(5)
β/deg	97.861(4)	95.805(7)	98.98(3)	91.42(5)
γ/deg	90	92.725(70	90	115.33(4)
V/Å^{-3}	6301(3)	2498(1)	1653.7(6)	1923(2)
Z	8	4	4	2
d_{calc}/g cm^{-3}	1.164	1.118	1.283	1.206
Color and habitus of crystals	Colorless needles	Colorless platelets	Colorless platelets	Colorless platelets
Crystal dimensions/mm^3	0.45×0.30×0.20	0.60×0.40×0.30	0.60×0.35×0.20	0.55×0.35×0.30
Diffractometer	«SMART Bruker»	«SMART Bruker»	«Enraf-Nonius CAD-4»	«Siemens P3/PC»
μ/cm^{-1}	2.05	2.29	0.85	1.86
T_{min}/T_{max}	0.187/0.968	0.219/0.862	—	—
Scan mode	ϕ/ω	ϕ/ω	$q - 5/3q$	$q - 2q$
$2\theta_{max}$/deg	52.22	56.56	50.00	48.22
Total number of reflections	20079	18651	5643	6504
Number of independent reflections (R_{int})	6201 (0.1115)	12248 (0.0204)	2900 (0.0313)	6059 (0.248)
R_1 (based on F for reflections with $I > 2\sigma(I)$)	0.0611 (1941)	0.0895 (6318)	0.0381 (1657)	0.0890 (3371)
wR_2 (based on F^2 for all reflections)	0.1789	0.2604	0.1371	0.2381
Number of parameters in refinement	352	612	285	455
Weighting scheme	$w^{-1} = \sigma^2(F_0^2) + (aP)^2 + bP$, where $P = 1/3(F_0^2 + 2F_0^2)$	$w^{-1} = \sigma^2(F_0^2) + (aP)^2 + bP$, where $P = 1/3(F_0^2 + 2F_0^2)$	$w^{-1} = \sigma^2(F_0^2) + (aP)^2 + bP$, where $P = 1/3(F_0^2 + 2F_0^2)$	$w^{-1} = \sigma^2(F_0^2) + (aP)^2 + bP$, where $P = 1/3(F_0^2 + 2F_0^2)$
A	0.0960	0.1780	0.1000	0.1250
B	0	0	0	0.7251
GOOF	0.714	0.910	0.856	1.031
R factor (%)	98.8	98.8	100.0	99.0
F(000)	2368	903	672	738
Residual electron density/e·Å^{-3}, ρ_{min}/ρ_{max}	0.298/−0.213	1.641/−0.419	0.129/−0.157	0.750/−0.320

sponds to that of pyrazoline **3**, which is indicative of the formation of phosphorus-containing pyrazoline of type **3**. However, attempts to isolate this compound and pyrazoline **11** in the individual state failed.

X-ray diffraction data sets for compounds **3**, **6**, **7**, and **10** were collected on automated diffractometers (Mo-Kα radiation) at ~20 °C. The structures were solved by direct methods and refined by the full-matrix least-squares method against F^2_{hkl}. All H atoms in the structure of **7** were revealed from difference electron density syntheses and refined isotropically. In molecules **3**, **6**, and **10**, all H atoms, except for the H atoms in the H_2O molecule and the NH groups, were placed in geometrically calculated positions and refined using the riding model with $B_{iso}(H) = 1.2B_{eq}(C)$, where $B_{eq}(C)$ are the equivalent thermal parameters of the C atoms to which the corresponding H atoms are bound. All calculations were carried out using the SHELXTL PLUS 5 program package.[9] The principal crystallographic data are given in Table 3. The selected geometric parameters are listed in Tables 1 and 2. The atomic coordinates and thermal parameters were deposited with the Cambridge Structural Database.

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