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Synthesis, Structure, and Properties of Phosphorus-Containing Bis(amidrazones)

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Abstract—Previously unknown ethenylphosphonic derivatives of bis(amidrazones) were prepared. According to spectroscopic data and quantum-chemical calculations, these compounds exist as phosphonium salts of a symmetrical linear structure with *trans* arrangement of the amidrazone fragments. In alkaline solutions, they are unstable and decompose to form triarylphosphine oxides. In contrast to ordinary amidrazones, their phosphorus-containing derivatives do not tend to form complexes with transition metals.

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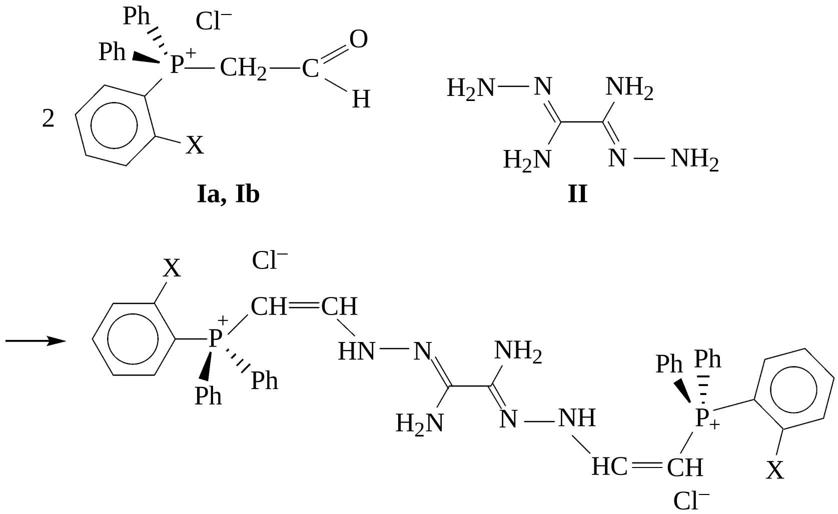
Amidrazones form a class of organic compounds whose structure and composition are represented by the formulas R–C(NH_2)=N–NH_2 or R–C(NH_2)=N–NH–R'. Amidrazones with various R and R' substituents have been described in the literature [1, 2], but there are no data on phosphorus-containing amidrazones. Due to the presence of several donor centers and acidic protons in the NH_2 groups, amidrazones are good complexants, in particular, for transition metal ions [3–7]. Amidrazones and amidrazone complexes exhibit high biological activity [8–10]. It seemed interesting to introduce a phosphorus-containing group into the amidrazone molecule and to reveal its effect on the amidrazone structure and properties, including complexation. For this purpose we synthesized amidrazones **IIIa** and **IIIb**.



Ia, Ib

II

IIIa, IIIb

X = H (**a**), OCH_3 (**b**).

The ^1H NMR spectra of **IIIa** and **IIIb** in DMSO-d_6 (25°C) contain signals of aromatic ring protons at 7.20–7.86 ppm; the spectrum of **IIIb** also contains a singlet of OCH_3 protons at 3.66 ppm. The signals of the NH and NH_2 protons appear as two broad singlets at 10.9–11.4 (2H) and 6.9–7.0 ppm (4H); the signals decrease on adding D_2O to the sample. The C*H*–NH protons give a two-proton doublet of triplets at

Table 1. Electronic absorption spectra of compounds **IIIa** and **IIIb**

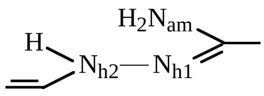
Comp. no.	Medium	λ, nm	ε	log ε
IIIa	Neutral	263 sh	8640	3.94
		269	9510	3.98
		276	9510	3.98
		348	28 100	4.45
	+ KOH	267	12 900	4.11
		385	10 150	4.01
	+ HCl	269	13 700	4.14
		355	13 820	4.14
IIIb	Neutral	268 sh	6520	3.81
		275 sh	8180	3.91
		293	10 760	4.03
		340	24 240	4.38
	+ KOH	285	11 330	4.05
		390	225 00	4.35
	+ HCl	276	13 790	4.14

6.4 ppm (J_{CHNH} = 4, J_{CHCH} = J_{CHP} = 14 Hz), and CHP protons, a two-proton doublet of doublets at 5.7–6.0 ppm (J_{CHP} = 16.5, J_{CHCH} = 14 Hz, exchanges with D_2O). The P–H coupling constants suggest the *trans* arrangement of ethylene protons in the $Ar_3P^+CH=CHNN$ fragment [11, 12].

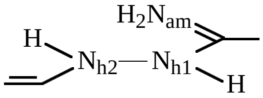
Thus, the ^1H NMR data show that at room temperature compounds **IIIa** and **IIIb** have a symmetrical linear structure with amidrazone fragments in the *trans* position.

The UV spectrum of **IIIa** (in methanol) contains a shoulder at λ_{max} 263 nm (log ε_{max} 3.94), two strong bands of $\pi \rightarrow \pi^*$ transition (*E* bands), λ_{max} 269 and 276 nm (both with log ε_{max} = 3.98), and one band of $\pi \rightarrow \pi^*$ transition (*K* band), λ_{max} 348 nm (log ε_{max} 4.45). On acidification (HCl) of a solution of **IIIa**, its UV spectrum changes insignificantly: a ~7-nm bathochromic shift of the long-wave band, accompanied by a hypochromic effect (ε_{max} decreses by ~14 000 units), is observed. Similar pattern is observed with **IIIb** (Table 1), suggesting similarity of the structures of both phosphonium salts.

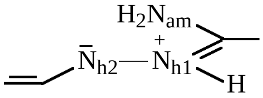
Insofar as molecules of **IIIa** and **IIIb** contain several donor centers and functional groups connected by a system of multiple bonds, they can exist as several relatively stable tautomers. The tautomerism within one amidrazone fragment can be represented as follows (N_{am} is amide nitrogen, N_{h1} and N_{h2} are the nitrogen atoms of hydrazone fragment):



A



B



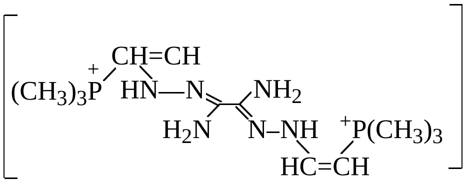
C

Table 2. Caculated [B3LYP, 6-31G(d,p)] total energies E_{tot} and energies relative to the most stable tautomer E_{rel} for various isomeric forms of **IV**

Comp. no.	Tautomer	E_{tot}, au	E_{rel}, kcal mol^{-1}
IVa	**A**	–1484.897325	0.0
IVb	**A**	–1484.897741	0.3
IVc	**A**	–1484.874523	14.6
IVd	**B**	–1484.867412	19.0
IVe	**C**	–1484.846792	32.0
IVf	**C**	–1484.856461	25.9
IVg	**A, B**	–1484.878314	12.2

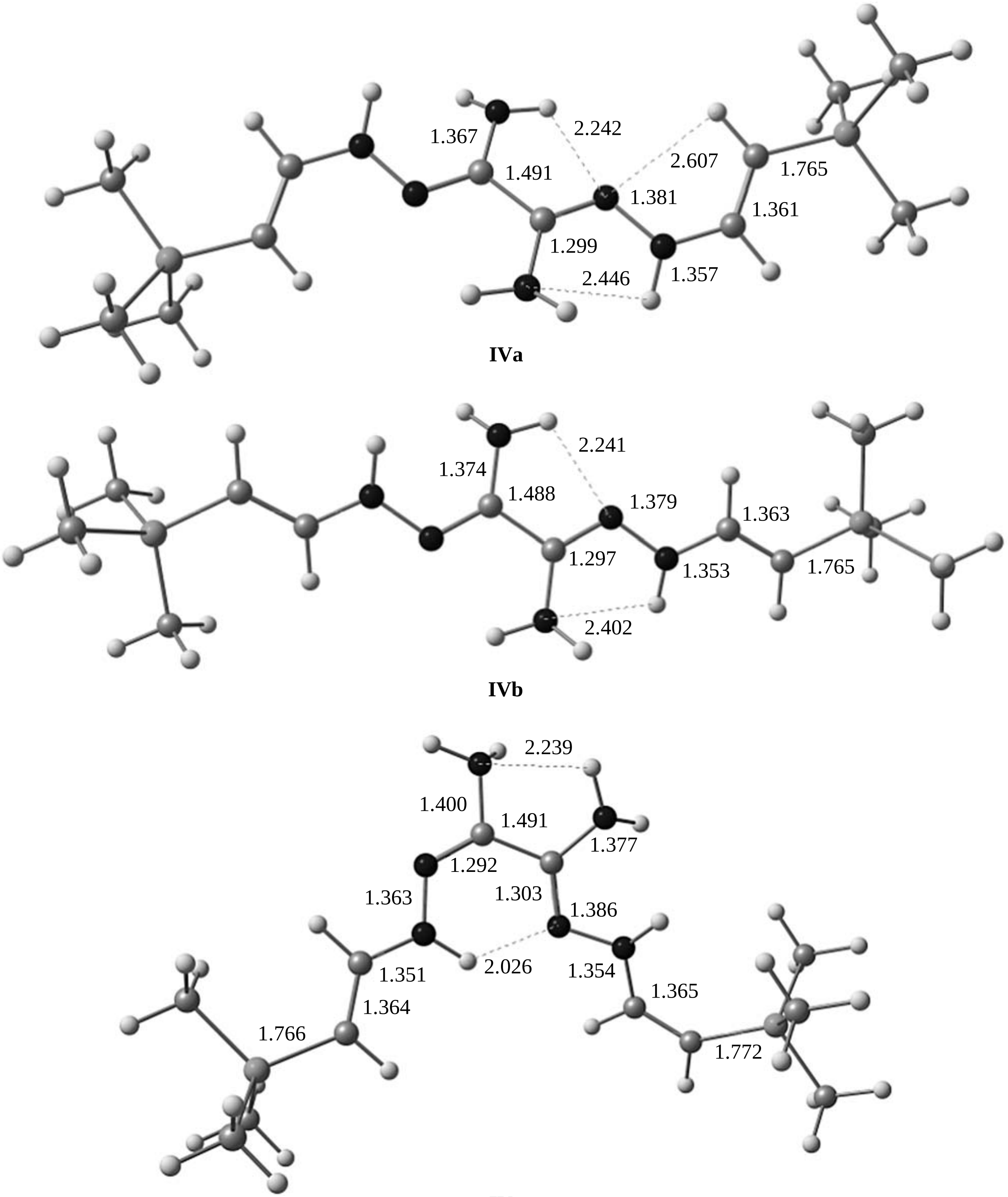
Each tautomer can exist in the form of various conformers differing in the steric repulsion of their fragments and in the number and strength of intramolecular H bonds.

To assess the relative stability of alternative molecular structures of **IIIa** and **IIIb**, we performed a quantum-chemical calculation of various structures of molecular dication **IV**. To reduce the computing time, the triphenylphosphonium fragments in **III** were replaced by trimethylphosphonium fragments.



The geometries of the optimized structures are shown in the figures below; their total and relative energies are listed in Table 2.

The most preferable are the conformations corresponding to tautomers **A** (**IVa**–**IVc**). Among them, the



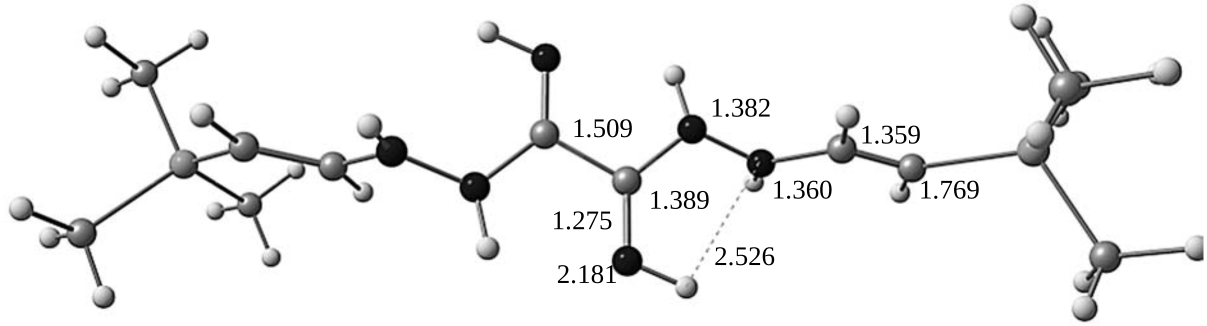
IVa

IVb

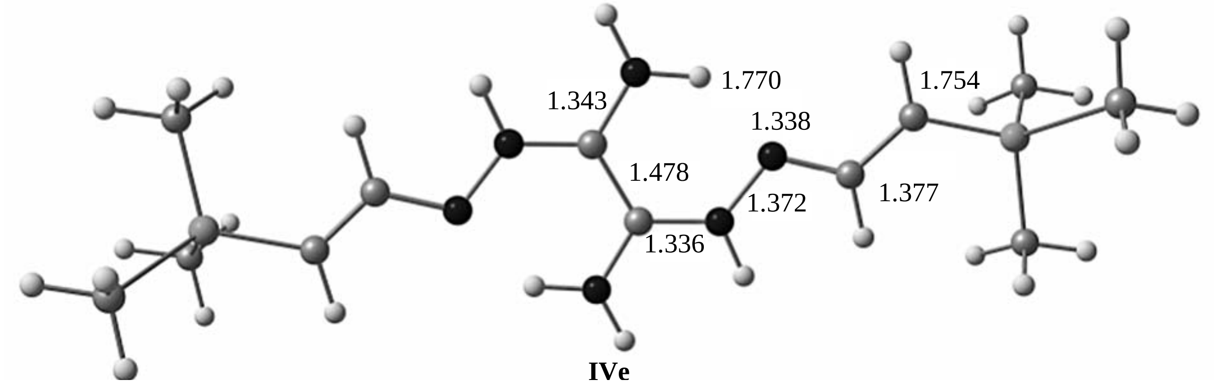
IVc

Fig. 1. Geometric structures of isomers **IVa–IVc**.

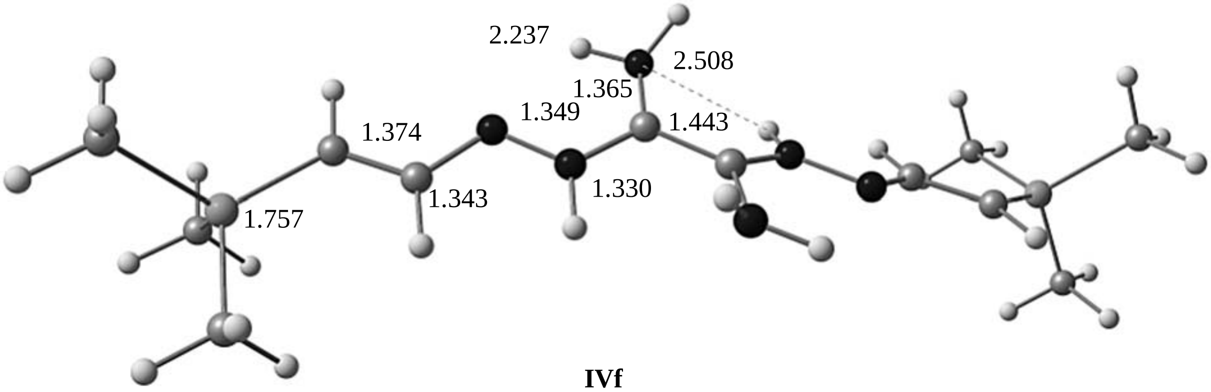
most stable are structures **IVa** and **IVb** with *trans* configuration of the bonds relative to the central C–C bond, which is stabilized by four relatively strong H bonds N_{am}–H···N_{h1} (2.242 Å) and N_{h2}–H···N_{am} (2.446 Å). Conformation **IVa** is slightly more preferable (by 0.3 kcal mol^{-1}) due to additional stabiliza-



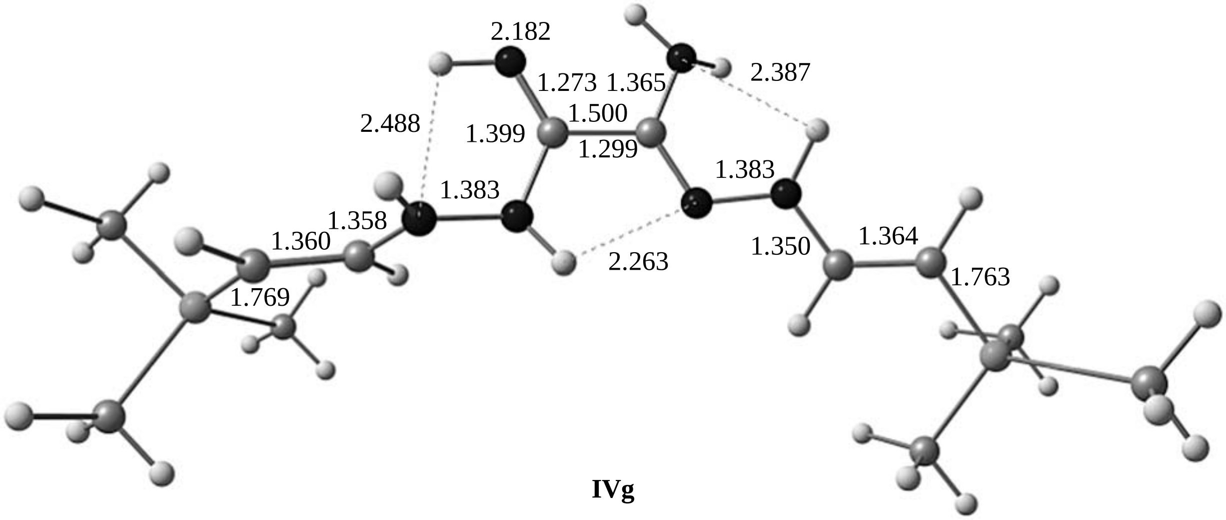
IVd



IVe



IVf



IVg

Fig. 2. Geometric structures of isomers **IVd–IVg**.

tion by the attracting interaction of the amidine nirtrogen atom N_{h1} and a proton in the ethylene group (the N_{h2}–H···N_{am} H-bond length increases from 2.402 in **IVb** to 2.446 Å in **IVa**, but owing to additional C–H···N_{h1} H bonding an energy gain is achieved). The central fragment of the molecule is essentially planar; the amide and N_{h2} nitrogen atoms are noticeable pyramidal.

The cisoid conformer (relative to the central C–C bond) **IVc** of tautomer of type **A** is considerably destabilized (by 14.6 kcal mol^{-1}) as compared to the transoid conformers (**IVa**, **IVb**). There are only two H bonds in its structure, and significant repulsion turns the amidrazone fragments by approximately 30° to opposite directions.

The tautomer of type **B** (structure **IVd**) is still less stable. Here the conjugation chain is the shortest, because the peripheral fragments of the molecule are turned by 90° around the single N–N bond of the hydrazone moiety to maintain the best conditions for hydrogen bonding N_{am}–H···N_{h2} in addition to N_{h1}–H···N_{am}.

The conformations of type **C**, **IVe** and **IVf**, are the least stable. The nonplanar structure **IVf** with four intramolecular H bonds (rotation by 25° around the central C–C bond) is preferable over the almost planar structure **IVe** with only two intramolecular H bonds.

Among the possible unsymmetrical tautomers, **IVg** is the most stable, due to formation of four different H bonds. It contains one amidrazone fragment in tautomeric form **A**, NH_2–C=N–NH, and the second fragment in form **B**, NH=C–NH–NH. The effect of H bonding on the stabilization in this structure is so strong that this structure is more favorable even than the *cis* conformer **IVc** of the type **A** tautomer.

Deprotonation of dication **IV** leads to a planar structure of type **V** with four practically equivalent H bonds formed by hydrogen atoms of NH_2 groups with the nitrogen atoms of hydrazine groups. The position of the long-wave maximum λ_{max} of **V**, calculated in the TDDFT approximation, is 338 nm, which is 24 nm higher than that calculated for conformer **IVa**, 314 nm. Thus, the bathochromic shift of the maximum of the long-wave absorption band upon alkalization in compounds **IIIa** ($\Delta\lambda_{max}$ 47 nm) and **IIIb** ($\Delta\lambda_{max}$ 50 nm) may be due to deprotonation of the parent cation.

A structural feature of **V** is the preference of the flagstaff conformation of trimethylphosphonium fragments relative to the plane of the central part of the molecule and significant loosening of one of the P–CH_3 bonds (elongation to 1.857 Å, as compared to 1.835 Å for the other bonds). This fact suggests easiness of chemical degradation processes and can be responsible for the observed instability of amidrazones **IIIa** and **IIIb** in alkaline medium.

Table 3. Calculated [B3LYP/6-31G(d,p)] parameters of vibrations of **IVa** in comparison with the experimental vibration frequencies of **IIIa**

Vibration mode	Frequency, cm^{-1}	
	calculated	experimental
NH_2 stretching (as)	3528 (2.30)	3380
NH_2 stretching (s)	3418 (1.27)	3250
NH stretching	3394 (1.54)	3185
Ethylene C–H stretching	3090 (0.2)	3060
C=C, C=N stretching	1656 (0.80)	1645
	1629 (5.00)	1625
	1597 (52.3)	1592
NH_2 bending	1576 (1.20)	1575 sh
NH bending	1493 (0.40)	1500

Thus, the calculation results and NMR data indicate that structure **IVa** prevails for the compounds synthesized.

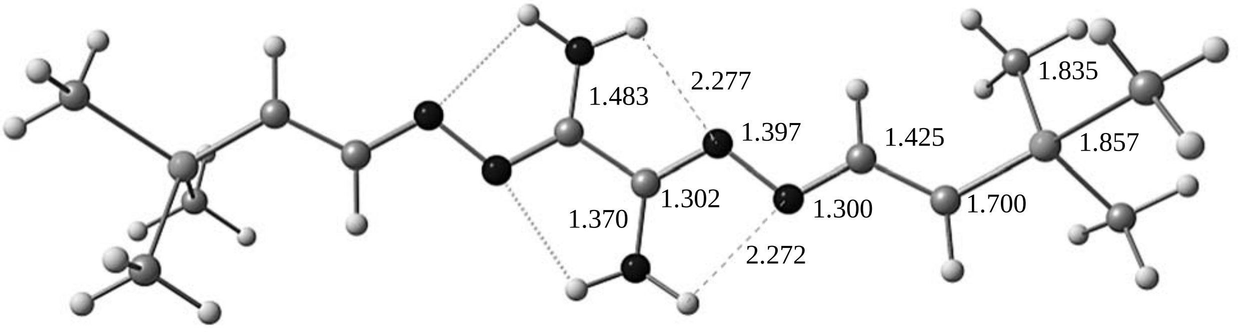
The IR spectra of the compounds contain the following bands: band in the region of 1440 cm^{-1} characteristic of a P–C bond [13], strong band in the region of 1600 cm^{-1} [probably due to overlapping ν(C=C) and ν(C=N) bands], and several bands at 3200–3500 cm^{-1} due to NH and NH_2 stretching vibrations.

To interpret the IR spectra, we calculated the frequency of the harmonic vibrations of **IVa** in the B3LYP/6-31G(d,p) approximation. The results obtained [an empirical factor of 0.9614 proposed by A. Scott and L. Radom [14] is taken to correct the frequency of the normal modes calculated in the framework of B3LYP/6-31G(d) approach] are compared in Table 3 with the experimental spectrum of **IIIa**.

The experimental and calculated parameters are well consistent, confirming correctness of determination of the most stable form of **IIIa** and **IIIb**.

One of our goals was the study of the complexing ability of bisphosphonium salts **IIIa** and **IIIb**. Data on the complextion of the related amidrazones with transition metal salts have been published [15–20].

Adding a methanolic solution of copper, nickel, or zinc acetate to a methanolic solution of a phosphonium salt **III** results in a change in the color. However, we failed to isolate a complex after prolonged



V

Fig. 3. Geometric structure of compound **V**.

refluxing of the reaction solution followed by evaporation. Attempted synthesis of a complex in an alkaline medium resulted in recovery of the corresponding triarylphosphine oxide contaminated with a metal salt. In our opinion, the low complexing ability of **IIIa** and **IIIb** is due to the presence in the ligand molecules of positive charges which decrease the donor power of the nitrogen lone pairs. Adding alkali to a solution of phosphonium salt **IIIa** or **IIIb** leads to its decomposition; therefore, it is impossible to prepare a complex with such a ligand in an alkaline medium. Thus, addition of the positively charged phosphonium group to the amidrazone fragment does not promote the complex formation.

EXPERIMENTAL

The IR spectra were recorded on a Unicam-SP1200 spectrophotometer from mulls in mineral oil. The ^{1}H NMR spectra were taken on a Bruker AM-300 instrument with internal TMS. The electronic spectra were measured on an SF-200 spectrophotometer in the range 220–500 nm from ethanolic solutions.

Oxamidrazone II. A mixture of 2.6 g of dithiooxamide (hydrorubeanic acid), 12 ml of ethanol, and 3 ml of 95% hydrazine hydrate was heated on a water bath for 30 min. The precipitate was filtered off, washed with ethanol, and recrystallized from aqueous methanol. Yield 75%, mp >300°C.

(1*Z*,2*Z*)-*N*'^{1},*N*'^{2}-Bis[(*E*)-2-triphenylphosphonio]-oxamidrazone chloride IIIa. To a hot solution of 0.002 mol of (formylmethyl)triphenylphosphonium chloride **Ia** [18] in 10 ml of ethanol, a hot solution of 0.001 mol of dihydrazide **II** [19] in 10 ml of ethanol was added, and the mixture was refluxed for 5 h. The precipitate of **IIIa** was filtered off, washed with ethanol, and recrystallized from methanol. Yield 75%, mp >300°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 5.98 d.d (2H, $P^+HC=$, J_{PH} 16.4, J_{CHCH} 14 Hz), 6.43 d.t (2H, H–C=C–H_{trans}N, J_{PH} 14, J_{CHCH} 14, J_{CHNH} 3.7 Hz), 6.92 br.s (4H, NH_2), 7.67–7.86 m (30H, C_6H_5), 10.93 br.s (2H, NH). Found, %: C 65.78; H 5.33; N 11.22; P 8.02; Cl 8.92. $C_{42}H_{40} \cdot N_6P_2Cl_2$. Calculated, %: C 66.23; H 5.29; N 11.03; P 8.13; Cl 9.31.

(1*Z*,2*Z*)-*N*'^{1},*N*'^{2}-Bis[(*E*)-2-{(2-methoxyphenyl)diphenyl}phosphonio]oxamidrazone chloride IIIb. To a hot solution of 0.002 mol of (formylmethyl)(2-methoxyphenyl)diphenylphosphonium chloride **Ib** (prepared by the same procedure as **Ia**) in 10 ml of ethanol, a hot solution of 0.001 mol of dihydrazine **II** in 10 ml of ethanol was added, and the mixture was refluxed for 5 h. Then the mixture was evaporated to 1/3 of the initial volume, and 15 ml of ethyl acetate was added. The precipitate of **IIIb** was filtered off, washed with ethyl acetate, and recrystallized from methanol–ethyl acetate, 1 : 3. Yield 58%, mp >300°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.66 s (6H, OCH_3), 5.73 d.d (2H, $P^+HC=$, J_{PH} 16.7, J_{CHCH} 14.1 Hz), 6.38 d.t (2H, H–C=C–H_{trans}N, J_{PH} 14, J_{CHCH} 14.1, J_{CHNH} 4.3 Hz), 7.01 br.s (4H, NH_2), 7.20–7.82 m (28H, Ar), 11.38 br.s (2H, NH). Found, %: C 64.78; H 5.43; N 9.75; P 7.72; Cl 8.42. $C_{44}H_{44}N_6P_2P_2Cl_2$. Calculated, %: C 64.31; H 5.40; N 10.23; P 7.54; Cl 8.63.

Quantum-chemical calculations. Geometry optimization and calculation of the electronic structure and vibration spectra of the conformers were performed in the framework of density functional theory (DFT) with B3LYP hybrid functional [20–22] in the 6-31G(d,p) basis set. All the calculations were performed using PCGAMESS package [23, 24]. Input data preparation, presentation of structures, and visualization of the calculation results were made using ChemCraft program [25]. The optical spectra of model compounds were calculated in the TDDFT approximation [26–28].

All the considered structures correspond to minima on the potential energy surface (no imaginary vibration frequencies).

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