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Quantum-Chemical Estimation of the Stability and Reactivity of Diphosphonium Salts

V. A. Zagumennov, A. N. Vedernikov, E. V. Nikitin, and B. N. Solomonov

Kazan State University, Kazan, Tatarstan, Russia

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Abstract—For a series of diphosphonium salts containing two positively charged covalently bonded phosphorus atoms, $X_nY_{3-n}P^+P^+X_nY_{3-n}$ (X = alkyl substituent, Y = amino group, n = 0–3), the stability, reactivity, and P–P bond strength were evaluated by various physicochemical methods. The P–P bond energy is appreciably influenced by both steric factors and donor properties of the substituents. The calculations confirmed that transformations of diphosphonium salts can involve cleavage of both P–P and P–N (or P–C) bonds.

It was shown previously that electrochemical oxidation of tertiary phosphines and aminophosphines in an inert solvent in the presence of a supporting electrolyte yields diphosphonium salts I [1–3]:

$$\begin{gathered} X_3P - e \longrightarrow X_3P^{+\cdot} \xrightarrow{+X_3P} [X_3PPX_3]^{+\cdot} \\ \xrightarrow[-e]{2ClO_4^-} \underset{\textbf{I}}{[X_3PPX_3]^{2+}(ClO_4^-)_2}, \qquad (1) \\ X = \text{Alk, Alk}_2\text{N}. \end{gathered}$$

Salts **I** are relatively stable [1]. Single-crystal X-ray diffraction data obtained for hexakis(diethylamino)diphosphonium diperchlorate, $[(Et_2N)_3PP(NEt_2)_3]^{2+} \cdot (ClO_4^-)_2$, show that salts **I** are phosphonium compounds with a covalent bond between two positively charged phosphorus atoms [2]. This result is unexpected, as a chemical bond between two atoms bearing like charges should destabilize the molecule. Therefore, it is interesting to study the stability and reactivity of salts **I** theoretically. In this work, we calculated quantum-chemically the geometries of a series of diphosphonium dications and the energies of homolytic and heterolytic cleavage of the P^+–P^+ and P–X bonds. As model compounds we chose a series of cations with the ethyl groups gradually substituted by dimethylamino groups: $Et_3P^+P^+Et_3$ (**II**), $Et_2 \cdot (Me_2N)P^+P^+(NMe_2)Et_2$ (**III**), $Et(Me_2N)_2P^+P^+ \cdot (NMe_2)_2Et$ (**IV**), and $(Me_2N)_3P^+P^+(NMe_2)_3$ (**V**). The calculations were performed with the isolated cations in the gas phase or a model solution; the effect of anions was neglected.

Calculations were performed by the following methods: density functional theory (DFT), with PBE functional [4] using Priroda program package [5]; Hartree–Fock and MP2 methods (MO *ab initio*), using GAMESS program package [6]. In calculations performed with various program packages, we used the Stevens–Bash–Krauss (SBK) basis sets [7]; their splitting was different for each program package (see Experimental). In all the cases, the geometries were fully optimized without symmetry constraints.

The principal geometric parameters of the hexakis(dimethylamino)diphosphonium ion $[(Me_2N)_3P^+P^+ \cdot (NMe_2)_3]$, calculated quantum-chemically (Fig. 1) are in good agreement with those determined by single-crystal X-ray diffraction for the salt of the hexakis(diethylamino) homolog [2]. The P–N and N–C bond lengths and the bond angles coincide within the experimental error. For the P–P bond length, the agreement is somewhat worse. The calculated value (0.242 nm) exceeds the experimental value (0.236 nm) by more than 2%; however, such a disagreement is quite acceptable. Good agreement of the calculated geometry of **V** with the experimental data for the $[(Et_2N)_3P^+P^+ \cdot (NEt_2)_3]$ salt demonstrates the adequacy of our quantum-chemical calculations.

The calculated (DFT) steric structure of hexaethyldiphosphonium dication **II** is shown in Fig. 2. According to the calculations, the ion has a typical phosphonium structure. The conformation along the P–P bond is intermediate between staggered and eclipsed (the CPPC torsion angles are about 40°). The P–C and C–C bond lengths are usual (0.185 and 0.154 nm, respectively). The P–P bond length, estimated at 0.230 nm, exceeds the P–P bond lengths in diphosphines (0.217–0.222 nm) [8]. The phosphorus and carbon atoms have a tetrahedral configuration with the bond angles close to 109°, suggesting that the steric strain in **II** is insignificant.

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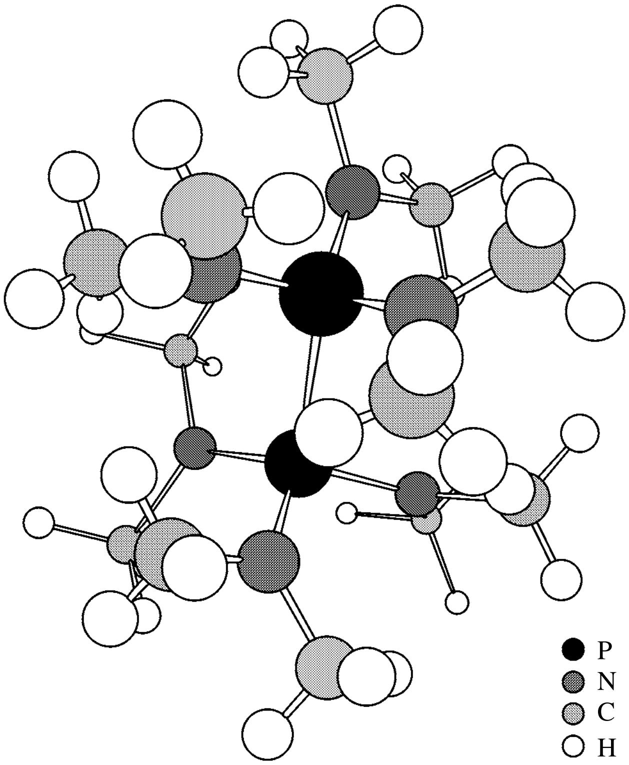

Fig. 1. Steric structure of the $(Me_2N)_3P^+P^+(NMe_2)_3$ dication (DFT calculations).

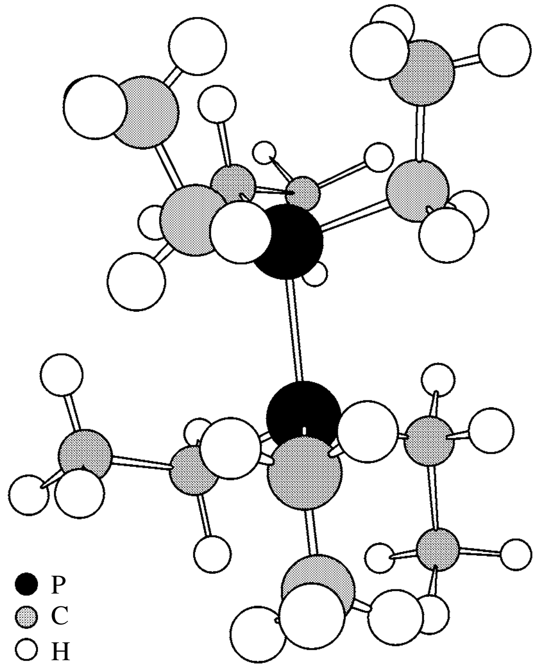

Fig. 2. Steric structure of the $Et_3P^+P^+Et_3$ dication (DFT calculations).

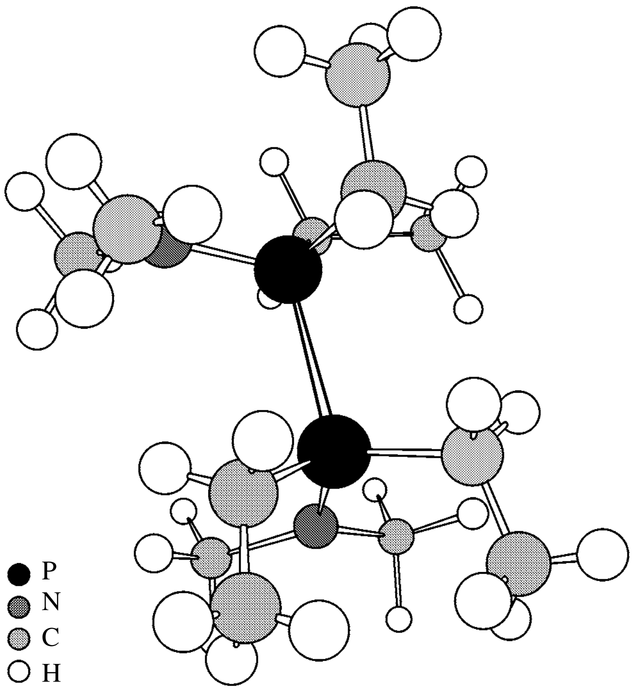

Fig. 3. Steric structure of the $Et_2(Me_2N)P^+P^+(NMe_2)Et_2$ dication (DFT calculations).

The results of geometry optimization for the bis(dimethylamino)tetraethyldiphosphonium dication (**III**) show (Fig. 3) that in this compound the P–P bond is longer than in **II**: 0.242 nm. At the same time, the P–N and P–C bond lengths are usual (0.167 and 0.185 nm, respectively). Analysis of the bond angles in **III** reveals an angular distortion of one of the two $[(Me_2N)Et_2P]$ fragments. Whereas in one of these fragments the bond angles at the P, C (~109°), and N (~120°) atoms have standard values, in the other fragment the CPN angle is as large as 116°–118°, with the CPC angle at the same P atom decreased to 102°. The arrangement of the N atoms relative to the P–P bond in **III** corresponds to the *trans* conformation.

Optimization of the structure of tetrakis(dimethylamino)diethyldiphosphonium dication (**IV**) leads to the geometry shown in Fig. 4. The calculated P–P, P–N, and P–C bond lengths in **IV** coincide with those obtained for **III** (0.242, 0.165, and 0.185 nm, respectively). In **IV**, in contrast to **III**, the geometries of both $[(Me_2N)_2EtP]$ fragments are similar: All the P and C atoms have a tetrahedral configuration (the bond angles are close to 109°), whereas the bond angles at the N atoms (118°–125°) are typical of the trigonal planar configuration.

The geometry of the hexakis(dimethylamino)diphosphonium ion (**V**) (Fig. 1) has certain specific features as compared to **III** and **IV**. For example, although the P–P and P–N bond lengths in **III**–**V** are essentially the same, the bond angles in **V** differ from those in **III** and **IV**. For example, the NPN bond angle is as small as 90°, and the NPP bond angles vary in a wide range (102°–128°); the nitrogen atom occurs in the sp^2 state, since the sum of the bond angles at this atom is about 360°. The NPPN dihedral angle is 60°.

The quantum-chemical calculations show (Figs. 1–4) that the geometries of the diphosphonium dications are influenced by substituents at the P atoms. For example, in hexaethyl derivative **II** the bond lengths and angles have close-to-optimum values. Replacement of ethyl groups by dimethylamino groups in **III**–**V** leads to lengthening of the P–P bond and distortion of the bond angles at the P and N atoms. It should also be noted that the nitrogen atoms in **III**–**V** tend to assume the sp^2 state rather than the sp^3 state characteristic of tertiary aliphatic amines.

The lengthening of the P–P bond in diphosphonium salts containing dimethylamino substituents may be due to two factors. First, the presence of more closely arranged (owing to shorter P–N and N–C bonds, as compared to P–C and C–C bonds: 0.165, 0.146 and 0.185, 0.154 nm, respectively) β-methyl groups should result in stronger repulsion of the two phosphonium fragments. Second, the dimethylamino group is a weaker donor than the alkyl group, which should result in a larger effective charge on the P atoms and hence in their stronger electrostatic repulsion. Indeed, the Mulliken charges on the P atoms, according to MO *ab initio* calculations, are −0.235 in the $Me_6P_2^{2+}$ dication and +0.289 in the simplest hexaaminodiphosphonium dication, $(H_2N)_6P_2^{2+}$. To evaluate the effect of steric factors on the P^+–P^+ bond length, we calculated by the DFT method the optimal geometry of the $[(H_2N)_3P^+P^+(NH_2)_3]$ dication **VI** containing no bulky β-methyl groups. The optimal structure of **VI** is shown in Fig. 5. It is seen that the structure is not distorted. The bond angles at the P and N atoms are close to 109° and 120°, respectively. The conformation of **VI** is almost eclipsed; the NPPN dihedral angle is 10°. The P–N bond lengths are the same as in **III**–**V** (0.165 nm). The P–P distance in **VI**, however, is as short as 0.230 nm and virtually coincides with the corresponding value calculated for the hexaethyl derivative **II**. Thus, the lengthening of the P–P bond in **III**–**V** is mainly due to the steric factors.

It is also interesting to study the stability and reactivity of diphosphonium salts **I**. These properties will be governed, in particular, by the relative strengths of the P–P, P–N, and P–C bonds. An important characteristic determining the stability and reactivity of compounds like **I** is the energy of homolytic cleavage of the P^+–P^+ bond. Since diphosphonium salts **I** have been prepared only recently, their properties have been studied insufficiently, and data on the P^+–P^+ bond energy are lacking. We calculated the energy of dissociation of **II**–**VI** across the P–P bond [Eq. (2)] by various quantum-chemical methods.

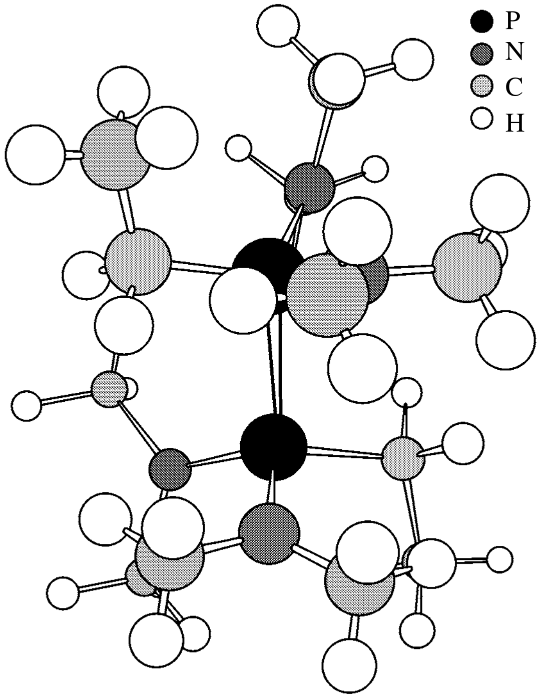

Fig. 4. Steric structure of the $Et(Me_2N)_2P^+P^+(NMe_2)_2Et$ dication (DFT calculations).

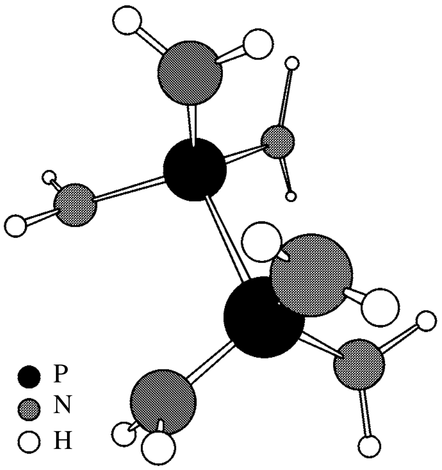

Fig. 5. Steric structure of the $(H_2N)_3P^+P^+(NH_2)_3$ dication (DFT calculations).

Table 1. Dissociation energies (δE) and lengths (l) of the P–P bond in hexaaminodiphosphonium dication $(H_2N)_3 \cdot P^+P^+(NH_2)_3$, calculated by the MP2 method with the Hartree–Fock (RHF) geometry using basis sets with different numbers of polarization d and p functions

Entry	Basis set in calculation		δE, kcal mol^{-1}	l, nm
	of energy (MP2)	of geometry (RHF)		
1	SBK+d	SBK	–3.5	0.2366
2	SBK+d	SBK+d	8.1	0.2225
3	SBK+d+p	SBK+d+p	6.7	
4	SBK+2d	SBK+2d	14.0	0.2233
5	SBK+3d	SBK+3d	15.5	0.2222

$$[X_3P^+P^+X_3] \longrightarrow 2X_3P^{+-}. \qquad (2)$$

Initially we calculated the P^+–P^+ bond energy in **II**–**VI** by the PBE method, because it gave good results as applied to calculations of the geometries of diphosphonium salts. The P^+–P^+ bond energies (δE) in **II**–**VI**, calculated by the PBE method, are given below.

Comp. no.	**II**	**III**	**IV**	**V**	**VI**	**II**
δE, kcal mol^{-1}	0.6	–16.8	–17.8	–17.3	–4.9	15.8[1]

It is seen that only hexaethyldiphosphonium cation **II** should be stable, as its dissociation energy is positive. The higher stability of **II**, compared to **III**–**VI**, may be due to the stronger donor effect of alkyl groups compared to amino groups and hence to lower positive charge on the P atoms and their weaker mutual repulsion. Although the delocalization of the positive charges over the N–P–P–N bond system in **III**–**VI** due to the overlap of the nitrogen p orbitals and phosphorus d orbitals is possible, as suggested by the tendency of the N atoms in these ions to assume the sp^2 state, it, apparently, exerts a weaker stabilizing effect on the P^+–P^+ bond as compared to the σ-donor effect of the alkyl substituents.

The PBE calculations of the P^+–P^+ bond energy suggest that amino-substituted diphosphonium cations **III**–**VI** should dissociate across the P–P bond [Eq. (2)] more readily. As the DFT calculations gave negative values of the P^+–P^+ dissociation energy, we also performed calculations by another method, MO *ab initio*.

The MP2 calculation of the P^+–P^+ bond energy using the geometry optimized on the RHF level shows that the dissociation energy in **II** is higher (by 16 kcal mol^{-1}) than that obtained by PBE calculations. The positive values obtained suggest that the MP2//RHF method describes the energy characteristics of diphosphonium salts **I** more accurately. Therefore, to evaluate the P^+–P^+ bond strength in amino-substituted diphosphonium cations, we calculated the dissociation energy of hexaaminodiphosphonium dication **VI** on the MP2//RHF level. Since the Priroda program package uses a more flexible (more split and diffuse) set of basis functions, the MP2//RHF calculations were performed with several basis sets differing in the number of diffuse d and p functions added to the atomic set of all the non-hydrogen and hydrogen atoms, respectively. Compound **VI** was chosen as a model for these calculations because of its simpler structure (which accelerates calculations) and the absence of β-methyl groups destabilizing the P^+–P^+ bond owing to the steric effect. The dissociation energies of **VI** calculated by the MP2 method with different basis sets are listed in Table 1.

Table 1 shows that the results of calculating the dissociation energy of **VI** strongly depend on the basis set used for geometry optimization. For example, when the geometry is optimized without polarization functions but these functions are subsequently included in the stage of energy calculation [MP2/(SBK + d)//RHF/SBK] (Table 1, entry no. 1), a negative P–P dissociation energy is obtained. When one polarization d function is added in the stage of geometry optimization (Table 1, entry no. 2) and the dissociation energy of **VI** is calculated at the MP2 level, also with addition of one polarization d function [MP2/(SBK + d)RHF/(SBK + d)], the dissociation energy becomes positive. Further extension of the basis set by adding polarization p functions only slightly affects (decreases) the P^+–P^+ bond energy (Table 1, entry no. 3); therefore, we did not add polarization p functions in the further calculations. Addition of the second polarization d function in the stages of geometry optimization (RHF) and energy calculation (RHF) leads to a further noticeable increase in the P^+–P^+ bond strength, and only the third polarization d function added in the stages of geometry optimization (RHF) and energy calculation (MP2) only slightly affects (increases) the energy of the cation dissociation across the P^+–P^+ bond. Thus, the quality of description of the valence shell of non-

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[1] The dissociation energy was calculated by the MP2/(SBK + d) method, and geometry, by the RHF/(SBK + d) method.

hydrogen (C, N, P) atoms is a decisive factor for valid calculation of the energy characteristics of diphosphonium cations.

The initial basis set used for optimizing the geometry of **VI** affects the calculation results not only for the $P^+–P^+$ bond energy but also for its length. For example, the $P^+–P^+$ bond length obtained by RHF/SBK calculations (Table 1, entry no. 1), i.e., without addition of polarization *d* and *p* functions, is 0.236 nm, whereas addition of polarization *d* functions (Table 1, entry nos. 2, 4, 5) gives shorter and approximately equal distances (0.222–0.223 nm). It should be noted that there is a certain correlation between the dissociation energies (δE) and $P^+–P^+$ bond lengths (l), calculated using different sets of basis functions (Table 1): More positive dissociation energies correspond to the shorter P–P bond in diphosphonium dications **I**. To a first approximation, the $P^+–P^+$ bond energy will depend on the length of this bond; therefore, with other conditions being the same, more accurate calculation of the P–P bond length in dications **I** will result in more accurate calculation of the energy parameters of these compounds.

To evaluate the reactivity of diphosphonium dications, we calculated the energies of the reactions of certain nucleophiles (NH_2^-, F^-) with hexaaminodiphosphonium (**VI**) and hexamethyldiphosphonium [$(CH_3)_3P^+P^+(CH_3)_3$ (**VII**)] cations chosen as models. The reaction energies were calculated for two possible pathways involving cleavage of the $P^+–P^+$ or $P^+–C$ ($P^+–N$) bond [Eqs. (3)–(10)]:

$$\mathbf{VI} + NH_2^- \longrightarrow (H_2N)_4P^+ + P(NH_2)_3, \quad (3)$$

$$\mathbf{VI} + 2NH_2^- \longrightarrow (H_2N)_2PP(NH_2)_2 + 2H_2NNH_2, \quad (4)$$

$$\mathbf{VII} + NH_2^- \longrightarrow (CH_3)_3P^+NH_2 + P(CH_3)_3, \quad (5)$$

$$\mathbf{VII} + 2NH_2 \longrightarrow (CH_3)_2PP(CH_3)_2 + 2H_2NCH_3, \quad (6)$$

$$\mathbf{VI} + 2F^- \longrightarrow (H_2N)_3PF_2 + P(NH_2)_3, \quad (7)$$

$$\mathbf{VI} + 2F^- \longrightarrow (H_2N)_2PP(NH_2)_2 + NH_2F, \quad (8)$$

$$\mathbf{VII} + 2F^- \longrightarrow (CH_3)_3PF_2 + P(CH_3)_3, \quad (9)$$

$$\mathbf{VII} + 2F^- \longrightarrow (CH_3)_2PP(CH_3)_2 + 2CH_3F, \quad (10)$$

Since the values initially afforded by quantum-chemical calculations refer to the gas phase, and for ionic species the solvation energy and hence the solvent effect on the reaction energy are very significant, we also calculated the energies of solvation of the ionic species in the ion–polarizable dielectric continuum approximation [9].

Table 2. Reaction energies (kcal mol^{-1}) in the gas phase and DMSO solution, according to MP2/(SBK + *nd*)// RHF(SBK + *nd*) calculations

Reaction	n	Gas	DMSO
(3)	1	–294.2	
(3)	2	–289.6	–87.8
(4)	1	–397.2	
(4)	2	–379.2	–44.8
(5)	1	–280.6	
(5)	2	–286.2	–85.5
(6)	1	–454.7	
(6)	2	–444.5	–113.9
(7)	1	–428.2	
(7)	2	–426.5	
(8)	1	–261.1	
(8)	2	–247.5	
(9)	1	–408.4	
(9)	2	–408.8	–242.6
(10)	1	–361.3	
(10)	2	–355.4	–190.1

The results of calculating the reactivity of **VI** and **VII** toward amide and fluoride ions in the gas phase and in a polar solvent (DMSO) are listed in Table 2. It is seen that the calculated reaction energies have very high negative values (from –250 to –450 kcal mol^{-1} for the gas phase) for all the considered pathways [Eqs. (3)–(10)], suggesting ready occurrence of these reactions. Calculations with the SBK + *d* and SBK + 2*d* basis sets give very similar results. Consideration of the solvation effects in DMSO considerably decreases the calculated negative reaction energies (Table 2, last column); however, the reaction energies remain negative, which suggests their ready occurrence in solution also. The weaker exothermic effect of the reaction in DMSO, compared to the gas phase, is due to considerably stronger solvation of the initial dication as compared to single-charged and neutral products.

The calculation results (Table 2) show that both hypothetical pathways of cleavage of diphosphonium salts are thermodynamically favorable. Thus, diphosphonium salts can exhibit dual reactivity. One of the reaction pathways is nucleophilic substitution at the phosphorus atom with cleavage of the P–P bond, elimination of a phosphine or aminophosphine molecule, and formation of single-charged phosphonium (quasiphosphonium) salts. Subsequent reaction of their cations with the second nucleophilic species yields phosphorane [Eqs. (3), (5), (7), (9)]. The second possible pathway is also nucleophilic substitution of phosphonium fragments, but it involves double substitution at the N [or C, in the case of reactions (6), (10)] atom. In the final substitution stage, the leaving group is tetrasubstituted diphosphine [Eqs. (4), (6), (8), (10)]. Comparison of the reaction energies (Table 2, third column) shows that, for the reactions of **VI** and **VII** with two equivalents of F^-, the first reaction pathway yielding difluorophosphoranes should be preferable [Eqs. (7), (9)]. This conclusion following from the results of quantum-chemical calculations is well consistent with the experiment. For example, Nikitin *et al.* [10, 11] showed that electrochemical oxidation of various organophosphorus compounds in the presence of fluorine-containing salts yields specifically difluorophosphoranes X_3PF_2. It should be noted that all the reactions (7)–(10) involve consumption of two equivalents of fluoride ion; hence, the energy required for desolvation of the nucleophile (very high in the case of compact fluoride ion) is the same for all the reactions. Since the double-charged diphosphonium cations under consideration have similar sizes and, correspondingly, similar solvation energies, it can be expected that the relative reactivities of these species toward two equivalents of fluoride ion will be similar in the gas phase and solution. The calculation results (Table 2) confirm this assumption.

Different conclusions can be made when analyzing the calculation results (Table 2) obtained for reactions of **VI** and **VII** with one [reactions (3), (5)] or two [reactions (4), (6)] amide ions. Since the number of reacting amide ions, which are capable of strong solvation, is different, it can be expected that the relative reactivities of diphosphonium cations in these reactions when performed in the gas phase and in solution will be different. It is seen that, with this nucleophile, the second pathway yielding diphosphines should be preferable [reactions (4), (6)]. This conclusion is apparently consistent with the experimental data on electrochemical oxidation of diaminophosphines [12]: Electrooxidation of $EtP(NEt_2)_2$ yielded as major product *sym*-bis(diethylamino)diethyldiphosphine $(Et_2N)\cdot(Et)PP(Et)(NEt_2)$. However, for hexaalkyldiphosphonium salts, the conclusion that in the reactions with amines the pathway involving cleavage of the P–C bond is preferable [Eq. (6)] disagrees with the experimental data. For example, Romakhin *et al.* [3] showed that hexaalkyldiphosphonium salts react with diethylamine in acetonitrile by the first pathway involving formation of the aminophosphonium salt and the starting tertiary phosphine [Eq. (11)]:

$$X_3P^+P^+X_3 + 2Et_2NH \longrightarrow X_3P^+NEt_2 + X_3P + Et_2N^+H_2. \tag{11}$$

Calculation of the energy of the reaction of **VII** with amide anion in dimethyl sulfoxide gives results that are better consistent with the experiment: The reaction energy for the first pathway (yielding phosphonium salt and tertiary phosphine) appeared to be more negative (–113.9 kcal mol^{-1}, against –85.5 kcal mol^{-1} for the second pathway). Thus, adequate consideration of the solvent effect on the reactivity of diphosphonium ions, indeed, may be of crucial importance.

It should also be noted that comparison of the calculation results and experimental data does not allow adequate predictions, because the actual reactivity, determined by the height of activation barriers, does not necessarily correlate with the thermodynamic characteristics of the reaction.

Thus, quantum-chemical evaluation of the stability of a new class of compounds, diphosphonium salts with two covalently bonded positively charged phosphorus atoms, showed that adequate description of the thermodynamics of these compounds is extremely sensitive to the quality of the basis set even in the stage of geometry optimization. The P–P bond energy is strongly affected by both steric factors and donor effects of substituents at the phosphorus atoms. Also, the calculations confirm that diphosphonium salts can exhibit dual reactivity: Their reactions with nucleophiles can follow pathways involving cleavage of either P–P or P–N (or P–C) bonds. Whether one or another pathway will be realized depends on the structure of the compound and specific reaction conditions.

EXPERIMENTAL

Complete geometry optimization at the restricted Hartree–Fock level was performed using the GAMESS program [6]. The inner electrons of atoms were taken into account by Stevens–Bash–Krauss effective core potentials (ECP) [7]. The Stevens–Bash–Krauss 31-split basis set for all main group elements (*ns, np*) was used. In this basis, which was extended in some cases by adding one, two, or three polarization *d* functions for all non-hydrogen atoms and one polarization p function for hydrogen atoms, we optimized the molecular geometry and calculated the vibration frequences by the restricted Hartree–Fock method. The MP2 energies and electronic properties were calculated in the basis that was extended in some cases by including additional polarization *p* and *d* functions. Calculations of MP2 corrections involved only outer shells of atoms. The reactants and products were assumed to occur in the singlet ground state. The Gibbs free energies of solvation of ions in dimethyl sulfoxide were calculated in terms of the polarizable continuum model using the solvent parameters included in the GAMESS package [9]. Complete geometry optimization at the level of the density functional theory (PBE functional [4]) was performed with the Priroda program [5]. In the calculations, we used the relativistic core potentials and the 311-split Stevens–Bash–Krauss basis set with two polarization *d* functions for nonhydrogen atoms and the 311-split basis set augmented with one polarization *p* function for hydrogen atoms. Frequency analysis was performed for all stationary points.

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