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Quantum-Chemical Investigation of Reactions of (Dialkylamino)ethynylphosphonates with Amines

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Abstract — Structural parameters and molecular energies of diethyl piperidylethynylphosphonate, dimethyl (diethylamino)ethynylphosphonate, dimethyl [2-(*t*-butylamino)-2-(diethylamino)vinyl]phosphonate, *N*,*N*-diethyl-*N*'-*t*-butyl(dimethoxyphosphinoyl)acetamidine, dimethyl [2-(diethylamino)-2-(phenylamino)vinyl]phosphonate, *N*,*N*-diethyl-*N*'-phenyl(dimethoxyphosphinoyl)acetamidine, and the cations formed by protonation of the phosphinoyl group, nucleophilic carbon atom, or nitrogen were determined by means of B3LYP/6-311G(d_5,p)&6-31G(d_5,p) quantum-chemical calculations. Acid–base properties of the related amines and their adducts with boron trifluoride in CCl_4 are estimated. The mechanism of the reactions of (dialkylamino)ethynylphosphonates with amines is discussed.

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Previously [1–4] we studied reactions of primary and secondary amines with (dialkylaminoethynyl)phosphonates. Chemo- and regiospecific addition of primary aromatic amines in the absence of acidic catalysis provides, after spontaneous prototropic isomerization, unsymmetrical phosphorylated acetamidines. By contrast, the reactions with primary aliphatic amines having bulky alkyl groups resulted in quantitative formation of (diaminovinyl)phosphonates [3]. Strong basic secondary amines add to (dialkylaminoethynyl)-phosphonates in the presence of catalysts only. With the boron trifluoride etherate catalyst in CCl_4, the reactions proceed regioselectively but not stereoselectively to form both *E* and *Z* isomers.

In this work, for explanation of the mechanism of reactions of (dialkylaminoethynyl)phosphonates with amines we performed quantum-chemical calculations of the energy and steric and electronic structure of diethyl piperidylethynylphosphonate (**I**), dimethyl (diethylamino)ethynylphosphonate (**II**), dimethyl (*Z*)- and (*E*)-[2-(*t*-butylamino)-2-(diethylamino)vinyl]-phosphonate (**III**), (*Z*)- and (*E*)-*N*,*N*-diethyl-*N*'-*t*-butyl-(dimethoxyphosphinoyl)acetamidine (**IV**), dimethyl (*Z*)- and (*E*)-[2-(diethylamino)-2-(phenylamino)vinyl]-phosphonate (**V**), (*Z*)- and (*E*)-*N*,*N*-diethyl-*N*'-phenyl-(dimethoxyphosphinoyl)acetamidine (**VI**), and cations $(\mathbf{II})_{=O}H^+$, $(\mathbf{II})_{C}H^+$, and $(\mathbf{II})_{N}H^+$, formed by protonation of molecule **II** by the phosphinoyl group, nucleophilic carbon atom, and nitrogen atom, respectively. The calculation is complicated due to the great number of possible conformers.

Molecular energies, equilibrium bond lengths, bond angles, and dihedral angles were calculated using the GAUSSIAN package [5] by the B3LYP method with the 6-311G(d_5,p) basis for the atoms entering (or belonging initially to) the amino and C≡C groups, as well as nitrogen and phosphorus, and with the 6-31G(d_5) basis for all the other atoms in the chemical compound. For each equilibrium configuration, the correspondence to a local energy minimum was confirmed by the calculated vibration spectrum. Solvent (CCl_4) effects were included by the polarized continuum model (PCM).

Atomic charges were calculated by three methods: (1) via atomic polar tensors (APT) [6], (2) via natural population analysis (NPA) [7], and (3) according to Mulliken (M) [8]. The ATP method was not applied with solvent effects included, since in this case the sum of atomic charges in a molecule or molecular ion differs from zero or ionic charge.

The nucleophilic free valence F^+ was defined as a difference between the valence {[9], formula (4.101)} and sum of bond indices [10] of a given atom and all other atoms of the virtual radical cation whose geometry is the same as the equilibrium geometry of the

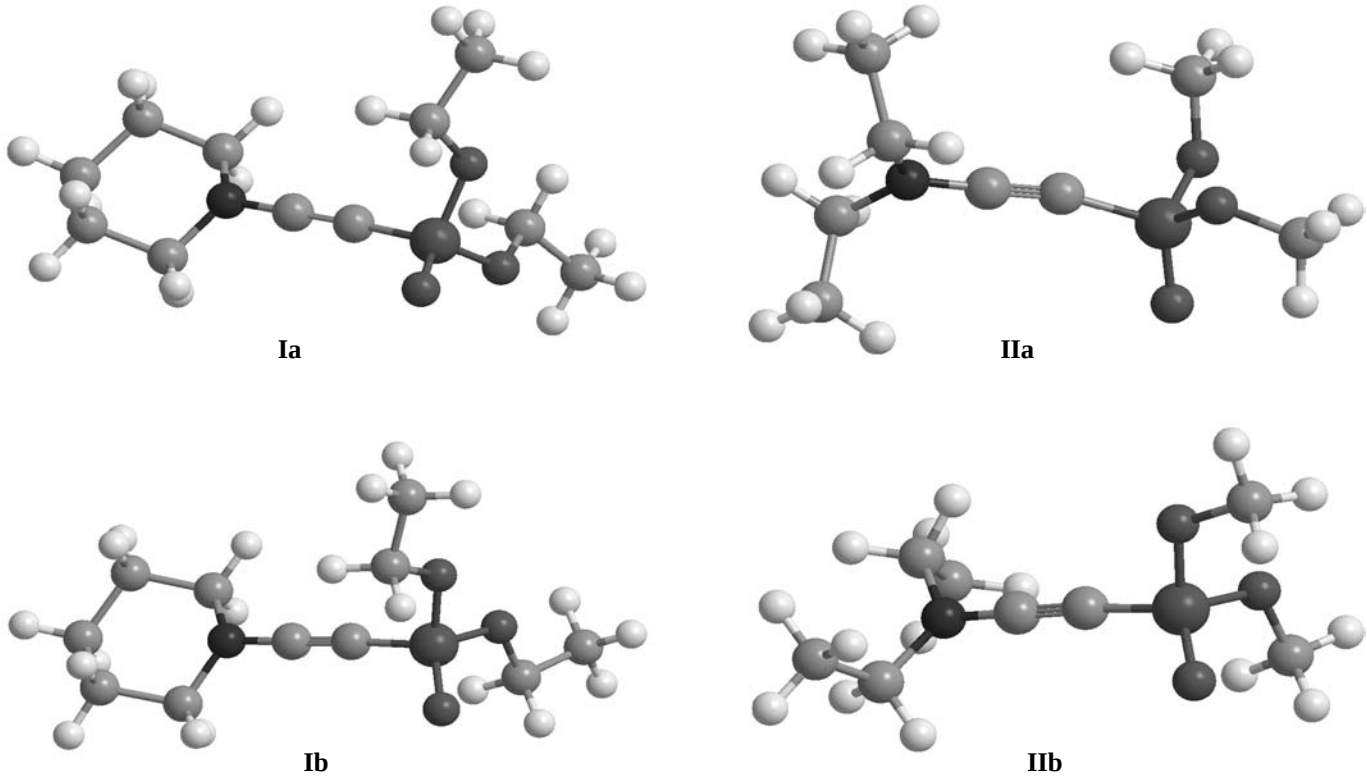


Fig. 1. Conformers (**a, b**) of (dialkylamino)ethynylphosphonates **I** and **II**.

parent molecule. From the relative F^+ values one can judge about the regioselectivity of reaction of the molecule with electrophiles.

The electrophilic free valence F^- is defined as a difference between the valence and sum of bond indices of a given atom and all other atoms of the virtual radical anion (with the geometry the same as the equilibrium geometry of the molecule) or virtual radical (with the geometry the same as the equilibrium geometry of the cation under consideration). From the relative F^- values one can judge about the regioselectivity of reaction of the molecule or cation with nucleophiles.

In the approximation used (B3LYP), the nucleophilic or electrophilic valences $F^{\pm}$ coincide with atomic spin populations and can also be calculated by an alternative formula, as a difference between the natural atomic α- and β-electron populations of the above virtual states of chemical compounds.

Molecules **I** and **II** are depicted in Fig. 1. The energy levels of conformers **b** lie below those of conformers **a**. For free molecules **I** and **II**, the energy gaps between the conformers are 0.5 and 1.6 kcal mol^{-1} and for solutions of **I** and **II** in CCl_4, 0.3 and 1.1 kcal mol^{-1}, respectively. The equilibrium structure of **I** and **II** includes the C≡C bond of normal length (1.22 Å) and carbon–nitrogen bonds much differing in length from each other: One of the NC bonds (1.32 Å) is shorter than two other N–CH_2 bonds (1.47 Å), being closer in length to an N=C double (1.26–1.30 Å [5]; 1.286–1.287 Å in **VI**) than to an N–C single bond. The phosphorus–carbon bond in the conjugated O=P–C≡C system (1.73–1.74 Å) is noticeably shorter than the single P–C bond (1.83 Å) in **VI**. The PC and C≡C bonds in (dialkylamino)ethynylphosphonates **I** and **II** are not quite collinear. The PCC angle is 174°–177° in **I** and 164°–177° in **II**. The sum of bond angles at the nitrogen atom in **I** is 354°–356°. In the equilibrium configuration of **II**, the nitrogen nucleus lies in the same plane as three neighboring carbon nuclei, and the sum of bond angles at the nitrogen atom achieves the limiting value of 360°. Obviously, the P=O and C≡C bonds and the lone electron pairs on nitrogen in **II** are stronger conjugated than in free molecule **I**.

The atomic charges and nucleophilic and electrophilic free valences are listed in Tables 1 and 2. The contrast charge distribution provides the high dipole moments of the molecules: 6–7 (**I**) and 5–6 D (**II**) in the free state and 7–9 (**I**) and 6–7 D (**II**) in CCl_4. The nitrogen nucleophilicity in **I** and **II** is very low.

Table 1. Charges Q (NPA, APT, and M) and free nucleophilic (F^+) and electrophilic (F^-) valences of atoms and atomic groups in molecule **I** and adduct **I**·BF_3 (for the lowest energy conformers)

Atom or group	Q			F^+		F^-	
	APT[a]	NPA[b]	M[a]	NPA[b]	M[c]	NPA[b]	M[c]
Compound **I**							
P	+2.66	+2.31	+1.42	0.00	0.00	0.14	0.19
C^1	–0.97	–0.57	–0.20	0.33	0.33	0.31	0.31
C^2	+0.72	+0.25	+0.08	0.06	0.08	0.35	0.32
N	–0.88	–0.49	–0.50	0.37	0.35	0.01	0.03
=O	–0.93	–1.04	–0.66	0.06	0.06	0.04	0.02
–O–	–1.14	–0.82	–0.60	0.03	0.03	0.01	0.01
C≡C	–0.25	–0.32	–0.12	0.39	0.41	0.66	0.63
P=O	+1.73	+1.27	+0.76	0.06	0.06	0.18	0.21
Adduct **I**·BF_3							
P	+2.77	+2.38	+1.52	0.00	0.02	0.17	0.21
C^1	–1.12	–0.66	–0.43	0.44	0.42	0.26	0.25
C^2	+0.92	+0.36	+0.29	0.02	0.05	0.37	0.35
N	–0.89	–0.46	–0.47	0.32	0.30	0.01	0.03
=O	–1.13	–1.01	–0.66	0.07	0.06	0.02	0.01
–O–	–1.11, –1.13	–0.83	–0.59, –0.61	0.01	0.01	0.03	0.01
C≡C	–0.22	–0.30	–0.14	0.46	0.47	0.64	0.60
P=O	+1.64	+1.37	+0.86	0.07	0.08	0.18	0.22

[a] One third of the trace of the atomic polar tensor. [b] Natural population analysis. [c] Mulliken method. The same in Tables 2, 4, and 6.

Table 2. Charges Q (NPA, APT, M) and free nucleophilic (F^+) and electrophilic (F^-) valences of atoms and atomic groups in molecule **II** and adduct **II**·BF_3 (for the lowest energy conformers)

Atom or group	Q			F^+		F^-	
	APT	NPA	M	NPA	M	NPA	M
Compound **II**							
P	+2.59	+2.30	+1.43	0.00	0.00	0.13	0.19
C^1	–0.98	–0.57	–0.19	0.36	0.36	0.31	0.31
C^2	+0.73	+0.26	+0.10	0.05	0.07	0.33	0.30
N	–0.90	–0.49	–0.49	0.38	0.36	0.01	0.03
=O	–0.91	–1.05	–0.66	0.06	0.05	0.04	0.02
–O–	–1.05, –1.10	–0.82	–0.60	0.02	0.02	0.01	0.01
C≡C	–0.25	–0.31	–0.09	0.41	0.43	0.64	0.61
P=O	+1.68	+1.25	+0.77	0.06	0.05	0.17	0.21
Adduct **I**·BF_3							
P	+2.70	+2.37	+1.51	0.01	0.02	0.17	0.22
C^1	–1.05	–0.63	–0.39	0.45	0.43	0.26	0.25
C^2	+0.83	+0.35	+0.29	0.02	0.04	0.36	0.34
N	–0.83	–0.45	–0.45	0.33	0.31	0.01	0.03
=O	–1.12	–1.03	–0.68	0.06	0.05	0.02	0.01
–O–	–1.03, –1.08	–0.81 –0.59	–0.58,	0.01	0.01	0.03	0.01
C≡C	–0.22	–0.28	–0.10	0.47	0.47	0.62	0.59
P=O	+1.58	+1.34	+0.83	0.07	0.07	0.19	0.23

Unlike piperidine and other amines listed in Table 3, these molecules are unable to expel diethyl ether from the $Et_2O \cdot BF_3$ adduct. The ester oxygen atoms in **I** and **II**, too, rank in their nucleophilicity below the oxygen in diethyl ether. When (dialkylamino)ethynylphosphonate replaces diethyl ether in $Et_2O \cdot BF_3$, it coordinates with BF_3 by the phosphinoyl group only (Figs. 2). According to quantum-chemical estimates, the bonds formed are stronger than in the boron trifluoride–aniline complex but weaker than in the complexes of boron trifluoride with *t*-butylamine or piperidine (Table 3).

The conjugation effects in adducts **I**·BF_3 or **II**·BF_3, as seen from the PC, NC, C≡C, and P=O bond lengths, are substantially stronger than in free molecules **I** and **II**. Note a strong disturbance in these adducts of the bond collinearity characteristic of the simplest acetylenes. The PCC bond angle is unexpectedly small: 131.3° in **I**·BF_3 and 134.5° in **II**·BF_3. Such bond angles are typical of a double rather than a triple CC bond. The length of the NC bond adjacent to C≡C in **I**·BF_3 and **II**·BF_3 (1.30 Å) corresponds to an N=C double bond [11].

Both these structural features of the adducts indicate an unusual cumulative nature of multiple bonds in a linear three-atomic CCN group comprising a three-coordinate nitrogen and a two-coordinate carbon atoms and suggests that the carbon atom nearest to phosphorus has a lone electron pair. Taking account of the equalization of the phosphorus–oxygen bonds, we can consider adducts **I**·BF_3 and **II**·BF_3 as phosphorylides with a basic carbon atom able to take up proton-donor amine molecules.

On adduct formation the Lewis acidity of BF_3 is transferred to its partner. The calculated electron affinities that measure the electrophilic properties of molecules **I** and **II** incorporated in adducts **I**·BF_3 and **II**·BF_3 are 21 kcal mol^{-1} higher than in the free molecules. The enhanced electrophilicity of the adducts allows them to take up nucleophiles, specifically

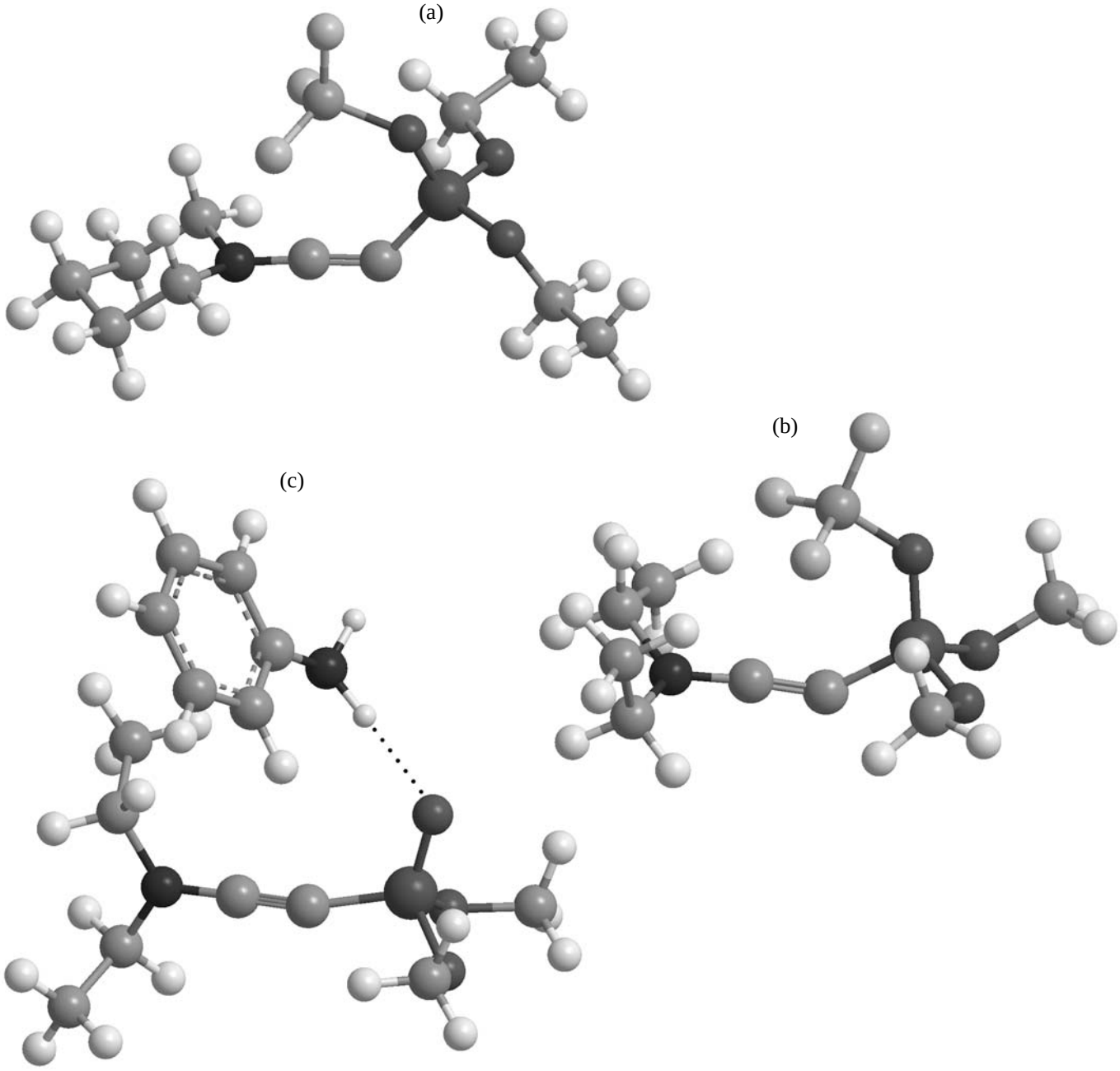


Fig. 2. Adducts of (dialkylamino)ethynylphosphonates **I** and **II** with boron trifluoride: phosphorylides (a) **I**·BF_3 and (b) **II**·BF_3 and (c) complex **II**·$PhNH_2$.

primary and secondary amines. As follows from the free electrophilic valence distributions (Tables 1 and 2), the nucleophilic nitrogen atom of the amine should attach to the carbon atom directly linked to a basic carbon atom. Thus, the reaction with amines involves the acetylenic group as a single whole; therewith, the amine H atom adds to a basic carbon atom, while the amine N atom, to an electrophilic carbon atom. In is natural to expect that such a regiospecific chemical reaction will proceed stereoselectively to form a *cis* product. The strong electric field in vicinity of the (dialkylamino)ethynylphosphonate molecule favors protolytic dissociation of thermally activated amine or its complex with boron trifluoride.

The solvent (CCl_4) reactive field increases the dipole moments of the molecules but only slightly affects the equilibrium bond lengths: The difference

Table 3. Calculated lengths and energies of the donor–acceptor bonds in boron trifluoride adducts with nucleophiles in CCl_4 [a]

Nucleophile	Bond length, Å	Bond energy, kcal mol^{-1}	Energy of replacement of diethyl ether, kcal mol^{-1}
$(CH_2)_5NH$ (ax)	1.650 (1.642)	28.8 (30.9)	13.8 (15.1)
$(CH_2)_5NH$ (eq)	1.655 (1.649)	26.9 (28.6)	11.9 (13.6)
Me_3CNH_2	1.661 (1.656)	25.0 (26.8)	10.0 (11.0)
$(MeO)_2P(\mathbf{O})C{\equiv}Et_2$	1.560	19.9	4.9
$(EtO)_2P(\mathbf{O})C{\equiv}CN(CH_2)_5$	1.560	19.5	4.5
$PhNH_2$	1.680 (1.671)	17.6 (20.1)	2.6 (4.3)
$(EtO)_2P(O)C{\equiv}C\mathbf{N}(CH_2)_5$	1.826	5.6	–9.4
Et_2O	1.650 (1.644)	15.0 (15.8)	0
$(Et\mathbf{O})_2P(O)C{\equiv}CN(CH_2)_5$	2.176	11.1	–3.9
$(EtO)_2P(O)\mathbf{C}{\equiv}CN(CH_2)_5$	1.741	10.8	–4.2
$(MeO)_2P(O)\mathbf{C}{\equiv}CNEt_2$	1.744	9.6	–5.4

[a] The coordination center in the (diethylamino)ethynylphosphonate molecule is printed bold; parenthesized are the results of higher accuracy calculations with the extended basis set 6-311G(d_5,p) not only for the NH_k atoms, but also for O, B, and F.

is no larger than 0.01 Å. An exception is boron bond lengths in the adducts: The BO distance in solvated adducts $\mathbf{I}\cdot BF_3$/solv. and $\mathbf{I}\cdot BF_3$/solv. is almost 0.02 Å shorter than in the free adducts. The minor changes in other bond lengths provide unambiguous evidence to show that solvent slightly enhances conjugation of chemical bonds in the adducts.

Along with the above-described phosphorylides $\mathbf{I}\cdot BF_3$ and $\mathbf{II}\cdot BF_3$, we detected an equilibrium $\mathbf{I}\cdot BF_3$ structure corresponding to a local energy minimum in which BF_3 is also coordinated with the phosphinoyl group of **I**, but the PC, C≡C and NC bonds are almost collinear, the conjugation effects are less pronounced, the bond energy between the components (17 kcal mol^{-1}1) is lower than in the phosphorylide and in the BF_3 adduct with aniline.

The phosphinoyl group in the (dialkylamino)ethynylphosphonate molecules is capable not only of coordinating with Lewis acids, but also of hydrogen bonding. We studied a complex of **II** with aniline, which includes an N–H···O=P bond. The hydrogen bond length is 3.01 Å, and the NHO and POH bond angles are 175° and 121°, respectively. The interaction energy between the polar molecules in the complex includes the electrostatic component and, therefore, cannot be related to the hydrogen bond only. This energy is 8 kcal mol^{-1} for the free complex and 11 kcal mol^{-1} for the complex in CCl_4.

The effect of hydrogen bonding on the structure of the (dialkylamino)ethynylphosphonates are similar to that of boron trifluoride but much weaker (see Tables 4 and 5). The PCC bond angle in the complex is reduced to 161° and the vertical electron affinity is 6 kcal mol^{-1} higher than in parent molecule **II**. Probably, the amine bound with the phosphinoyl group favors nucleophilic addition in the absence of catalysts. As follows from the calculation, the amine hydrocarbon fragment partially shields reaction centers in the (dialkylamino)ethynylphosphonate in complex $\mathbf{II}\cdot PhNH_2$, thus favoring *cis* addition of the second amine molecule (Fig. 2). However, cleavage of the hydrogen bond and amine addition to the electrophilic acetylenic group seems more probable.

The protonation of phosphonate **II** in CCl_4 by the basic carbon atom is preferred by 7.2 kcal mol^{-1} over the protonation by the phosphinoyl group and by 25.5 kcal mol^{-1} over the protonation by nitrogen (Fig. 3).

Table 4. Charges Q (NPA, APT, M) and free nucleophilic (F^+) and electrophilic (F^-) valences of atoms and atomic groups in complex $\mathbf{II}\cdot PhNH_2$ (for the lowest energy conformer)

Atom or group	Q			F^-	
	APT	NPA	M	NPA	M
P	+2.70	+2.32	+1.48	0.10	0.14
C^1	–1.04	–0.60	–0.33	0.22	0.23
C^2	+0.76	+0.30	+0.20	0.24	0.23
N	–0.88	–0.48	–0.48	0.01	0.02
=O	–1.04	–1.08	–0.70	0.03	0.02
–O–	–1.07, –1.11	–0.82	–0.59	0.01	0.00
C≡C	–0.28	–0.30	–0.13	0.46	0.46
P=O	+1.66	+1.24	+0.78	0.13	0.16

Table 5. Calculated bond lengths (Å) in molecules **I**–**VI** (the lowest energy conformers of compounds **III**–**VI** are taken)

Compound	Stereoisomer or conformer	CC	PC	NC	CN'	P=O	P–O
I	**a**	1.217	1.743	1.324	–	1.475	1.605, 1.619
	b	1.217	1.740	1.323	–	1.481	1.609, 1.609
I·BF_3	**a**	1.239	1.724	1.294	–	1.528	1.585, 1.596
	b	1.237	1.723	1.297	–	1.536	1.586, 1.587
I·BF_3/solv.	**a**	1.241	1.721	1.291	–	1.535	1.583, 1.593
	b	1.240	1.721	1.292	–	1.541	1.584, 1.585
II	**a**	1.219	1.737	1.317	–	1.477	1.619, 1.620
	b	1.218	1.728	1.317	–	1.482	1.608, 1.623
II·BF_3	**a**	1.234	1.714	1.297	–	1.522	1.587, 1.598
	b	1.237	1.709	1.296	–	1.536	1.586, 1.597
II·BF_3/solv.	**a**	1.235	1.710	1.295	–	1.528	1.585, 1.596
	b	1.239	1.708	1.293	–	1.540	1.584, 1.595
II·$PhNH_2$	**a**	1.223	1.732	1.312	–	1.484	1.601, 1.618
	b	1.223	1.721	1.310	–	1.491	1.606, 1.618
II·$PhNH_2$/solv.	**a**	1.224	1.729	1.310	–	1.486	1.603, 1.617
	b	1.223	1.719	1.309	–	1.492	1.607, 1.618
III	*Z*	1.372	1.756	1.391	1.382	1.486	1.622, 1.638
	E	1.377	1.756	1.382	1.390	1.484	1.631, 1.642
IV	*Z*	1.534	1.827	1.403	1.277	1.484	1.614, 1.618
	E	1.531	1.828	1.397	1.278	1.485	1.614, 1.617
V	*Z*	1.368	1.760	1.383	1.397	1.485	1.620, 1.637
	E	1.371	1.761	1.384	1.394	1.483	1.632, 1.633
VI	*Z*	1.526	1.827	1.379	1.286	1.483	1.613, 1.614
	E	1.526	1.827	1.376	1.287	1.483	1.613, 1.621

The weak proton-acceptor capacity of nitrogen in the (dialkylamino)ethynylphosphonates is explainable by the above-mentioned conjugation of its lone electron pair with the acetylenic bond. The vertical electron affinities of cations $(\mathbf{II})_C H^+$, $(\mathbf{II})_{=O} H^+$, and $(\mathbf{II})_N H^+$ in CCl_4 equal 132, 67, and 41 kcal mol^{-1}, respectively.

The conjugation effects in the $(\mathbf{II})_{=O} H^+$ cation reveal themselves in shortening of the PC and NC bonds and elongation of the C≡C and P=O bonds. The disturbed collinearity of the PC and CC bonds is characterized by the PCC bond angle of 158°. The length of the NC bond adjacent to C≡C (1.29 Å) corresponds to an N=C double bond [12]. The electronic effects of protonation by the phosphinoyl group are similar to those of boron trifluoride addition (cf. Tables 2 and 6).

On the contrary, the protonation by the nitrogen in dimethyl (diethylamino)ethynylphosphonate results in weakening of the conjugation effects in the O=P–C≡C–N chain and elongates all the three nitrogen–carbon bonds to 1.398, 1.546, and 1.556 Å. The P=C and C≡C bonds become almost collinear (angle 175.4°).

The most interesting is to consider the protonation by the basic carbon atom, yielding an ordinary carbon–hydrogen bond at the quasiallenic >C=C=N< group. The PCC bond angle is reduced to 117.4°. The bonds at the terminal atoms of this group occupy two orthogonal planes and the sums of bond angles at the >C= and =N< atoms are 360° each. The regiospecificity of reactions of cation $(\mathbf{II})_C H^+$ with nucleophiles is uniquely determined by the dominating electrophilic free valence of the carbon atom nearest to nitrogen (Table 6).

Addition of *t*-butylamine to **II** (**II** + *t*-$BuNH_2$ → *Z*-**III**) in CCl_4 reduces the energy of the molecular system by 23 kcal mol^{-1} (25 kcal mol^{-1} without inclusion of solvent effects); addition of aniline (**II** + $PhNH_2$ → **V** → **VI**) reduces the energy by 27 kcal mol^{-1} (30 kcal mol^{-1} without inclusion of solvent effects) for (*Z*)-**VI** and 31 kcal mol^{-1} (36 kcal mol^{-1} without inclusion of solvent effects) for (*E*)-**VI**. The energy levels of **VI** are below those of assumed intermediate **V**.

Similar amidine **IV** is not formed in the reaction **II** + *t*-$BuNH_2$ → **III**. Intramolecular hydrogen transfer

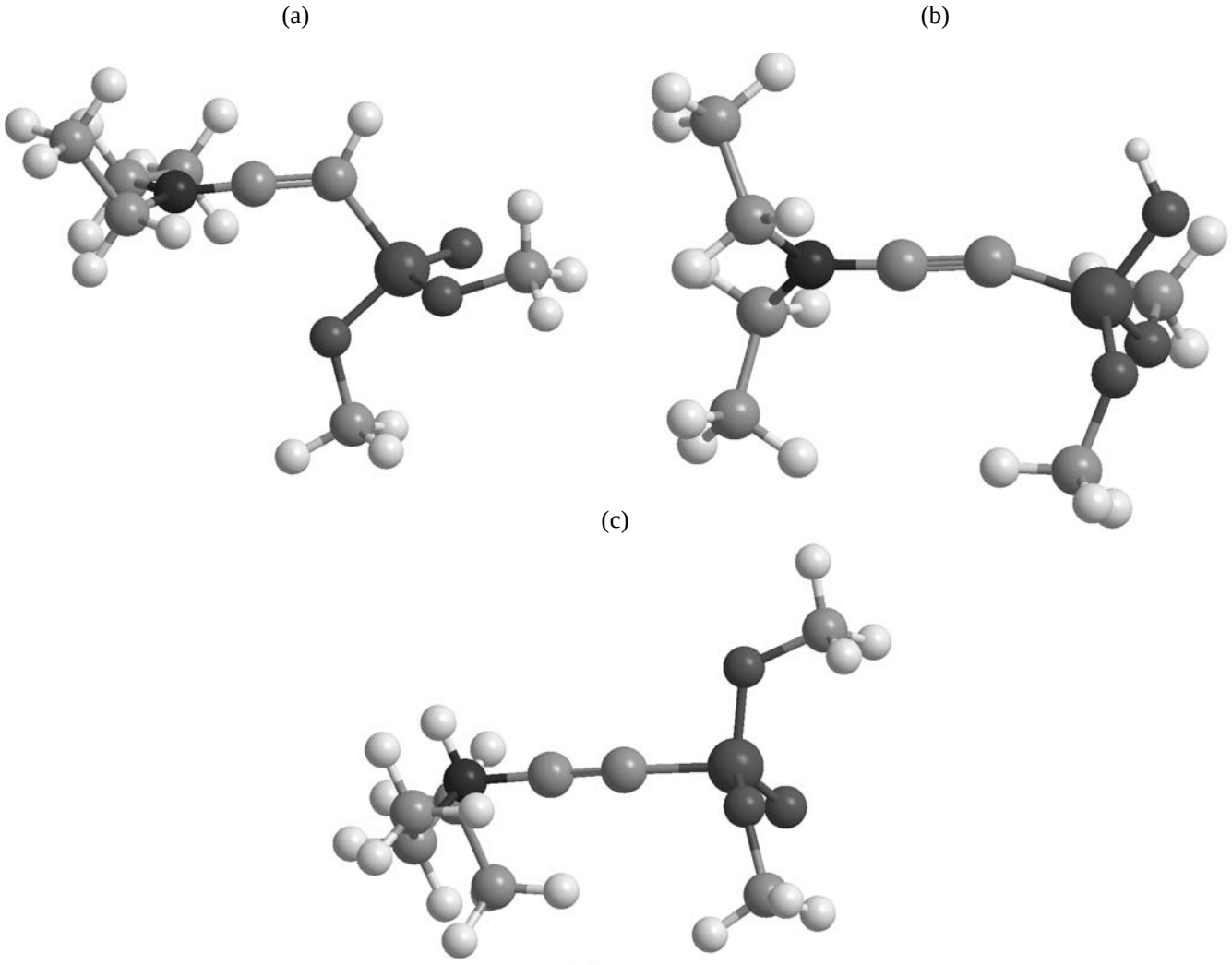


Fig. 3. Protonated forms of dimethyl (diethylamino)ethynylphosphonate (**II**) in CCl_4: (a) $(\mathbf{II})_C H^+$, (b) $(\mathbf{II})_{=O} H^+$, and (c) $(\mathbf{II})_N H^+$.

in **III** having a configuration favorable for the prototropic isomerization **III** → **IV** would produce stereoisomer (*Z*)-**IV** whose energy is higher that that of the respective conformer of molecule **III**. Moreover, it is obvious that *t*-butylamine cannot promote this prototropic isomerization of **III** by steric reasons. Forma-

Table 6. Charges *Q* (NPA, APT, M) and electrophilic free valences (F^-) of atoms and atomic groups in the protonated forms of compound **II**/solv. (solvent CCl_4)

Atom or group	*Q*		F^-		Atom or group	*Q*		F^-	
	NPA	M	NPA	M		NPA	M	NPA	M
Cation $\mathbf{II}_{=O}H^+$									
P	+2.36	+1.60	0.19	0.23	–O–	–0.80, –0.81	–0.57, –0.58	0.02	0.01
C^1	–0.71	–0.39	0.23	0.22					
C^2	+0.40	+0.26	0.39	0.37	H^+	+0.55	+0.38	0.01	0.03
N	–0.44	–0.47	0.01	0.02	C≡C	–0.31	–0.13	0.62	0.59
=O	–0.94	–0.58	0.03	0.01	P=O	+1.42	+1.02	0.22	0.24

Table 6. (Contd.)

Atom or group	Q		F^-		Atom or group	Q		F^-	
	NPA	M	NPA	M		NPA	M	NPA	M
	Cation $\mathbf{II}_C H^+$					Cation $\mathbf{II}_N H^+$			
P	+2.33	+1.47	0.07	0.06	P	+2.32	+1.47	0.06	0.08
C^1	–0.58	–0.31	0.01	0.03	C^1	–0.31	–0.06	0.22	0.20
C^2	+0.48	+0.38	0.56	0.58	C^2	+0.14	+0.07	0.20	0.20
N	–0.33	–0.41	0.22	0.20	N	–0.45	–0.50	0.04	0.02
=O	–1.02	–0.63	0.01	0.01	=O	–1.03	–0.58	0.02	0.01
–O–	–0.82, –0.84	–0.60, –0.62	0.00	0.00	–O–	–0.82, –0.81	–0.60	0.01	0.00
H^+	+0.30	+0.24	0.08	0.05	H^+	+0.47	+0.34	0.32	0.38
C≡C	–0.10	+0.07	0.57	0.61	C≡C	–0.17	+0.01	0.42	0.40
P=O	+1.31	+0.84	0.08	0.07	P=O	+1.29	+0.89	0.08	0.09

Table 7. Calculated dihedral angles (deg) in molecules **III**–**VI** (for the lowest energy conformers)

Comp. no.	Compound	Conformer	PCCN	PCCN'	CCN'C'	NCN'C'	NCN'H
III	$(MeO)_2P(O)CH=C(NEt_2)N'HCMe_3$	*Z*	–28.8	152.2	–17.3	163.6	–28.9
		E	166.5	–17.7	120.0	–64.0	158.4
IV	$(MeO)_2P(O)CH_2–C(NEt_2)=N'CMe_3$	*Z*	–95.0	84.4	167.5	–13.2	–
		E	66.1	–112.3	–1.1	–179.4	–
V	$(MeO)_2P(O)CH=C(NEt_2)N'HPh$	*Z*	–28.4	134.5	–22.4	160.0	–33.8
		E	169.4	–12.9	129.8	–52.2	154.9
VI	$(MeO)_2P(O)CH_2–C(NEt_2)=N'Ph$	*Z*	–88.7	89.4	171.2	–11.1	–
		E	78.9	–103.2	5.6	–176.4	–

Table 8. Calculated energies for compounds **II**–**VI**[a] in the free state and in CCl_4, kcal mol^{-1} (for the lowest energy conformers)

Comp. no.	Conformer	Free molecule	Molecule in solution
II	–	0	0
III	*Z*	–24.7	–22.6
	E	–26.9	–24.7
IV	*Z*	–20.3	–17.6
	E	–29.0	–25.2
V	*Z*	–25.5	–22.6
	E	–30.3	–27.8
VI	*Z*	–30.2	–27.0
	E	–35.7	–31.1

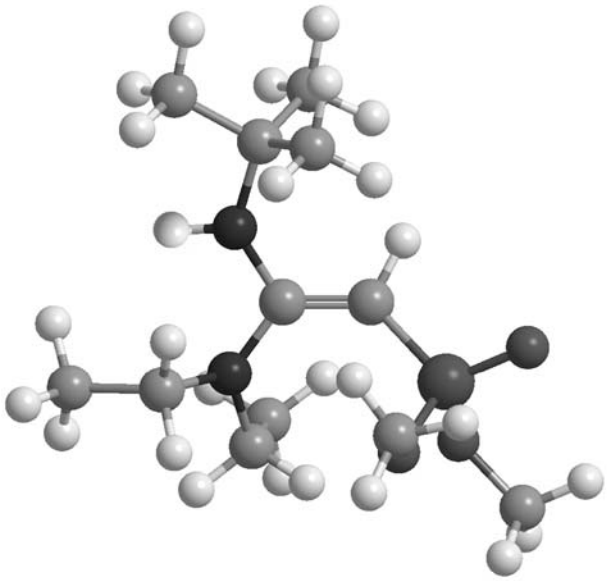
[a] The formulas of compounds **III**–**VI** are given in Table 7; compound **II** is $(MeO)_2P(O)C–CNEt_2$.

tion of (*Z*)-**IV** is unfavored by energy. However, the calculated energy of a hypothetical molecule (*E*)-**IV** is lower than those of isomers (*Z*)- and (*E*)-**III**.

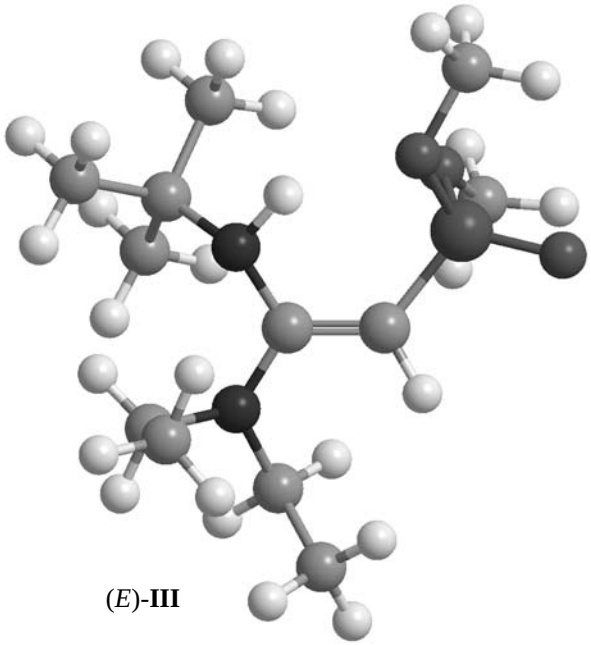
Molecules **III**–**VI** are depicted in Fig. 4. The bond lengths and angles are listed in Tables 5 and 7 and the relative energies, in Table 8.

The basicity of amines in water is thoroughly studied. However, the considered reactions of amines with (dialkylamino)ethynylphosphonates were carried out in nonaqueous media, mostly in anhydrous CCl_4. To assess the relative basicity of amines and other Lewis bases of interest in this solvent, we performed quantum-chemical calculations of formation energies for their adducts with boron trifluoride (Table 3).

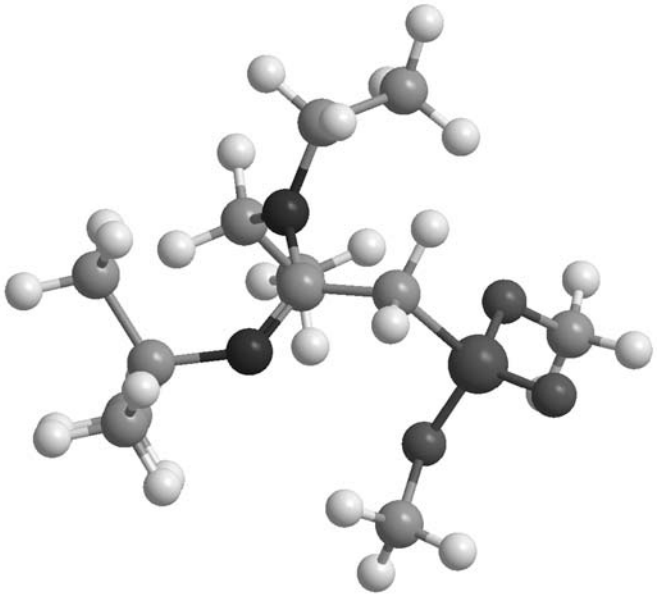
In the adducts formed by boron trifluoride (specifically, boron trifluoride etherate) with amines, the N–B bond lengths increase as the energy of the donor–acceptor bond decreases. Similar dependence is observed for the O–B donor–acceptor bond.



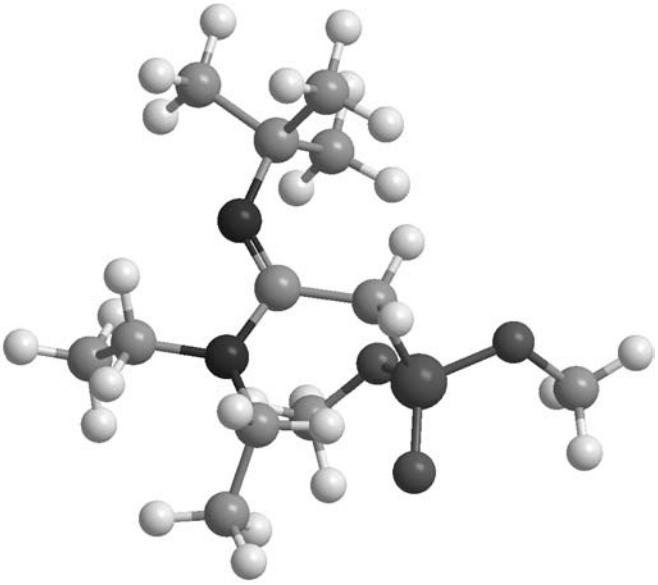
(*Z*)-**III**



(*E*)-**III**



(*Z*)-**IV**



(*E*)-**IV**

Fig. 4. Dimethyl 2-amino-2-(diethylamino)vinylphosphonate (**III**) and *N*,*N*-diethyl(dimethoxyphosphinoyl)acetamidine (**IV**).

On adduct formation between primary or secondary amines and boron trifluoride, the Lewis acidity of BF_3 endows the partner molecule, RNH_2 or R_2NH, with Brønsted acidity. This reduces the energy of proton transfer from one amine molecule to another. The calculated energy of generation of separated ion pairs $[RNH_3]^+\&[BF_3RNH]^-$ and $[R_2NH_2]^+\&[BF_3R_2N]^-$ in CCl_4 (66, 69 and 63 kcal mol^{-1} for piperidine, *t*-butylamine, and aniline, respectively) are 41–54 kcal mol^{-1} lower than those for $[RNH_3]^+\&[RNH]^-$ and $[R_2NH_2]^+\&[R_2N]^-$ (112, 123, and 105 kcal mol^{-1} in the same series). For comparison, the calculated energy of generation of the separated ion pair $[PhNH_3]^+\&[PhNH]^-$ in neat aniline is 70 kcal mol^{-1}.

The energy of proton transfer from the adducts

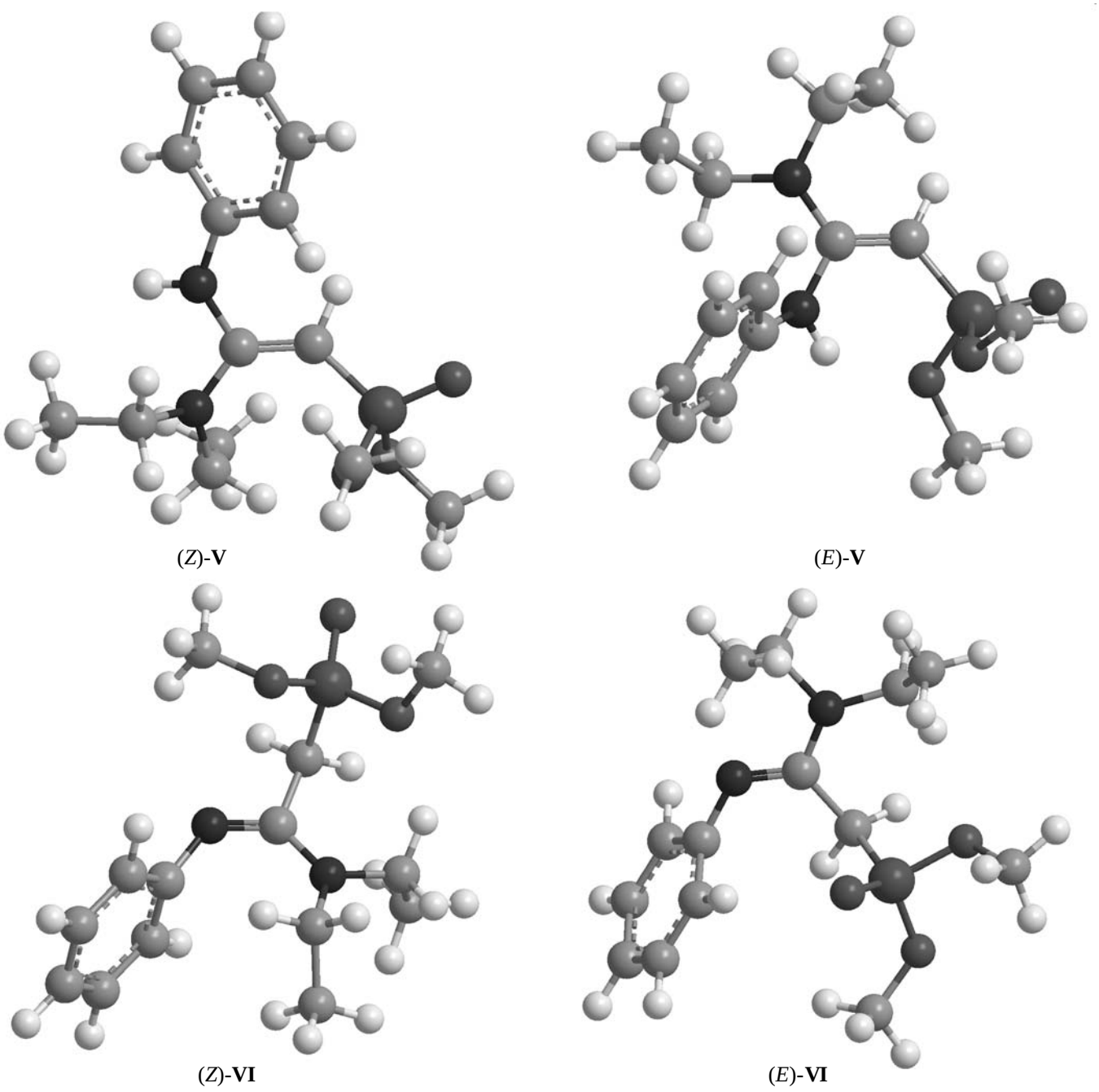


Fig. 5. Dimethyl 2-amino-2-(diethylamino)vinylphosphonate (**V**) and *N*,*N*-diethyl(dimethoxyphosphinoyl)acetamidine (**VI**).

with boron trifluoride in CCl_4 (71, 70, and 52 kcal mol^{-1} in the above series) and, in particular, from free amines (117, 123 and 93 kcal mol^{-1}) to the basic carbon atom in the (dialkylamino)ethynylphosphonates (without formation of contact ion pairs) are too high, and appearance in CCl_4 of free cations and anions in the absence of acid catalyst (Brønsted acid) seems unlikely. The contact ion pairs stabilized by Coulomb attraction between the components are more favorable, but they cannot be stable, since the distance between the nucleophilic nitrogen atom in the amine and the electrophilic carbon atom in the dialkyl aminoethynylphosphonate is too short. The short life of such an ion pair should be completed by formation of a covalent C–N chemical bond, that is, by regio- and stereospecific *cis* addition of the amine to (dialkylamino)ethynylphosphonate.

Thus, (dialkylamino)ethynylphosphonates are higly polar compounds with effective conjugation of the multiple bonds and the nitrogen lone pair. Their protonation by carbon is preferred over the protonation by the phosphinoyl group or nitrogen. Their adducts with boron trifluoride coordinated by the phosphinoyl oxygen atom are characterized by the phosphorylide structure with enhanced electrophilicity of chemically polarized acetylenic fragment which includes an electrophilic and a basic carbon atoms. Primary and secondary amines can substitute diethyl ether from boron trifluoride etherate and thus enhance their reactivity toward the basic carbon atom of the activated acetylene. *cis* Addition of amines to the acetylenic fragment is more probable than *trans* addition, and it is followed by prototropic isomerization to unsymmetrical phosphorylated amidines. But in the case of bulky aliphatic amines, the configuration of the primary adduct is unfavorable for hydrogen transfer, and the reaction stops in on)diaminovinyl)phosphonate formation.

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