Physical Chemistry

Intramolecular Y←O (Y = N, P, As, Sb, Bi) coordination in organopnictogen compounds: an *ab initio* and DFT study

V. I. Minkin, R. M. Minyaev, A. A. Milov, and T. N. Gribanova*

Institute of Physical and Organic Chemistry at Rostov State University, 194/2 prosp. Stachki, 344090 Rostov-on-Don, Russian Federation. Fax: +7 (863 2) 43 4667. E-mail: minkin@ipoc.rsu.ru

The molecular structure and rearrangements of β-pnictogenovinylaldehydes and 1,6-dioxa-6aλ^5-pnictapentalenes (Pn = N, P, As, Sb, and Bi) were studied using the *ab initio* and DFT approach. According to calculations, the quasi-cyclic conformation of β-pnictogenovinylaldehyde molecules is much more stable than their free of strain, *trans-s-trans* conformation. This stabilization is achieved due to the formation of a rather strong secondary Pn←O bond of the hypervalent type. Bicyclic structures of 1,6-dioxa-6aλ^5-pnictapentalenes (Y = P, As) with the three-center, four-electron hypervalent O—Y—O bonds are more energetically favorable than isomeric sterically unstrained monocyclic structures. The strength of the intramolecular coordination bonds (R)Y←O in β-pnictogenovinylaldehydes and of the hypervalent bonds O—Y(R)—O in 1,6-dioxa-6aλ^5-pnictapentalenes increases in the order Y = N, P, As, Sb, and Bi and with an increase in the electronegativity of the substituent R = H, Cl, and F. In contrast to their chalcogen-containing analogs, the above-mentioned quasi-cyclic and bicyclic structures of organopnictogen compounds possess low aromatic character.

Keywords: intramolecular coordination, organopnictogen compounds, molecular and electronic structure, nonempirical quantum-chemical calculations, aromaticity, heterapentalenes, hypervalent bonding, β-pnictogenovinylaldehydes.

Intra- and intermolecular donor-acceptor interactions between electron-rich centers (*viz.*, main group element atoms) determine the molecular structure of compounds;[1—6] the secondary and tertiary structures of proteins; biological activity of various enzymes and phosphorus- and selenium-containing proteins and nucleosides;[7—9] and the modes of molecular packing in crystals.[10—12] Intramolecular hypervalent coordination Chalc←O(N) (Chalc = S, Se, and Te) plays an important role in the stabilization of some thermodynamically and kinetically unstable organochalcogen compounds[4,13,14] and is responsible for the stereochemistry of the reactions at the chalcogen center.[15] A recently proposed new concept of pharmacophore bonding[16] is also based on the assumption of a specific role of intermolecular non-covalent S...O interaction between the sulfur-containing bioactive compound and the O atom of the peptide bond of an enzyme or corresponding receptor.

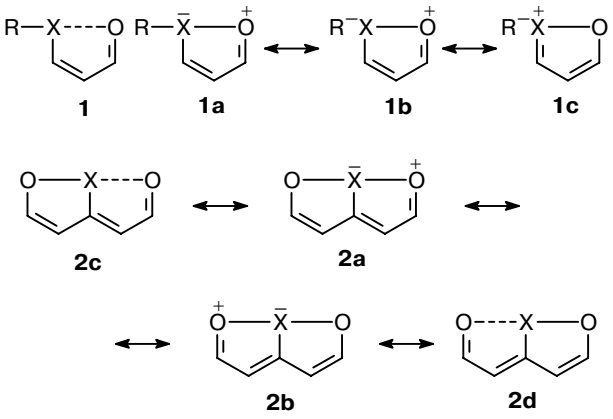
The nature of the attractive intramolecular nonbonded interaction between the chalcogen and O (or N) atoms, as well as the structural and chemical consequences of

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 11, pp. 1938—1954, November, 2001.

1066-5285/01/5011-2028 $25.00 © 2001 Plenum Publishing Corporation

this interaction (they are determined by short contact between these atoms) have been studied experimentally and theoretically in considerable detail.[1—6,17—19] The shortest Chalc←O(N) contacts occur in the case of 1,5-interaction where both atomic centers are involved in the π-conjugated system. The molecules of β-chalcogenovinylaldehydes (**1**) and 1,6-dioxa-6aλ^4-chalcapentalenes (**2**) are typical representatives of this class of systems. The electronic structures of molecules **1** and **2** are described[20—24] as the no bond resonance systems with a π-electron sextet and decet, respectively (Scheme 1).

Scheme 1



X = S, Se, Te

The strength of the secondary bonds X...O in compounds **1** and **2** can be estimated[18,19] as the difference between the total energies (ΔE) of quasi-cyclic *cis-cis* molecular conformations **1** and **2** and the corresponding free of strain, *trans-s-trans* conformations (**3** and **4**, respectively). The Chalc...O distances and ΔE values obtained from *ab initio* calculations[18,19] of these compounds and the homodesmotic stabilization energies (*HSE*),[25,26] which characterize the contribution of the aromatic stabilization energy to ΔE, are presented in Fig. 1. To provide the possibility of comparing the parameters of the secondary, or "premature hypervalent,"[17] bonds with the corresponding standard values for covalent bonds, it is convenient to introduce[27] the so-called covalency ratio factor, χ, which is calculated using the formula

$$\chi = \frac{(R_A + R_B) - d_{AB}}{(R_A + R_B) - (r_A + r_B)}.$$

Here, R_A and R_B are the van der Waals radii of the interacting nonbonded atoms; r_A and r_B are their covalent radii, and d_{AB} is the distance between the interacting centers, which is determined either experimentally or from calculations. The χ values for some chalcogen-containing compounds are also given in Fig. 1.

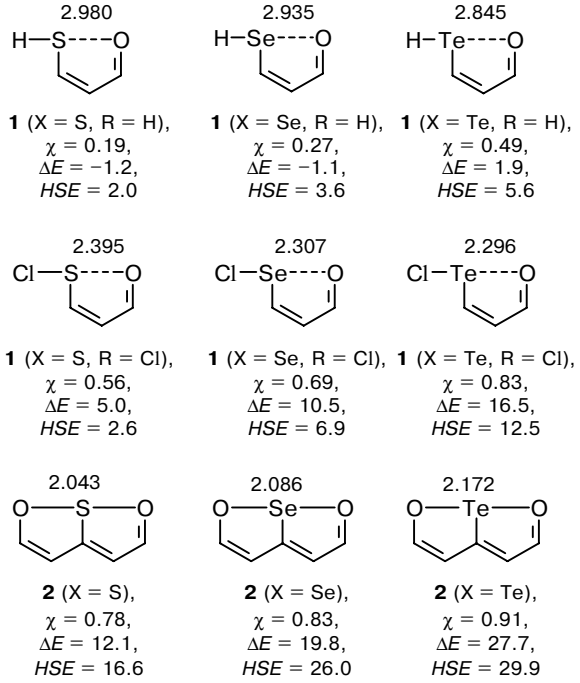
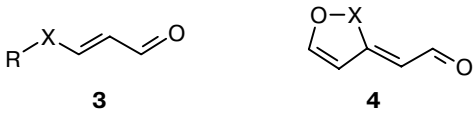


Fig. 1. Distances Chalc...O[18] (in Å); covalency ratio factors χ for Chalc...O bonds (the covalent and van der Waals radii of corresponding atoms were taken from Ref. 28**)**; energy differences (ΔE/kcal mol^{-1}) between the cyclic (**1**) and open (**3**) β-chalcogenovinylaldehyde isomers and between the bicyclic (**2**) and corresponding monocyclic (**4**) structures, and the homodesmotic stabilization energies (*HSE*/kcal mol^{-1}) calculated by the MP2(fc)/LanL2DZ method. Positive values correspond to stabilization of the cyclic structures.



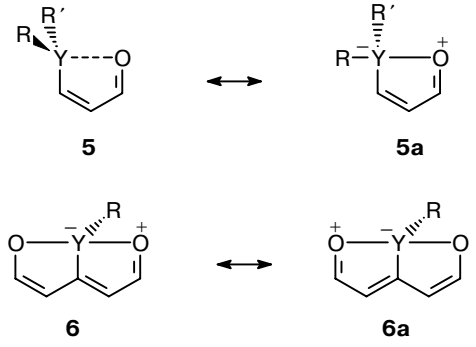
X = S, Se, Te

Analysis of the numerical data presented in Fig. 1 shows that the strength of the Chalc...O bond increases (i) in the order X = S, Se, and Te and (ii) as the electronegativity of the substituent at the chalcogen atom increases. The *cis-s-cis* conformers of molecules **1** (X = S, Se; R = H) are less energetically favorable than their sterically unstrained isomers **3**. However, replacement of the H atom at the chalcogen center by the Cl atom leads to substantial stabilization of the quasi-cyclic structure **1**. This can be explained assuming that the energy levels of the orbitals involved in the $n_O \rightarrow \sigma^*_{X-R}$ donor-acceptor interaction responsible for the energy of the secondary bond[2—6,16—19,29,30] come closer together. The aromaticity of cyclic structures **1** and **2**, which is characterized by the *HSE* values, makes the largest contribution to ΔE and increases as the covalency ratio

factor of the secondary bond Chalc...O increases. It is aromatic stabilization that is responsible for symmetric C_{2v} molecular structures of 1,6-dioxa-6aλ^4-chalcapentalenes **2**.

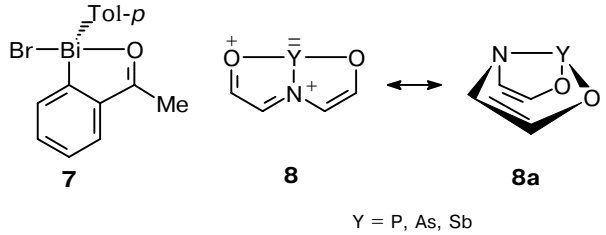
The well-studied β-chalcogenovinylaldehydes **1** and 1,6-dioxa-6aλ^4-chalcapentalenes **2** have the corresponding isoelectronic analogs **5** and **6** containing pnictogen centers (Pn = N, P, As, Sb, and Bi). However, these organopnictogen compounds have not been theoretically studied as yet, though the possibility for similar cooperative effects of hypervalent bonding and aromatic stabilization of quasi-cyclic structures to occur in molecules **5** and **6** (Scheme 2) seems not to be improbable.

Scheme 2



The ability of the pnictogen center to form hypervalent bonds in systems of the types **5** and **6** can be illustrated by the results of X-ray diffraction studies of (2-acetylphenyl)bromo(4-methylphenyl)bismuthane (**7**)[31] and 5-aza-2,8-dioxa-1-pnictabicyclo[3.3.0]octa-2,4,6-trienes (ADPnO) (**8**)[32,33] (Scheme 3).

Scheme 3



A rather strong hypervalent bond O—Bi—Br in compound **7** is due to the intramolecular coordination of the carbonyl O atom to the Bi atom. The intramolecular contact Bi...O (2.519 Å) is 1.2 Å shorter than the sum of the van der Waals radii of Bi and O atoms (this corresponds to $\chi = 0.74$). Compounds **8** are isostructural with and isoelectronic to 1,6-dioxa-6aλ^4-chalcapentalenes **2**. The barriers to stereochemical vertex inversion at the Pn center lie between 5 and 35 kcal mol^{-1} for NH_3 and NF_3 and between 35 and 85 kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}) for the trihydrides and trifluorides of other pnictogens.[34—37] Hence, one can expect that isomeric classical structure **8a** with two pyramidal, tricoordinate pnictogen centers will be much more stable than the planar conformation **8**. However, high 10π-electron aromaticity of the bicyclic pentalene-type structure **8** provides stabilization of the planar conformation **8** with a T-shaped bond configuration at the pnictogen center, as in the case of chalcogen-containing analogs **2**. Recent calculations[38] revealed the absence of local minima on the potential energy surface (PES) of classical isomer **8a** (Y = As). In contrast to this, a shallow minimum was found[38] on the PES of the phosphorus derivative with pyramidal structure **8a** (Y = P). This minimum lies only 16.6 kcal mol^{-1} higher than that corresponding to planar isomer **8** on the energy scale.

The main goal of this study was to estimate the effects of hypervalent bonding in the R—Pn—O triad and aromatic stabilization in model compounds **5** and **6** and to compare the magnitudes of these effects with those found for chalcogen-containing compounds **1** and **2** (X = S, Se, and Te).

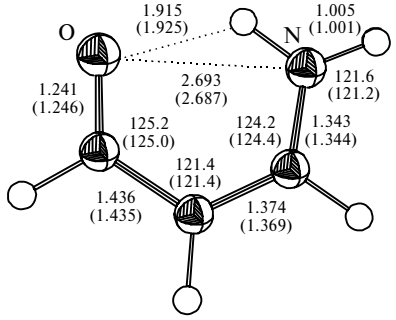
Calculation Procedure

Calculations were carried out using the *ab initio* computational scheme (MP2(full)/6-31G** and MP2(fc)/LanL2DZ)[39] and DFT approach (B3LYP/6-31G**, B3LYP/LanL2DZ) with the GAUSSIAN-94[40] and GAMESS[41] program packages. The geometries of the structures corresponding to the stationary points on the PES were optimized with the "tight" convergence criterion (GAUSSIAN-94) and up to a value of 10^{-5} au for the RMS and gradients (GAMESS). The correspondence between the structures found and the stationary points on the PES was proved by calculating the harmonic vibrational frequencies. Relativistic effects for the Sb- and Bi-containing systems were partially included by the use of the LanL2DZ pseudopotential basis set. The basis set superposition error (*BSSE*)[42] was ignored following the known recommendations.[43]

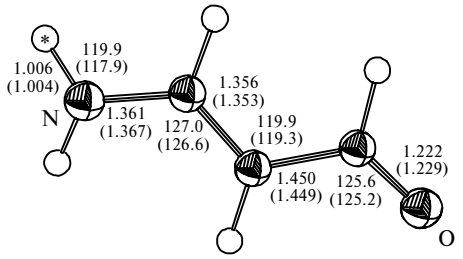
Results and Discussion

β-Pnictogenovinylaldehydes 5. According to calculations of systems **5** and **9** (Table 1, Figs. 2—5), only the molecule of β-aminovinylaldehyde **5** (Y = N, R = R′ = H) has a planar C_s conformation due to the formation of a strong intramolecular bond O...H—N.

For all other compounds **5** including those containing two H atoms at the pnictogen center, the geometry of the coordination site is mainly determined by the intramolecular interaction O→Y—R of the hypervalent type, which provides a nearly linear configuration of the O...Y—R (R = Cl, F, H) triad. The calculated angles O...Y—R lie between 150 and 167° (*cf.* 160.8° for the O...Bi—Br angle in compound **7** obtained from X-ray diffraction experiments[31]). An increase in the atomic

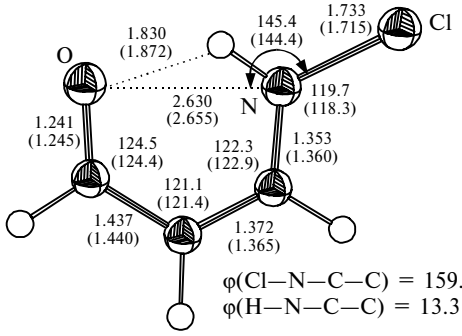


5 (Y = N, R = R′ = H), C_s



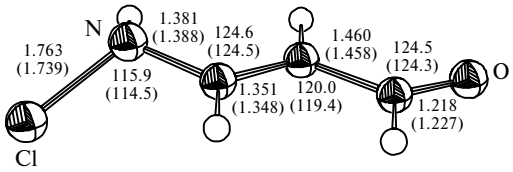
φ(H*—N—C—C) = 166.7 (159.8)

9 (Y = N, R = R′ = H), C_s



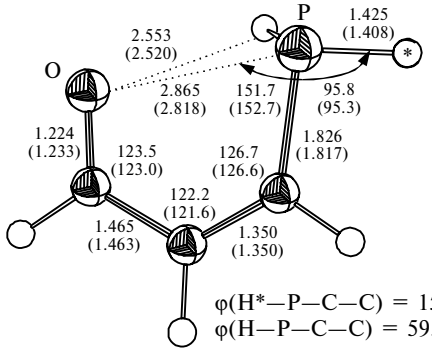
φ(Cl—N—C—C) = 159.8 (157.3)
φ(H—N—C—C) = 13.3 (16.3)

5 (Y = N, R = Cl, R′ = H), C_1



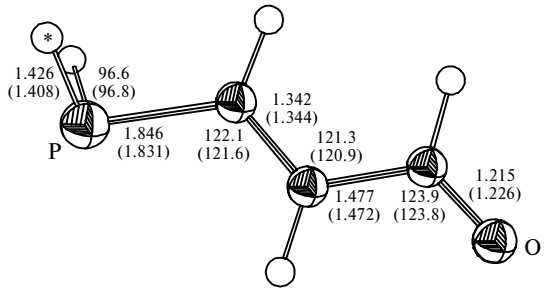
φ(Cl—N—C—C) = 147.0 (145.7)

9 (Y = N, R = Cl, R′ = H), C_1



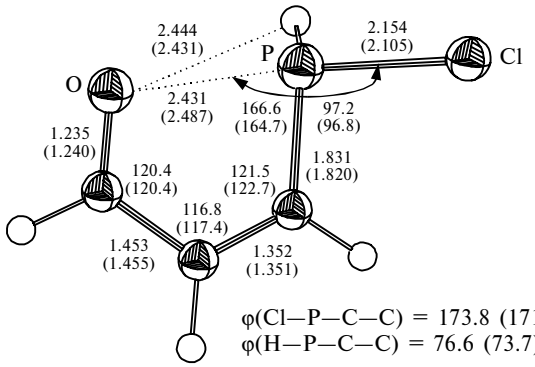
φ(H*—P—C—C) = 156.9 (158.4)
φ(H—P—C—C) = 59.0 (60.0)

5 (Y = P, R = R′ = H), C_1



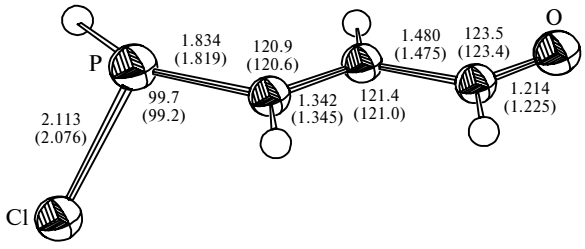
φ(H*—P—C—C) = 133.4 (132.7)

9 (Y = P, R = R′ = H), C_1



φ(Cl—P—C—C) = 173.8 (171.9)
φ(H—P—C—C) = 76.6 (73.7)

5 (Y = P, R = Cl, R′ = H), C_1



φ(Cl—P—C—C) = 135.8 (133.6)

9 (Y = P, R = Cl, R′ = H), C_1

Fig. 2. Geometric parameters of the molecules of *cis*- and *trans*-isomers of β-aminovinylaldehydes and β-phosphinovinylaldehydes and their chloro derivatives calculated by the B3LYP/6-31G** and MP2(full)/6-31G** (figures in parentheses) methods. The bond lengths are given in Å and the bond angles and dihedral angles (φ) are given in degrees.

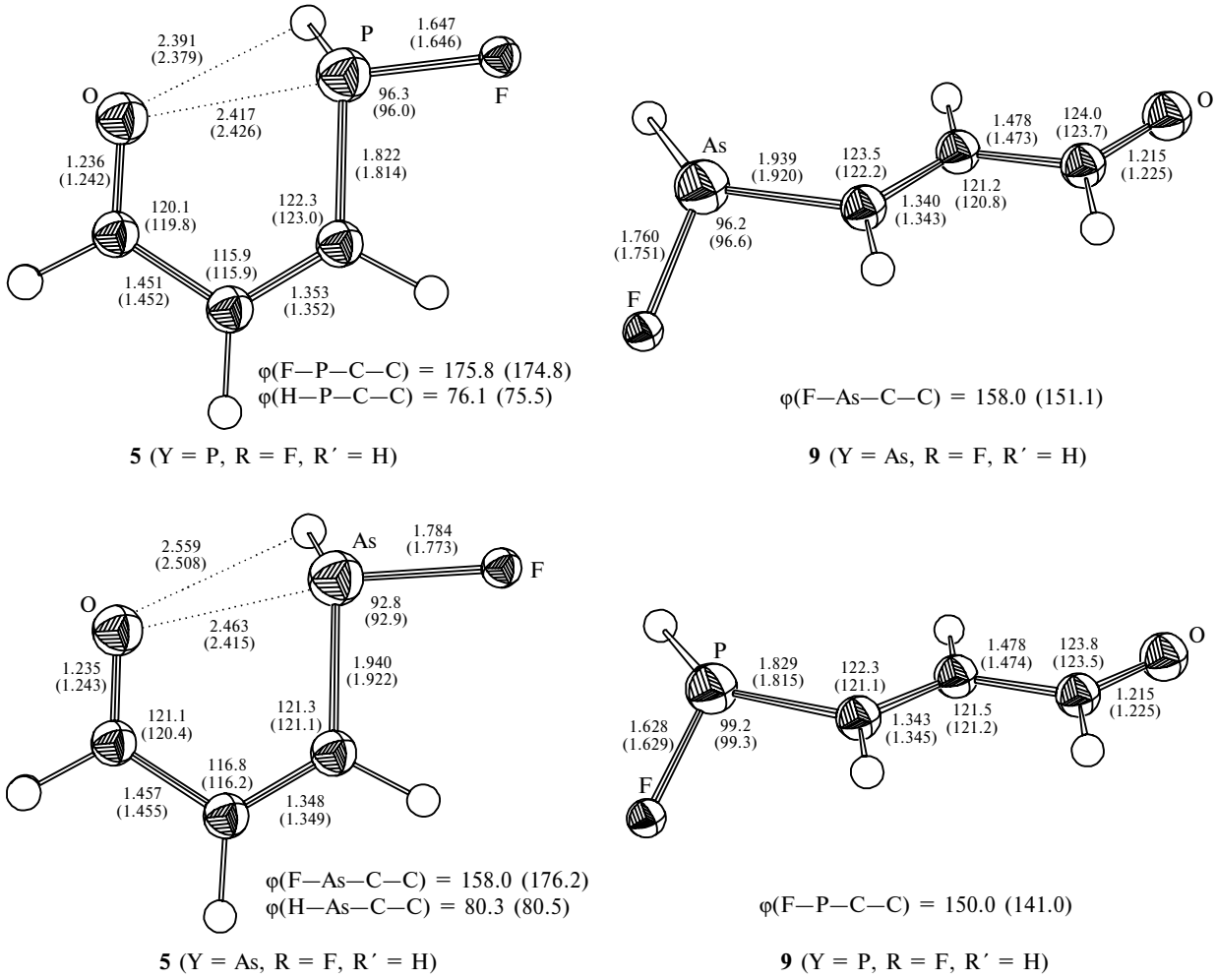
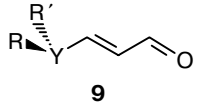


Fig. 3. Geometric parameters of the molecules of *cis*- and *trans*-isomers of β-fluorophosphinovinylaldehydes and β-fluoroarsinovinylaldehydes obtained from B3LYP/6-31G** and MP2(full)/6-31G** (figures in parentheses) calculations. The bond lengths are given in Å and the bond angles and dihedral angles (φ) are given in degrees.

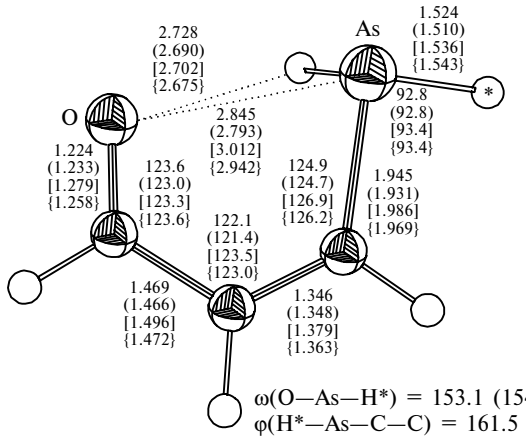
number of the pnictogen center in compounds **5** and in the electronegativity of substituent R leads to substantial increase in the angle O...Y—R. The calculated Y...O contacts in molecules **5** (Y = P, As, Sb, and Bi) are much shorter (by ~0.5—1.1 Å) than the sums of the van der Waals radii of the corresponding atoms and decrease in the order Y = P, As, Sb, and Bi (Table 2). The same is also observed for β-chalcogenovinylaldehydes **1** (X = S, Se, Te), *viz.*, the secondary bond Y...O is shortened while its covalency ratio factor χ increases as the atomic number of Y and the electronegativity of substituent R (R = H, Cl, F) increase (see Fig. 1).

Intramolecular Y←O coordination makes the *cis-s-cis* conformation **5** more stable than the strain-free *trans-s-trans* conformation **9**. The stabilization energies (ΔE) estimated as the differences between the total energies of conformations **5** and **9** are listed in Table 3. The relative thermodynamic characteristics of these conformations (they are also given in Table 3) allow one to follow the same tendency to strengthening of the hypervalent bond O→Y as that illustrated in Fig. 1.



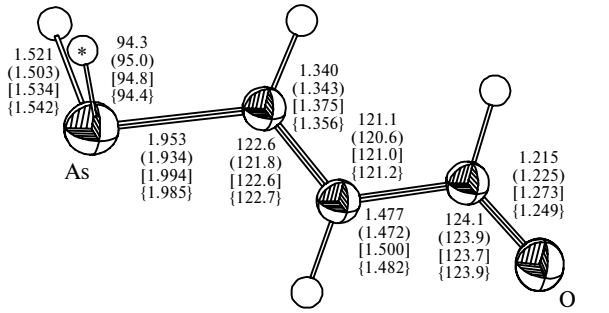
9

According to RHF calculations, the quasi-cyclic system **5** (R = R′ = H) is less energetically favorable than isomeric structure **9**. The inclusion of electron correlation, which is known to be of crucial importance for correct description of hypervalent interactions,[44] leads in the case of MP2 calculations to equalization of the energies of conformers **5** and **9** (ΔE = 1—2 kcal mol^{-1}). Indeed, in some cases[18,19,44] attempts at finding intra- and intermolecular attractive hypervalent interactions using the RHF approximation failed. The ΔE value (the energy preferableness of structure **5**) monotonically increases in the order Y = P, As, Sb, Bi and as the electronegativity of the substituent R increases. For instance, for compounds with Y = Sb (Bi) and R = Cl the ΔE values lie between 10 and 11 kcal mol^{-1}, which is comparable with the energy of a rather strong hydrogen bond.[45,46] Calculations with the LanL2DZ pseudo-



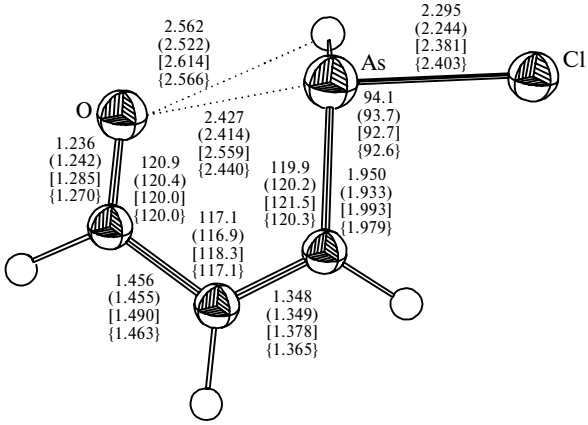
ω(O—As—H*) = 153.1 (154.2) [148.5] {149.6}
φ(H*—As—C—C) = 161.5 (163.0) [156.6] {157.7}
φ(H—As—C—C) = 69.4 (70.3) [60.9] {62.1}

5 (Y = As, R = R′ = H), C_1



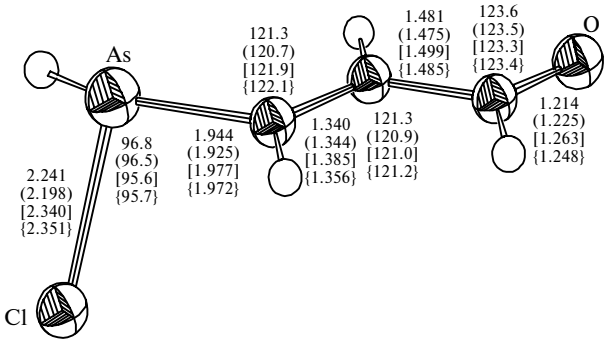
φ(H*—As—C—C) = 134.7 (134.1) [133.3] {134.0}

9 (Y = As, R = R′ = H), C_1



ω(O—As—Cl) = 164.6 (163.9) [161.2] {163.0}
φ(Cl—As—C—C) = 173.6 (173.1) [171.4] {173.3}
φ(H—As—C—C) = 81.0 (80.0) [77.5] {79.8}

5 (Y = As, R = R′ = H), C_1



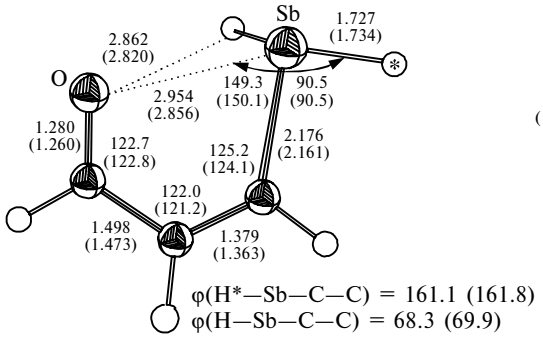
φ(Cl—As—C—C) = 125.1 (121.4) [134.1] {135.1}

9 (Y = As, R = Cl, R′ = H), C_1

Fig. 4. Geometric parameters of the molecules of *cis*- and *trans*-isomers of β-arsinovinylaldehyde and β-chloroarsinovinylaldehydes calculated by the B3LYP/6-31G**, MP2(full)/6-31G** (figures in parentheses), MP2/LanL2DZ (figures in brackets), and B3LYP/LanL2DZ (figures in braces) methods. The bond lengths are given in Å and the bond angles and dihedral angles (φ) are given in degrees.

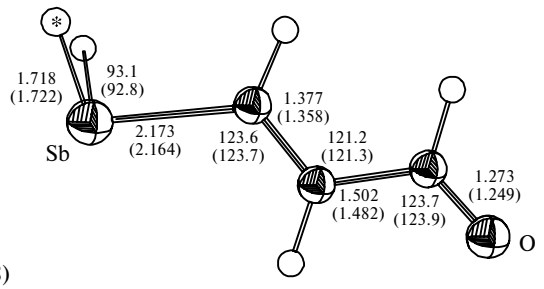
potential basis set (see Tables 2 and 3) lead to underestimation of hypervalence effects. A possible explanation consists in the fact that this basis set is not augmented with polarization functions necessary for correct description of long-range interactions.

Table 4 lists selected results obtained from analysis of the electronic structure of compounds **5** in the framework of the Natural Bond Orbital scheme (NBO analysis)[27] and we can now explain the nature of the attractive interaction between the pnictogen center and the carbonyl O atom. The energy of the stabilizing orbital interaction (see Table 4) is defined[3] as the total energy of all two-electron orbital interactions involved in electron transfer from the lone electron pair (LEP) orbital of the O atom to the antibonding Y—R orbital of the pnictogen center. The largest contribution to this energy comes from interaction between the n_O and σ^*_{Y-R} orbitals oriented along the direction of the O...YR bond. According to calculations for compounds **5** (Y = As, Sb, and Bi), the LEP of the O atom donates up to 0.15 e to the σ^*_{Y-R} orbital of the axial bond Y—Hal, whereas the degree of charge transfer to the σ^*_{Y-H} orbital of compounds **5** with R = H is nearly an order of magnitude lower. By and large, from the data listed in Table 4 it follows that the tendency to strengthening of the RY...O bonds in compounds **5** with an increase in the atomic number of Y and in the electronegativity of substituent R, found when analyzing the calculated distances Y...O and ΔE values, correlates with an increase in both the total energies of the attractive orbital interactions and the energies of the orbital interaction $n_O \rightarrow \sigma^*_{Y-R}$. This correlation emphasizes an important role of the orbital



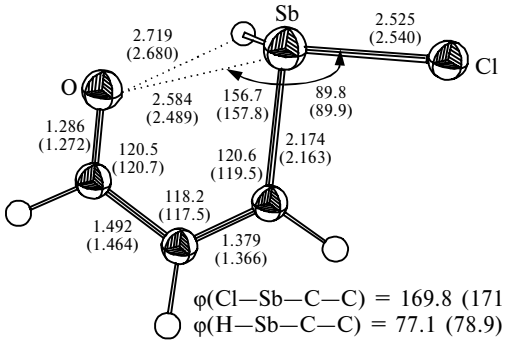
φ(H*—Sb—C—C) = 161.1 (161.8)
φ(H—Sb—C—C) = 68.3 (69.9)

5 (Y = Sb, R = R′ = H), C_1



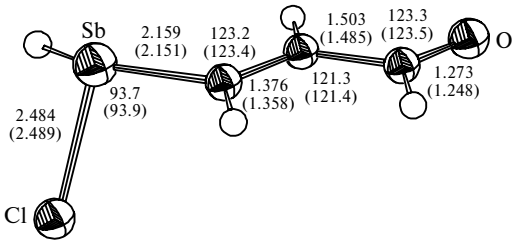
φ(H*—Sb—C—C) = 134.0 (134.7)

9 (Y = Sb, R = R′ = H), C_1



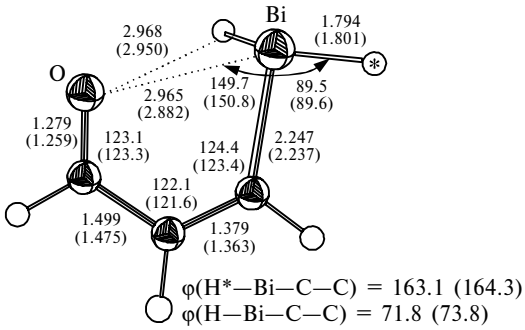
φ(Cl—Sb—C—C) = 169.8 (171.3)
φ(H—Sb—C—C) = 77.1 (78.9)

5 (Y = Sb, R = Cl, R′ = H), C_1



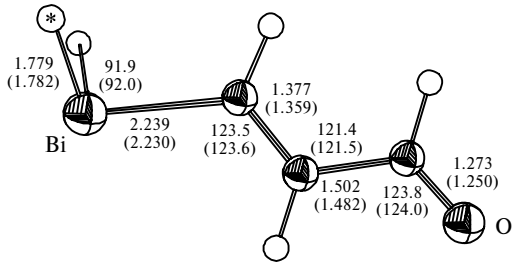
φ(Cl—Sb—C—C) = 137.3

9 (Y = Sb, R = Cl, R′ = H), C_1



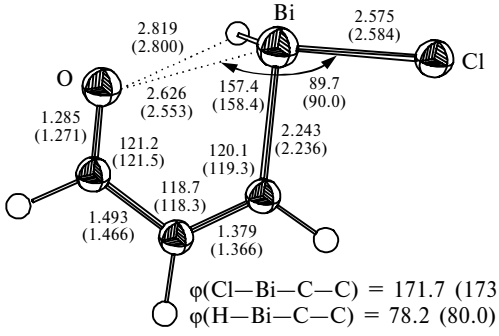
φ(H*—Bi—C—C) = 163.1 (164.3)
φ(H—Bi—C—C) = 71.8 (73.8)

5 (Y = Bi, R = R′ = H), C_1



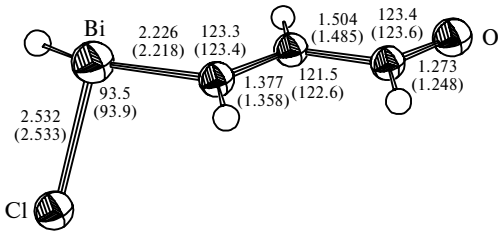
φ(H*—Bi—C—C) = 134.7 (135.2)

9 (Y = Bi, R = R′ = H), C_1



φ(Cl—Bi—C—C) = 171.7 (173.3)
φ(H—Bi—C—C) = 78.2 (80.0)

5 (Y = Bi, R = Cl, R′ = H), C_1



φ(Cl—Bi—C—C) = 135.9 (139.1)

9 (Y = Bi, R = Cl, R′ = H), C_1

Fig. 5. Geometric parameters of the molecules of *cis*- and *trans*-isomers of β-stibinovinylaldehydes and β-bismuthinovinylaldehydes and their derivatives obtained from MP2/LanL2DZ and B3LYP/LanL2DZ (figures in parentheses) calculations. The bond lengths are given in Å and the bond angles and dihedral angles (φ) are given in degrees.

Table 1. Total energies (E_{tot}), zero-point vibrational energy corrections (*ZPE*), and the lowest harmonic frequencies (ω_1) calculated by different quantum-chemical methods for the isomers **5** and **9** of β-pnictogenovinylaldehydes

YR′	Isomer	R	Computational method	$-E_{tot}$ / au	*ZPE* / au	ω_1 / cm^{-1}
NH	**5**	H	MP2(full)/6-31G**	246.585076	0.081273	170
			B3LYP/6-31G**	247.296673	0.079978	233
		Cl	MP2(full)/6-31G**	705.565577	0.071389	93
			B3LYP/6-31G**	706.842064	0.069825	93
	9	H	MP2(full)/6-31G**	246.577418	0.080813	143
			B3LYP/6-31G**	247.296673	0.079978	233
		Cl	MP2(full)/6-31G**	705.557828	0.070887	89
			B3LYP/6-31G**	706.833049	0.069422	88
PH	**5**	H	MP2(full)/6-31G**	532.780558	0.072397	141
			B3LYP/6-31G**	533.865406	0.070434	128
		F	MP2(full)/6-31G**	631.831994	0.066726	23
			B3LYP/6-31G**	633.129131	0.065201	133
		Cl	MP2(full)/6-31G**	991.837229	0.065408	99
			B3LYP/6-31G**	993.488716	0.063832	100
	9	H	MP2(full)/6-31G**	532.778814	0.071300	99
			B3LYP/6-31G**	533.865406	0.070443	128
		F	MP2(full)/6-31G**	631.823054	0.065642	56
			B3LYP/6-31G**	633.119800	0.064023	65
		Cl	MP2(full)/6-31G**	991.830729	0.064560	57
			B3LYP/6-31G**	993.481501	0.063074	47
AsH	**5**	H	MP2(full)/6-31G**	2424.102714	0.070830	136
			B3LYP/6-31G**	2426.272736	0.068977	128
			MP2/LanL2DZ	197.633745	0.067650	111
			B3LYP/LanL2DZ	198.586138	0.068162	115
		F	MP2(full)/6-31G**	2523.156261	0.065225	22
			B3LYP/6-31G**	2525.537395	0.063570	126
		Cl	MP2(full)/6-31G**	2883.174803	0.064441	96
			B3LYP/6-31G**	2885.910190	0.062800	95
			MP2/LanL2DZ	211.823249	0.061243	80
			B3LYP/LanL2DZ	212.969615	0.061892	89
	9	H	MP2(full)/6-31G**	2424.099280	0.069709	78
			B3LYP/6-31G**	2426.270156	0.068066	79
			MP2/LanL2DZ	197.633649	0.066810	91
			B3LYP/LanL2DZ	198.585155	0.067300	62
		F	MP2(full)/6-31G**	2523.140997	0.063900	57
			B3LYP/6-31G**	2525.523759	0.062372	62
		Cl	MP2(full)/6-31G**	2883.162099	0.063287	48
			B3LYP/6-31G**	2885.897651	0.061848	36
			MP2/LanL2DZ	211.814911	0.060461	47
			B3LYP/LanL2DZ	212.958242	0.061092	41
SbH	**5**	H	MP2/LanL2DZ	196.915161	0.065205	116
			B3LYP/LanL2DZ	197.864525	0.065894	122
		Cl	MP2/LanL2DZ	211.125892	0.059911	82
			B3LYP/LanL2DZ	212.267299	0.060551	86
	9	H	MP2/LanL2DZ	196.913275	0.064379	8
			B3LYP/LanL2DZ	197.861408	0.065021	61
		Cl	MP2/LanL2DZ	211.112535	0.058883	43
			B3LYP/LanL2DZ	212.250749	0.059564	39
BiH	**5**	H	MP2/LanL2DZ	196.949150	0.064053	117
			B3LYP/LanL2DZ	197.904831	0.064718	125
		Cl	MP2/LanL2DZ	211.316769	0.059062	72
			B3LYP/LanL2DZ	212.316769	0.059695	75
	9	H	MP2/LanL2DZ	196.946869	0.063352	81
			B3LYP/LanL2DZ	197.901494	0.064056	67
		Cl	MP2/LanL2DZ	211.154938	0.058112	40
			B3LYP/LanL2DZ	212.298735	0.058824	35

Table 2. Contacts Y...O (*r*) in the molecules of *cis-s-cis* conformers of β-pnictogenovinylaldehydes **5** and the covalency ratio factors (χ) for secondary bonds Y...O calculated by the MP2(full)/6-31G** (*A*) and MP2/LanL2DZ (*B*) methods

Y—R′	R	*r*/Å		χ	
		A	*B*	*A*	*B*
N—H	H	2.687	—	0.18	—
	Cl	2.655	—	0.20	—
P—H	H	2.818	—	0.33	—
	Cl	2.487	—	0.54	—
	F	2.426	—	0.58	—
As—H	H	2.690	2.702	0.48	0.47
	Cl	2.522	2.614	0.59	0.53
	F	2.415	—	0.65	—
Sb—H	H	—	2.862	—	0.50
	Cl	—	2.719	—	0.59
Bi—H	H	—	2.968	—	0.53
	Cl	—	2.819	—	0.62

Table 3. Energy differences calculated without (ΔE) and with inclusion of zero-point vibrational energy correction (ΔE_{ZPE}), standard enthalpy differences ($\Delta H°$), and free Gibbs energy differences ($\Delta G°$) between the *cis-s-cis* conformers of β-pnictogenovinylaldehydes **5** and isomers **9** calculated by different quantum-chemical methods

YR′	R	Computational method	ΔE / kcal mol^{-1}	ΔE_{ZPE} / kcal mol^{-1}	$\Delta H°$ / kcal mol^{-1}	$\Delta G°$ / kcal mol^{-1}
NH	H	MP2(full)/6-31G**	5.2	4.9	5.1	4.8
		B3LYP/6-31G**	5.2	4.7	5.0	4.4
	Cl	MP2(full)/6-31G**	4.9	4.6	4.8	4.2
		B3LYP/6-31G**	5.7	5.4	5.7	5.1
PH	H	MP2(full)/6-31G**	1.1	0.4	0.8	−0.2
		B3LYP/6-31G**	0.9	0.4	0.7	−0.4
	F	MP2(full)/6-31G**	5.6	4.9	5.4	4.0
		B3LYP/6-31G**	5.9	5.1	5.6	4.0
	Cl	MP2(full)/6-31G**	4.1	3.6	3.9	2.7
		B3LYP/6-31G**	4.5	4.1	4.4	3.0
AsH	H	MP2(full)/6-31G**	2.2	1.5	1.9	0.7
		B3LYP/6-31G**	1.6	1.0	1.4	0.3
		MP2/LanL/2DZ	0.1	−0.5	−0.2	−1.0
		B3LYP/LanL2DZ	0.8	0.1	0.5	−0.7
	F	MP2(full)/6-31G**	9.6	8.7	9.2	7.5
		B3LYP/6-31G**	8.6	7.8	8.3	7.0
	Cl	MP2(full)/6-31G**	8.0	7.3	7.6	6.1
		B3LYP/6-31G**	7.9	7.3	7.7	6.0
		MP2/LanL2DZ	5.2	4.7	5.1	3.7
		B3LYP/LanL2DZ	7.1	6.6	7.0	5.4
SbH	H	MP2/LanL2DZ	0.7	1.2	0.5	−0.5
		B3LYP/LanL2DZ	2.0	1.4	1.8	0.5
	Cl	MP2/LanL2DZ	8.4	7.7	8.1	6.5
		B3LYP/LanL2DZ	10.4	9.8	10.2	8.4
BiH	H	MP2/LanL2DZ	1.4	1.0	1.3	0.3
		B3LYP/LanL2DZ	2.1	1.7	2.1	0.8
	Cl	MP2/LanL2DZ	9.5	8.9	9.3	7.6
		B3LYP/LanL2DZ	11.3	10.8	11.2	9.4

Note. Positive ΔE values denote stabilization of the cyclic structures **5**.

Table 4. Total energies (E) of the orbital interaction between the YHR fragment and the carbonyl O atom in structures **5** calculated in the framework of the NBO analysis by the MP2(full)/6-31G** and MP2/LanL2DZ methods

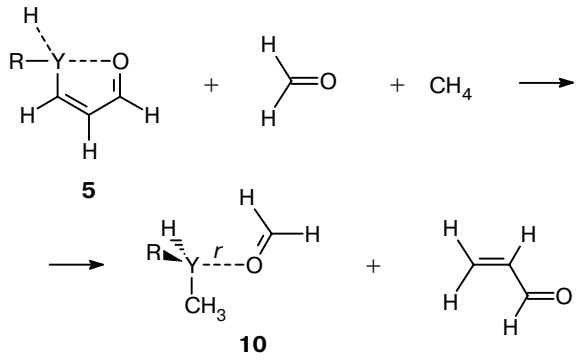
YR′	R	E/kcal mol^{-1}	
		MP2(full)/6-31G**	MP2/LanL2DZ
PH	H	3.0 (2.1)	—
	F	15.9 (11.6)	—
	Cl	19.2 (14.3)	—
AsH	H	4.8 (3.3)	3.6 (2.4)
	F	21.1 (15.4)	—
	Cl	26.5 (19.8)	30.3 (22.7)
SbH	H	—	7.3 (4.0)
	Cl	—	29.4 (20.3)
BiH	H	—	8.0 (4.3)
	Cl	—	27.3 (19.0)

Note. Figures in parentheses correspond to the strongest orbital interaction $n_O \rightarrow \sigma^*_{Y-R}$.

interaction $n_O \rightarrow \sigma^*_{Y-R}$ in the determination of the properties of the secondary pnictogen—oxygen bonds in compounds **5**, similarly to the case of their chalcogen-containing analogs **1**.[2,3,6,16—19,47] Yet another important component of the O→Pn interaction, which stabilizes the conformation **5**, is electrostatic attraction between the positively charged pnictogen atom (according to NBO analysis data, the Pn atom carries a charge ranging from +0.35e for the P atom at R = R′ = H to +1.17e for the Bi atom at R = Cl, R′ = H) and negatively charged O atom of the carbonyl group whose charge varies between −0.5 and −0.6e.

As mentioned above, stabilization of the *cis-s-cis* conformation of β-chalcogenovinylaldehydes **1** (X = S, Se and Te)[19] is to a great extent due to the large contribution of the aromaticity of the 6π-electron pseudocyclic structure of these compounds. In β-pnictogenovinylaldehydes **5** the lone electron pair of the pnictogen center can also be involved in the formation of the π-electron sextet. To estimate the contribution of aromatic stabilization of molecules **5** to ΔE, we calculated the *HSE* values for the reaction shown in Scheme 4.

Scheme 4



This reaction is analogous to that used previously[19] in the evaluation of homodesmotic stabilization energies of β-chalcogenovinylaldehyde molecules **1** (X = S, Se, and Te).

The *HSE* values represent the energy contribution of cyclic electron delocalization and can be considered as analogs of Dewar′s resonance energy.[26,48] Although no unambiguous homodesmotic reaction (in which the number of chemical bonds of each formal type is retained in both reactants and products) can be constructed for compounds **5**, the reaction shown in Scheme 4 can serve as a reasonable approximation for estimating the *HSE* values. The only deviation from the above condition is the difference between the number of C_{sp^3}—H and C_{sp^2}—H bonds in reactants (four and five, respectively) and products (three and six, respectively). However, a small difference in the energies of these bonds has little effect on the *HSE* values obtained and, hence, does not affect the principal conclusions. To exclude overestimated stabilization of the bimolecular complexes **10** due to the formation of not only the coordination bond, but also additional hydrogen bonds YH...O and CH...Cl between monomers (see, *e.g.*, the structures[18] of bimolecular complexes $H_2CO...R_2X$, where X = S, Se, and Te), the dimer energies (Table 5) were calculated for the conformation **10** in which only the RY...O interaction occurs. (The angles Me—Y—O and Y—O—CH_2 were assumed to be equal to 90° and 120°, respectively, while the rest geometric parameters were treated as independent variables.) As could be expected, variation of the pnictogen center (in the order Y = N, P, As, Sb, Bi) and substituent at Y (in the order R = H, Cl, F) leads to an increase in the stabilization energy of complex **10** and to a progressive shortening of the Y...O distance (r) as compared to the sum of the van der Waals radii. It should be emphasized that the adducts **10** formed by amines (Y = N) and methylphosphine (Y = P, R = H) are stabilized ($E_{st} > 0$) solely by the electrostatic interaction. The calculated Y...O distances in these complexes are longer than the sum of the van der Waals radii of corresponding atoms.

From the data listed in Table 5 it follows that, in contrast to high *HSE* of β-chalcogenovinylaldehydes **1** (see Fig. 1), the *HSE* values calculated for all compounds **5**, except for the nitrogen derivatives (Y = N), are rather small or negative. This suggests the absence of aromaticity in β-pnictogenovinylaldehydes **5** (Y = P, As, Sb, and Bi) and is also supported by retention of considerable variations in the lengths of the alternating carbon—carbon bonds, $\Delta l = l_{C-C} - l_{C=C}$ ($\Delta l \approx 0.11$—0.13 Å) in the quasi-cyclic structures **5**, similarly to those found for the open conformations **9** (see Figs. 2—5 and Table 6). On the other hand, β-chalcogenovinylaldehydes **1** are characterized by substantial equalization of the carbon—carbon bond lengths (*i.e.*, by a decrease in Δl) as compared to linear isomers **3**, especially for the compounds with electronegative substituent (Cl) at the chalcogen center.

Table 5. Total energies (E_{tot}/au), distances Y...O (r/Å), and stabilization energies (E_{st}/kcal mol^{-1}) of complexes **10** and the homodesmotic stabilization energies (*HSE*/kcal mol^{-1}) of β-pnictogenovinylaldehydes **5** calculated by different quantum-chemical methods

YR′	R	Computational method	$-E_{tot}$	r	E_{st}[a]	*HSE*
N	H	MP2(full)/6-31G**	209.751327	3.25	0.8	21.2
		B3LYP/6-31G**	210.367356	3.36	0.3	24.2
	Cl	MP2(full)/6-31G**	668.745239	3.05	2.2	12.8
		B3LYP/6-31G**	669.927864	3.13	1.6	14.7
P	H	MP2(full)/6-31G**	495.974747	3.35	1.9	3.7
		B3LYP/6-31G**	496.970238	3.53	1.0	2.7
	F	MP2(full)/6-31G**	595.0231112	3.04	3.6	0.0
		B3LYP/6-31G**	596.229281	3.12	2.5	−0.2
	Cl	MP2(full)/6-31G**	955.030647	3.15	3.3	4.1
		B3LYP/6-31G**	956.592969	3.10	2.9	3.1
As	H	MP2(full)/6-31G**	2387.298857	3.21	3.8	2.4
		B3LYP/6-31G**	2389.383494	3.21	5.1	−1.0
		MP2/LanL2DZ	160.871849	3.58	1.0	2.3
		B3LYP/LanL2DZ	161.697108	3.70	0.5	0.8
	F	MP2(full)/6-31G**	2486.347236	2.86	7.2	−3.9
		B3LYP/6-31G**	2488.639711	2.92	6.1	−4.2
	Cl	MP2(full)/6-31G**	2846.368742	2.92	7.1	0.3
		B3LYP/6-31G**	2849.017857	2.89	7.9	1.0
		MP2/LanL2DZ	175.060970	2.95	4.5	−2.7
		B3LYP/LanL2DZ	176.078692	2.90	3.4	3.5
Sb	H	MP2/LanL2DZ	160.151659	3.61	1.3	2.2
		B3LYP/LanL2DZ	160.973861	3.65	0.8	0.6
	Cl	MP2/LanL2DZ	174.359225	2.99	5.3	−3.1
		B3LYP/LanL2DZ	175.372058	2.96	4.8	−5.1
Bi	H	MP2/LanL2DZ	160.185060	3.53	1.7	2.3
		B3LYP/LanL2DZ	161.013676	3.53	1.1	0.6
	Cl	MP2/LanL2DZ	174.402857	2.95	6.4	−3.8
		B3LYP/LanL2DZ	175.421043	2.93	5.8	−5.7

[a] Calculated as the difference between the total dimer energy and the sum of the total energies of isolated monomers.

The electronic structures of β-chalcogenovinylaldehydes **1** (X = Chalc) and their pnictogen-containing analogs **5** (Y = P, As, Sb, and Bi) differ in that the Pn atom has only one LEP n_Y and that the LEP orientation controlled by the stereochemistry of the coordination site in molecules **5** is unfavorable for optimum interaction with the π-system of the fragment —CH=CH—CH=O. As follows from NBO analysis data, the angle between the orbital n_Y and the five-membered ring plane varies from ~30° to 45°, the LEP orbital is characterized by rather low p-character, and its hybridization lies between $sp^{0.6}$ for the phosphorus derivative **5** (Y = P, R = H) and $sp^{0.2}$ for the bismuth derivative **5** (Y = Bi, R = Cl). Figure 6 shows that the coordination polyhedron of bonds at the pnictogen atom in molecules **5** corresponds to a distorted trigonal bipyramid with the LEP (a phantom ligand) in equatorial position. This geometry of the coordination site seems to be less favorable for cyclic π-electron delocalization compared to that of the chalcogen-containing analogs **1**, in which one of the LEP orbitals of the hypervalent center is an unperturbed p_z-orbital.[50]

Table 6. Alternation degree of carbon—carbon bonds, $\Delta l = l_{C-C} - l_{C=C}$, in the cyclic (*A*) and open (*B*) conformations of β-chalcogenovinylaldehydes (**1** and **3**, respectively) and β-pnictogenovinylaldehydes (**5** and **9**, respectively), and homodesmotic stabilization energies (*HSE*) for the cyclic structures **1** and **5** calculated by the MP2/LanL2DZ method

X[a] or YH	R	Δ*l*/Å		*HSE* /kcal mol^{-1}
		A	*B*	
		β-Chalcogenovinylaldehydes[18,19]		
S[b]	H	0.098	0.110	2.0
	Cl	0.062	0.113	2.6
Se	H	0.106	0.118	3.6
	Cl	0.067	0.125	6.9
Te	H	0.098	0.137	5.6
	Cl	0.048	0.124	12.5
		0.056[c]	—	—
		β-Pnictogenovinylaldehydes		
PH[d]	H	0.113	0.128	3.7
	Cl	0.104	0.130	4.1
AsH	H	0.117	0.125	2.3
	Cl	0.112	0.114	−2.7
SbH	H	0.120	0.125	2.2
	Cl	0.113	0.127	−3.1
BiH	H	0.120	0.125	2.3
	Cl	0.114	0.127	−3.8

[a] Listed are the substituents X for β-chalcogenovinylaldehydes or YH for β-pnictogenovinylaldehydes.
[b] Obtained from MP2/6-31+G** calculations.[18]
[c] Calculated by the MP2/6-31G** method.
[d] The results of X-ray study of 3-(*p*-methoxyphenyl)-5-phenyl-1,2-oxatellurolyl-1-ium chloride.[49]

β-Aminovinylaldehydes and β-*N*-(chloro)aminovinylaldehydes **5** (Y = N) represent a distinct exception. As a result of planarity of their structure (the sum of the bond angles at the N atom is 360 and 351°, respectively), in both molecules the LEP axis of the N atom is normal to the plane of the conjugated ring stabilized by the intramolecular bond N—H...O. This leads to rather high *HSE* values and to considerable equalization of the carbon—carbon bond lengths in the conformation **5** (Y = N) of these compounds as compared to structure **9** (see Fig. 2). Important role of the resonance stabiliza-

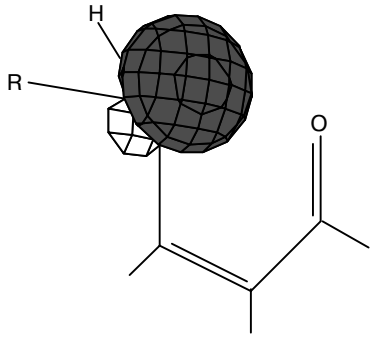


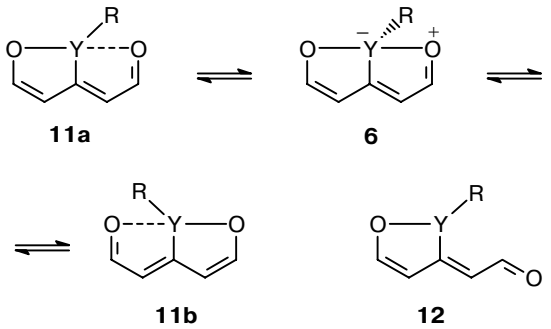
Fig. 6. Orientation of the hybrid LEP orbital of the P atom in molecule **5** (Y = P, R = Cl) determined in the framework of the NBO analysis by the RHF/6-31G** method.

tion of conjugated systems with intramolecular hydrogen bonds was repeatedly pointed out.[45,46,51]

The aforesaid suggests that considerable stabilization of the quasi-cyclic conformation **5** of β-pnictogenovinylaldehyde molecules compared to their free of strain, *trans-s-trans* conformation **9**, clearly indicated by substantially shortened Y...O contacts and positive ΔE values (see Tables 2 and 3, respectively), is mainly due to the factors responsible for the formation of secondary bonds Y...O of the hypervalent type (*i.e.*, electrostatic attraction and the $n_O \rightarrow \sigma^*_{Pn-R}$ orbital interaction). In contrast to β-chalcogenovinylaldehydes **1**, aromatic stabilization in molecules **5** is relatively weak or even absent.

1,6-Dioxa-6aλ^5-pnictapentalenes 6. Formally, these unknown at present compounds can be obtained by "fusing" the five-membered furan ring with the *cis*-β-pnictogenovinylaldehyde molecules **5**. Compounds **6** are isoelectronic to both 1,6-dioxa-6aλ^4-chalcapentalenes **2** and ADPnO **8** and possess the same type of the heterapentalene backbone. Similarly to molecules **2**, alternative structural forms of the heterapentalene system **6** can be represented either by the equilibrium between topomers **11** (here, structure **6** is a transition state) or by isomers with respect to acyclic bonds, *e.g.*, **12** (Scheme 5).

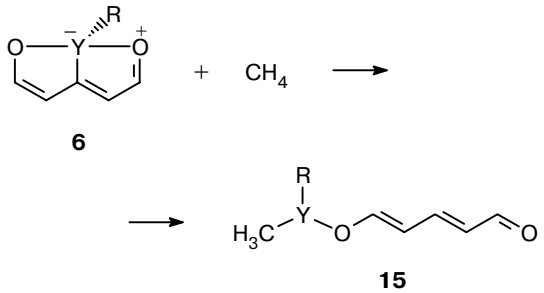
Scheme 5



The formation of strong 3c-4e bonds O—Y—O with Y = P and As is readily apparent from the results of calculations listed in Tables 7 and 8. These bonds stabilize the *cis*-configuration with respect to the C=C bonds, thus providing the possibility of formation of stable quasi-heterapentalene structures **6** of corresponding compounds. Bicyclic hypervalent structures **6** (Y = P, As) are more energetically favorable than sterically unstrained monocyclic isomers **12**. The energy differences between **6** and **12** increase on going from Y = P to Y = As and from R = H to R = F. For nitrogen derivative (Y = N, R = H) the most stable is monocyclic *cis*-structure **11** with intramolecular coordination O←N. Only one similar structure was found in the calculations of 1,6-dioxa-6a-fluoro-6aλ^5-arsapentalene (Y = As, R = F); however, its formation should be considered as a consequence of a slight distortion of the C_s-structure **6** of this compound. The total energies of structures **6** and **11** (Y = As, R = F) virtually coincide (see Tables 7 and 8). The symmetric structure of 1,6-dioxa-6aλ^5-azapentalene **6** (Y = N, R = H) corresponds to a saddle point rather than a minimum on the PES and represents a transition state (TS) of the N—O bond switching reaction between the topomers **11a** and **11b**. This rearrangement is likely to proceed as intramolecular S_N2-substitution at the tricoordinate N atom and structure **6** exactly meets corresponding stereoelectronic conditions. The energy barrier to the rearrangement is characterized by the ΔE values for structure **6** (Y = N, R = H) listed in Table 8. They are close to the height of the barrier to intramolecular nucleophilic substitution at the tetrahedral C atom in the structurally identical 2,3-dihydro-3-formylmethylenefuran (27.7 kcal mol^{-1} at the MP2(full)/6-31G** level of theory).[52] The results obtained from MP2 and DFT calculations are in reasonable agreement. The sole exception is the structure of 1,6-dioxa-6a-fluoro-6aλ^5-arsapentalene **6** (Y = As, R = F). The optimized geometric parameters of the molecules of 1,6-dioxa-6aλ^5-pnictapentalenes **6**, monocyclic isomers **12**, structures **14** (TS of topomerization of compounds **6**), and their isomers **13** are presented in Figs. 7—11.

The aromaticity of 1,6-dioxa-6aλ^4-chalcapentalenes **2** (X = S, Se, Te) and ADPnO **8** is readily apparent from complete analogy between the electronic structures of these compounds and pentalene dianion.[18—20,23,26,38] On the other hand, aromaticity of 1,6-dioxa-6aλ^5-pnictapentalenes **6** should depend on the degree of involvement of the LEP of the pnictogen atom in cyclic π-conjugation. According to NBO analysis data, the angle between the LEP axis and the direction of the C(3a)—Y bond varies from 121 to 136° while the p-character of the LEP orbital decreases in the order Y = N, P, As and on going from R = H to R = F as well. To estimate the *HSE* values for molecules **6** and compare them with the results obtained for compounds **2** (X = S, Se, and Te), we calculated the heats of the reactions presented in Scheme 6 (see Table 9).

Scheme 6



As can be seen from the data listed in Table 9, the *HSE* values for 1,6-dioxa-6aλ^5-pnictapentalenes **6** are much lower than those found for their chalcogen-con-

Table 7. Total energies (E_{tot}), zero-point vibrational energy corrections (*ZPE*), and the lowest (ω_1) or imaginary (iω) harmonic frequencies calculated by different quantum-chemical methods for the isomers of 1,6-dioxa-6aλ^5-pnictapentalenes

Y	R	Structure, symmetry	Computational method	$-E_{tot}$	*ZPE*	ω_1 or iω /cm^{-1}
				au		
N	H	**6**, C_s (TS)	MP2(full)/6-31G**	397.498813	0.095644	i522
			B3LYP/6-31G**	398.623735	0.093882	i827
		11, C_1	MP2(full)/6-31G**	397.545085	0.095823	130
			B3LYP/6-31G**	398.660682	0.095823	129
		12, C_1	MP2(full)/6-31G**	397.5300698	0.096580	130
			B3LYP/6-31G**	398.645741	0.095523	104
		13, C_1	MP2(full)/6-31G**	397.469870	0.097190	114
			B3LYP/6-31G**	398.577292	0.095408	61
P	H	**6**, C_s	MP2(full)/6-31G**	683.842165	0.092334	198
			B3LYP/6-31G**	685.324322	0.090485	208
		12, C_1	MP2(full)/6-31G**	683.818268	0.090207	84
			B3LYP/6-31G**	685.300733	0.088793	92
		14, C_{2v} (TS)	MP2(full)/6-31G**	683.830488	0.092412	i469
			B3LYP/6-31G**	685.300094	0.091065	i501
		13, C_s	MP2(full)/6-31G**	683.849301	0.094820	72
			B3LYP/6-31G**	685.318688	0.092583	115
	F	**6**, C_s	MP2(full)/6-31G**	782.886848	0.085420	153
			B3LYP/6-31G**	784.581297	0.083974	151
		12, C_1	MP2(full)/6-31G**	782.880243	0.085659	67
			B3LYP/6-31G**	784.571782	0.082815	70
		14, C_{2v} (TS)	MP2(full)/6-31G**	782.861978	0.086008	i282
			B3LYP/6-31G**	784.541226	0.084978	i318
		13, C_s	MP2(full)/6-31G**	782.856234	0.085659	98
			B3LYP/6-31G**	784.544256	0.084226	108
As	H	**6**, C_s	MP2(full)/6-31G**	2575.173224	0.090599	177
			B3LYP/6-31G**	2577.740592	0.088883	172
		12, C_1	MP2(full)/6-31G**	2575.146512	0.089296	87
			B3LYP/6-31G**	2577.714006	0.087641	93
		14, C_{2v} (TS)	MP2(full)/6-31G**	2575.137735	0.090579	i502
			B3LYP/6-31G**	2577.688536	0.088787	i612
		13, C_s	MP2(full)/6-31G**	2575.173900	0.092826	100
			B3LYP/6-31G**	2577.727408	0.091254	119
	F	**6**, C_s	MP2(full)/6-31G**	2674.217242	0.083767	i25 (TS)
			B3LYP/6-31G**	2676.995877	0.082311	100
		11, C_1	MP2(full)/6-31G**	2674.217242	0.083772	37
		12, C_1	MP2(full)/6-31G**	2674.202564	0.082784	64
			B3LYP/6-31G**	2676.979308	0.081601	75
		14, C_{2v} (TS)	MP2(full)/6-31G**	2674.165059	0.084412	i266
			B3LYP/6-31G**	2676.921458	0.082941	i329
		13, C_s	MP2(full)/6-31G**	2674.180730	0.084361	97
			B3LYP/6-31G**	2676.953467	0.082920	110

taining analogs **2**. The higher the p-character of the LEP centered on the Pn atom in molecules **6**, the higher the *HSE* value and, hence, the aromaticity of the compound. The homodesmotic stabilization energies found for systems **6** and **2** (see Table 9) were compared with the corresponding values calculated for the most aromatic bicyclic naphthalene structure with a π-electron decet. The results obtained using the same procedure (Scheme 7) were 62.2 (MP2(full)/6-31G**) and 53.7 kcal mol^{-1} (B3LYP/6-31G**). As can be seen, the *HSE* values are nearly 50% of the latter estimate for 1,6-dioxa-6aλ^4-chalcapentalenes **2**, much lower for compounds **6**, and virtually insignificant for 6a-fluoro derivatives. These results indicate that heterapentalenes **6** are much less aromatic than compounds **2**. As in the case of β-pnictogenovinylaldehydes, this can be due to the fact that both hybridization and orientation of the

Scheme 7

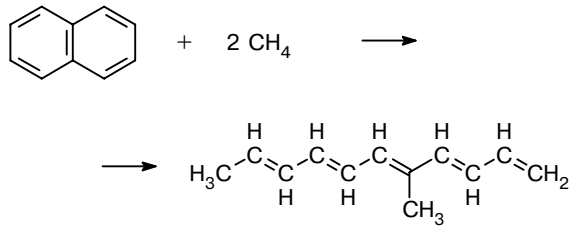


Table 8. Relative energies calculated without (ΔE) and with inclusion of zero-point vibrational energy correction (ΔE_{ZPE}), standard relative enthalpies ($\Delta H°$), and standard free Gibbs energies ($\Delta G°$) of the isomers of 1,6-dioxa-6aλ^5-pnictapentalenes

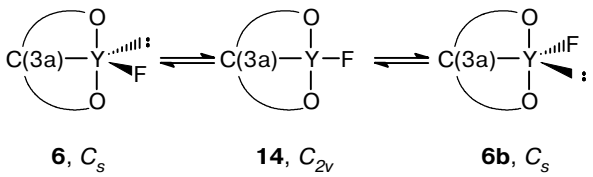
Y	R	Structure, symmetry	Computational method	ΔE	ΔE_{ZPE}	$\Delta H°$	$\Delta G°$
				kcal mol^{-1}			
N	H	**11**, C_1	MP2(full)/6-31G**	0	0	0	0
			B3LYP/6-31G**	0	0	0	0
		6, C_s (TS)	MP2(full)/6-31G**	29.0	28.2	27.8	28.6
			B3LYP/6-31G**	23.2	22.0	21.7	22.3
		12, C_1	MP2(full)/6-31G**	9.4	9.2	9.4	8.7
			B3LYP/6-31G**	9.4	9.2	9.4	8.7
		13, C_1	MP2(full)/6-31G**	47.2	47,3	46.8	47.8
			B3LYP/6-31G**	52.3	52.1	51.8	52.3
P	H	**6**, C_s	MP2(full)/6-31G**	0	0	0	0
			B3LYP/6-31G**	0	0	0	0
		12, C_1	MP2(full)/6-31G**	15.0	13.7	14.3	12.5
			B3LYP/6-31G**	14.8	13.7	14.2	12.7
		14, C_{2v} (TS)	MP2(full)/6-31G**	7.3	7.4	6.9	8.1
			B3LYP/6-31G**	15.2	15.6	15.0	16.4
		13, C_s	MP2(full)/6-31G**	−4.5	−2.9	−2.8	−3.3
			B3LYP/6-31G**	3.5	4.8	4.6	4.9
	F	**6**, C_s	MP2(full)/6-31G**	0	0	0	0
			B3LYP/6-31G**	0	0	0	0
		12, C_1	MP2(full)/6-31G**	4.1	3.2	3.7	2.1
			B3LYP/6-31G**	6.0	5.2	5.6	4.2
		14, C_{2v} (TS)	MP2(full)/6-31G**	15.6	16.0	15.2	17.0
			B3LYP/6-31G**	25.1	25.8	24.9	26.9
		13, C_s	MP2(full)/6-31G**	19.2	19.4	19.1	19.6
			B3LYP/6-31G**	23.2	23.4	23.1	23.7
As	H	**6**, C_s	MP2(full)/6-31G**	0	0	0	0
			B3LYP/6-31G**	0	0	0	0
		12, C_1	MP2(full)/6-31G**	16.8	15.9	16.3	15.0
			B3LYP/6-31G**	16.7	15.9	16.2	15.1
		14, C_{2v} (TS)	MP2(full)/6-31G**	22.3	22.3	21.7	23.3
			B3LYP/6-31G**	32.7	32.6	32.1	33.6
		13, C_s	MP2(full)/6-31G**	−0.4	1.0	0.7	1.1
			B3LYP/6-31G**	8.3	9.8	9.5	10.0
	F	**6**, C_s	MP2(full)/6-31G**	0	0	0	0
			B3LYP/6-31G**	0	0	−0.5	1.1
		11, C_1	MP2(full)/6-31G**	0	0	0	0
			B3LYP/6-31G**	0	0	0	0
		12, C_1	MP2(full)/6-31G**	9.2	8.6	8.8	8.3
			B3LYP/6-31G**	10.4	9.9	10.1	9.4
		14, C_{2v} (TS)	MP2(full)/6-31G**	32.7	33.1	32.1	35.2
			B3LYP/6-31G**	46.7	47.1	46.1	48.7
		13, C_s	MP2(full)/6-31G**	22.9	23.3	22.7	24.4
			B3LYP/6-31G**	26.6	27.0	26.5	27.7

LEP of the pnictogen center in molecules **6** are unfavorable for providing the maximum overlap with the π-system of the molecular skeleton.

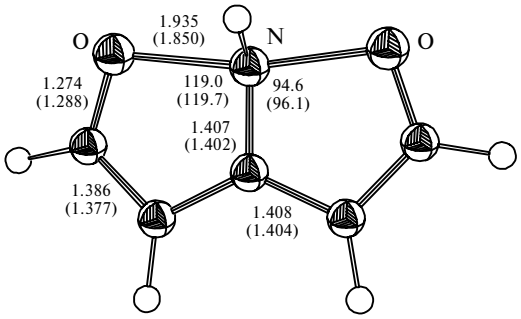
All the bicyclic structures **6** shown in Figs. 7—11 are characterized by slight folding along the Y—C(3a) bond. Planar structures **14** with C_{2v} symmetry represent transition states of a specific polytope rearrangement of quasi-trigonalbipyramidal (bisphenoid) structures **6** (Y = P, As; see Scheme 8).

A salient feature of the mechanism of this rearrangement is planarity of the tetracoordinate inversion center, whereas topomerization of strain-free bisphenoid structures occurs usually *via* a square-pyramidal TS (see, *e.g.*, Ref. 53). Calculations performed for the phosphorus derivative **6** (Y = P, R = H) predict a rather low energy barrier to the topomerization (~7 kcal mol^{-1} at the MP2/6-31G** level of theory). For the As derivative, as

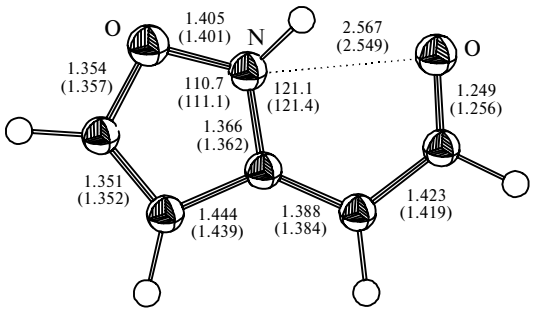
Scheme 8



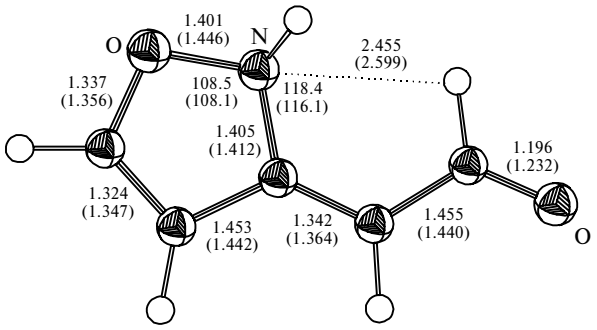
6, C_s **14**, C_{2v} **6b**, C_s



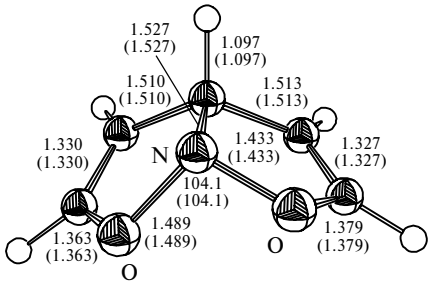
6 (Y = N, R = H), C_s



11 (Y = N, R = H), C_1

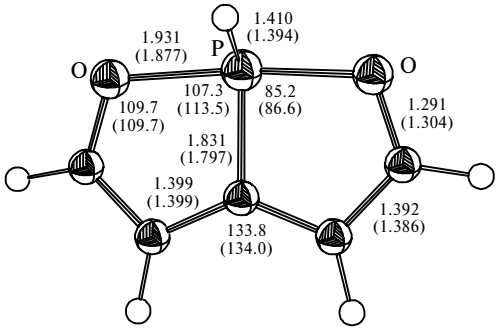


12 (Y = N, R = H), C_1

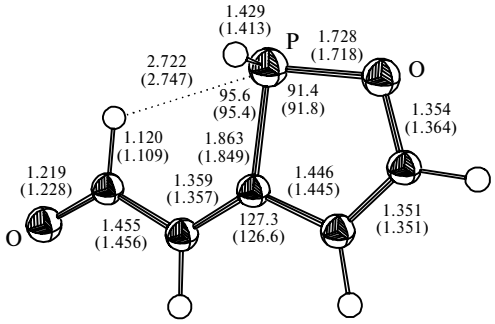


13 (Y = N, R = H), C_1

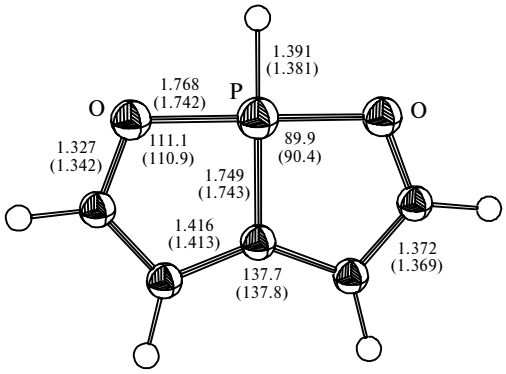
Fig. 7. Geometric parameters of the 4,5-dihydro-5-formylmethyleneoxazole isomers and bicyclic structure **6** (a TS of interconversion between topomers **11a** and **11b**) calculated by the B3LYP/6-31G** and MP2(full)/6-31G** (figures in parentheses) methods. The bond lengths are given in Å and the bond angles are given in degrees.



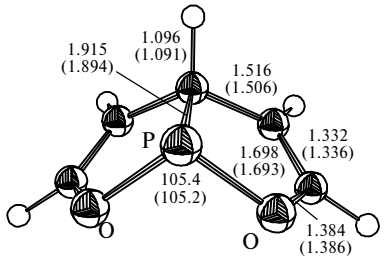
6 (Y = P, R = H), C_s



12 (Y = P, R = H), C_1

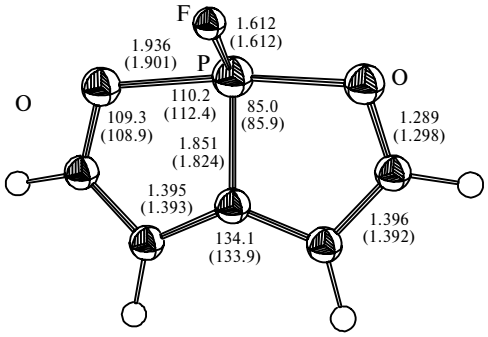


14 (Y = P, R = H), C_{2v}

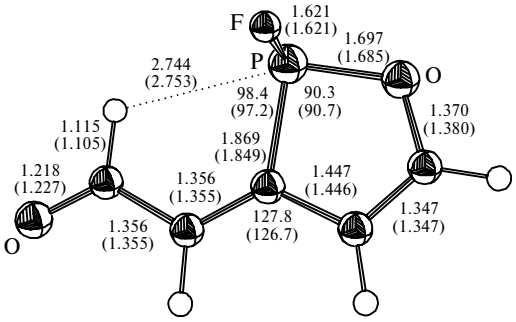


13 (Y = P, R = H), C_s

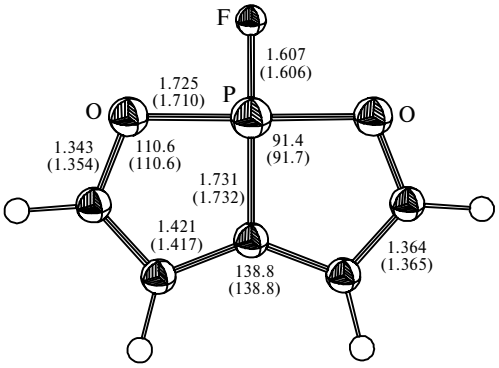
Fig. 8. Geometric parameters of the molecule of 1,6-dioxa-6aλ^5-phosphapentalene (**6**), structure **14** (a TS of topomerization of **6**), and isomers **12** and **13** calculated by the B3LYP/6-31G** and MP2(full)/6-31G** (figures in parentheses) methods. The bond lengths are given in Å and the bond angles are given in degrees.



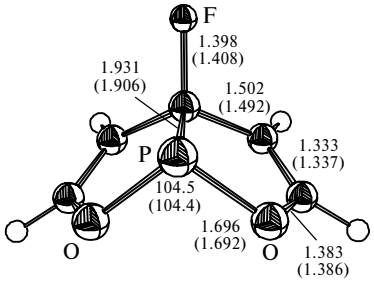
6 (Y = P, R = F), C_s



12 (Y = P, R = F), C_1

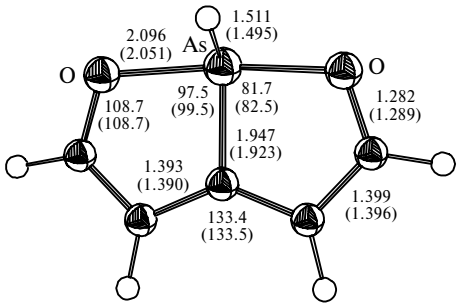


14 (Y = P, R = F), C_{2v}

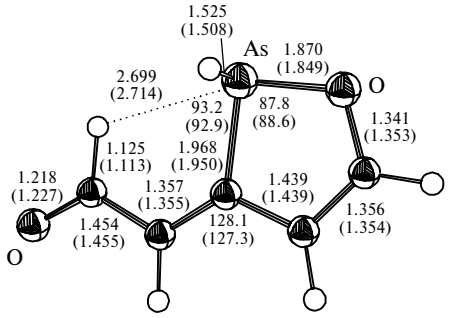


13 (Y = P, R = F), C_s

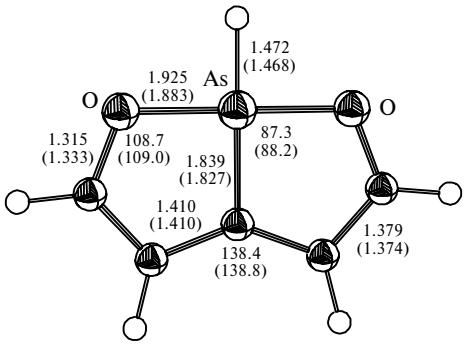
Fig. 9. Geometric parameters of the molecule of 1,6-dioxa-6a-fluoro-6aλ^5-phosphapentalene (**6**), structure **14** (a TS of topomerization of **6**), and isomers **12** and **13** calculated by the B3LYP/6-31G** and MP2(full)/6-31G** (figures in parentheses) methods. The bond lengths are given in Å and the bond angles are given in degrees.



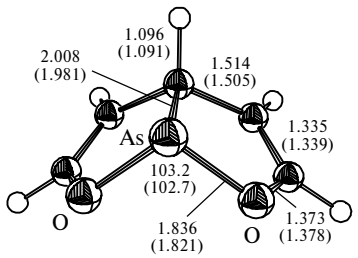
6 (Y = As, R = H), C_s



12 (Y = As, R = H), C_1

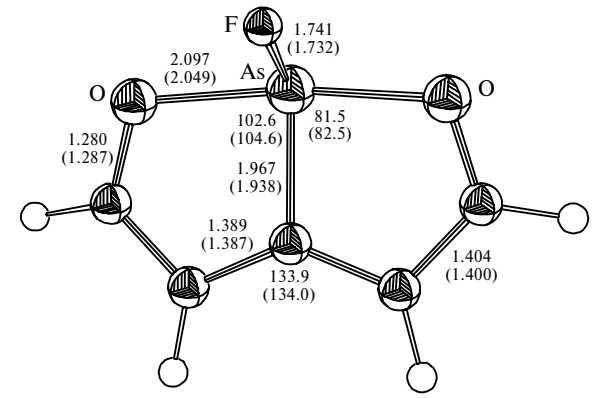


14 (Y = As, R = H), C_{2v}

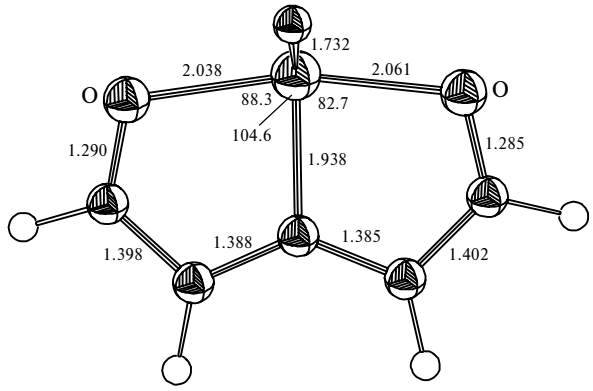


13 (Y = As, R = H), C_s

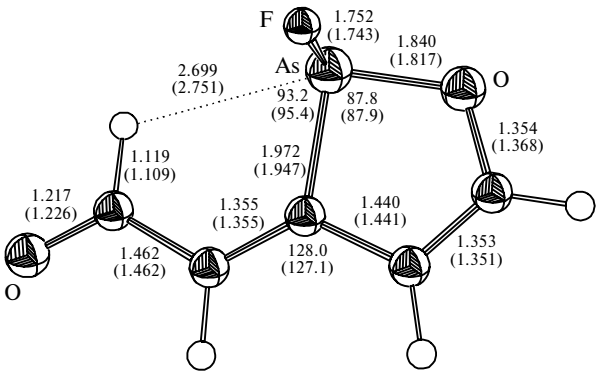
Fig. 10. Geometric parameters of the molecule of 1,6-dioxa-6aλ^5-arsapentalene (**6**), structure **14** (a TS of topomerization of **6**), and isomers **12** and **13** calculated by the B3LYP/6-31G** and MP2(full)/6-31G** (figures in parentheses) methods. The bond lengths are given in Å and the bond angles are given in degrees.



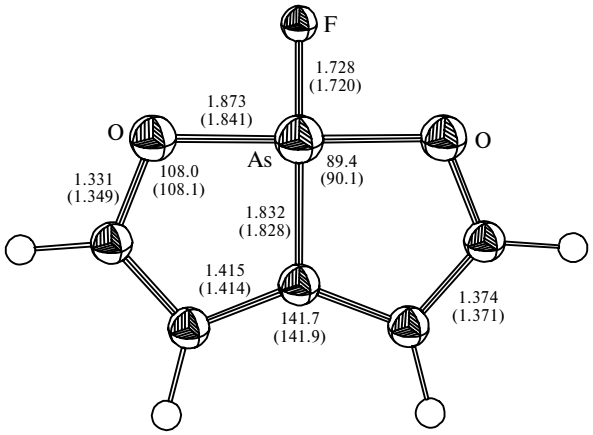
6 (Y = As, R = F), C_s



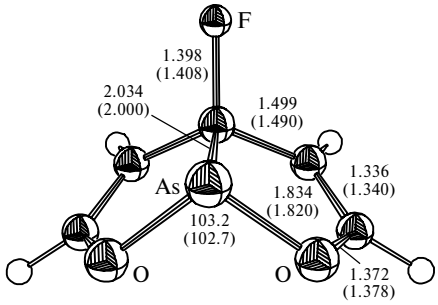
11 (Y = As, R = F), C_1



12 (Y = As, R = F), C_1



14 (Y = As, R = F), C_{2v}



13 (Y = As, R = F), C_s

Fig. 11. Geometric parameters of the molecule of 1,6-dioxa-6a-fluoro-6aλ^5-arsapentalene (**6**), structure **14** (a TS of topomerization of **6**), and isomers **12** and **13** calculated by the B3LYP/6-31G** and MP2(full)/6-31G** (figures in parentheses) methods. The bond lengths are given in Å and the bond angles are given in degrees.

well as upon replacement of the H atom at the pnictogen center by the more electronegative atom F the barrier to the topomerization ("cuneal inversion"[54]) becomes much higher.

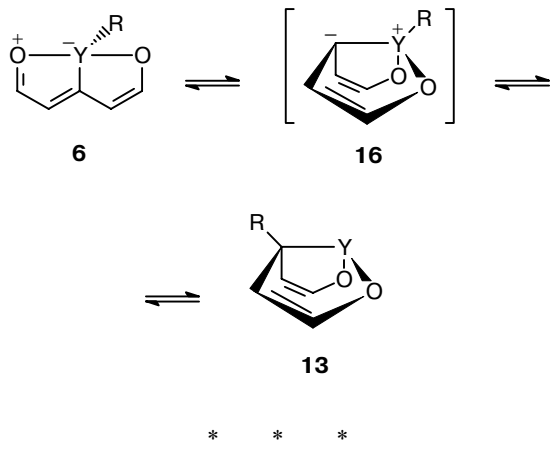
It was also of interest to assess the possibility for "electromorphism" to occur in structures **6** due to "forced" distortion of their geometries, similarly to that proposed for 5-aza-2,8-dioxa-1-pnictabicyclo[3.3.0]octa-2,4,6-trienes (ADPnO) **8**.[32,33] No stationary points corresponding to the structure of intermediate (or TS) **16** and isoelectronic to **8a** were located on the PES of systems **6**. Nevertheless, we found that folding of these structures along the Y—C(3a) bond immediately results in isomeric 2,8-dioxa-1-pnictabicyclo[3.3.0]octa-2,4,6-trienes **13** that are formed as a result of migration of the substituent R (R = H, F) from Y to the C(3a) atom (Scheme 9). The relative energies of the phospha and arsa derivatives **13** (Y = P, As; R = H) listed in Table 8 nearly coincide with those of hypervalent isomers **6**. In the case of nitrogen derivatives **13** (Y = N) and com-

Table 9. Homodesmotic stabilization energies (*HSE*/kcal mol^{-1}) and the LEP orbital hybridization (*LP*) for the atomic centers X (in compounds **2**) or Y (in compounds **6**), and the total energies (E_{tot}/au) of polyenes **15**

Structure	X (Y)	R	Computational method	$-E_{tot}$(**15**)	*HSE*	*LP*
2 [18]	S	—	MP2/LanL2DZ	392.074416	16.6	p
			B3LYP/6-31G**	782.028589	23.4	—
			MP2(fc)/6-31+G**	780.349761	24.9	—
	Se	—	MP2/LanL2DZ	391.206449	26.0	—
			MP2(full)/6-31G**	2780.483483	39.0	—
	Te	—	MP2/LanL2DZ	390.059210	29.9	—
6	N	H	MP2(full)/6-31G**	437.849479	12.6	$sp^{1.8}$
			B3LYP/6-31G**	439.164601	12.6	—
	P	H	MP2(full)/6-31G**	724.187519	15.4	$sp^{0.9}$
			B3LYP/6-31G**	725.827966	12.8	—
		F	MP2(full)/6-31G**	823.253858	1.8	$sp^{0.6}$
			B3LYP/6-31G**	825.104195	0.7	—
	As	H	MP2(full)/6-31G**	2615.510667	20.3	$sp^{0.6}$
			B3LYP/6-31G**	2618.236579	17.6	—
		F	MP2(full)/6-31G**	2714.579446	7.2	$sp^{0.4}$
			B3LYP/6-31G**	271.509987	6.6	—

pounds with the F atom in position 5, structures **6** are more energetically favorable.

Scheme 9



* * *

Intramolecular coordination Y←O in the *cis-s-cis* conformers of β-pnictogenovinylaldehydes **5** leads to their stabilization as compared to the uncoordinated sterically unstrained *trans-s-trans* conformers **9**. This effect is almost entirely due to the factors responsible for the formation of secondary bonds Y...O of the hypervalent type, *viz.*, electrostatic attraction and the $n_O \rightarrow \sigma^*_{Pn-R}$ orbital interaction. In contrast to β-chalcogenovinylaldehydes **1**, aromatic stabilization in molecules **5** is insignificant or even absent. According to calculations, bicyclic hypervalent structures of 1,6-dioxa-6aλ^5-pnictapentalenes **6** (Y = P and As) are much more stable than the strain-free monocyclic isomers **12**. In addition, aromaticity of heterapentalenes **6** is much weaker than that of their chalcogen-containing analogs **2** (X = S, Se, and Te). As in the case of β-pnictogenovinylaldehydes **5**, this can be explained by non-optimum hybridization and orientation of the LEP of the pnictogen center, which precludes a maximum overlap with the π-system of the molecular skeleton. It should be emphasized again that correct estimate of the strengths and lengths of the secondary bonds Chalc...O (in β-chalcogenovinylaldehydes **1**) and Pn...O (in β-chalcogenovinylaldehydes **1** and β-pnictogenovinylaldehydes **5**), as well as the three-center, four-electron hypervalent bonds O—X—O (in 1,6-dioxa-6aλ^4-chalcapentalenes **2**) and O—Y—O (in 1,6-dioxa-6aλ^5-pnictapentalenes **6**) requires the inclusion of electron correlation.

This work was carried out with the financial support of the Russian Foundation for Basic Research (Project Nos. 00-15-97320 and No. 01-03-32546). V. I. Minkin gratefully acknowledges the support of the Alexander von Humboldt Foundation (Germany, 1999 Alexander von Humboldt Research Award).

References

1. A. Kucsman and I. Kapovits, in *Organic Sulfur Chemistry: Theoretical and Experimental Advances*, Eds. I. G. Csizmadia, A. Mangini, and F. Bernardi, Elsevier, Amsterdam, 1985, 191.
2. D. H. R. Barton, M. B. Hall, Z. Lin, S. I. Parekh, and J. Reibenspies, *J. Am. Chem. Soc.*, 1993, **115**, 5056.
3. M. Iwaoka and S. Tomoda, *J. Am. Chem. Soc.*, 1996, **118**, 8077.
4. W. R. McWhinnie, I. D. Sadekov, and V. I. Minkin, *Sulfur Repts.*, 1996, **18**, 295.
5. G. D. Markham and C. W. Bock, *J. Mol. Struct. (THEOCHEM)*, 1997, **418**, 139.
6. V. I. Minkin, *Ross. Khim. Zh.* (*Zh. Ross. Khim. Obshch. im. D. I. Mendeleeva*), 1999, **43**, 10 [*Mendeleev Chem. J.*, 1999, **43** (Engl. Transl.)].
7. F. T. Burling and B. M. Goldstein, *J. Am. Chem. Soc.*, 1992, **114**, 2313.
8. C. L. Perrin and J. B. Nielsen, *Ann. Rev. Phys. Chem.*, 1997, **48**, 511.
9. O. Epp, R. Ladenstein, and A. Wendel, *Eur. J. Biochem.*, 1983, **133**, 51.
10. J. D. Dunitz, *X-Ray Analysis and the Structure of Organic Molecules*, Cornell Univ. Press, Ithaca—London, 1979.
11. G. R. Desiraju, *Crystal Engineering. The Design of Organic Solids*, Elsevier, Amsterdam, 1989.
12. L. G. Kuz′mina, *Koord. Khim.*, 1999, **25**, 643 [*Russ. J. Coord. Chem.*, 1999, **25** (Engl. Transl.)].
13. I. D. Sadekov and V. I. Minkin, *Usp. Khim.*, 1995, **64**, 491 [*Russ. Chem. Rev.*, 1995, **64** (Engl. Transl.)].
14. K.-y. Akiba, *Chemistry of Hypervalent Compounds*, Wiley-VCH, New York, 1999.
15. V. I. Minkin, I. D. Sadekov, B. B. Rivkin, A. V. Zakharov, V. L. Nivorozhkin, O. E. Kompan, and Yu. T. Struchkov, *J. Organomet. Chem.*, 1997, **536—537**, 233.
16. Y. Nagao, T. Hirata, S. Goto, S. Sano, A. Kakehi, K. Iizuka, and M. Shiro, *J. Am. Chem. Soc.*, 1998, **120**, 3104.

17. J. G. Ángyán, R. A. Poirier, A. Kucsman, and I. G. Csizmadia, *J. Am. Chem. Soc.*, 1987, **109**, 2237.
18. R. M. Minyaev and V. I. Minkin, *Canad. J. Chem.*, 1998, **76**, 766.
19. V. I. Minkin and R. M. Minyaev, *Mendeleev Commun.*, 2000, 171.
20. R. Gleiter and R. Gygax, *Top. Curr. Chem.*, 1976, **63**, 49.
21. M. R. Detty and B. J. Murray, *J. Am. Chem. Soc.*, 1983, **105**, 883.
22. M. R. Detty and J. Peristein, *Organometallics*, 1987, **6**, 1597.
23. I. D. Sadekov, A. A. Maksimenko, A. G. Maslakov, and V. I. Minkin, *J. Organomet. Chem.*, 1990, **391**, 179.
24. R. Cimiraglia and H.-J. Hoffmann, *J. Am. Chem. Soc.*, 1991, **113**, 6449.
25. P. George, M. Trachtman, C. W. Bock, and A. Brett, *Theor. Chim. Acta*, 1975, **38**, 121.
26. V. I. Minkin, M. M. Glukhovtsev, and B. Ya. Simkin, *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*, Wiley, New York, 1994.
27. A. E. Reed, L. A. Curtiss, and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899.
28. J. Emsley, *The Elements*, Clarendon Press, Oxford, 1991.
29. V. I. Minkin and R. M. Minyaev, *Chem. Rev.*, 2001, **101**, 1247.
30. M. Iwaoka and S. Tomoda, *J. Org. Chem.*, 1995, **60**, 5299.
31. T. Murafuji, T. Mutoh, K. Satoh, K. Tsunenari, N. Azuma, and H. Suzuki, *Organometallics*, 1995, **14**, 3848.
32. A. J. Arduengo, III, C. A. Stewart, F. Davidson, D. A. Dixon, J. Y. Becker, S. A. Culley, and M. Mizen, *J. Am. Chem. Soc.*, 1987, **109**, 627.
33. A. J. Arduengo, III, and C. A. Stewart, *Chem. Rev.*, 1994, **94**, 1215.
34. R. Stecler and D. J. Truhlar, *J. Chem. Phys.*, 1990, **93**, 6570.
35. D. A. Dixon and A. J. Arduengo, III, *J. Am. Chem. Soc.*, 1987, **109**, 338.
36. J. Moc and K. Morokuma, *Inorg. Chem.*, 1994, **33**, 551.
37. P. Schwerdtfeger, P. D. W. Boyd, T. Fischer, P. Hunt, and M. Liddell, *J. Am. Chem. Soc.*, 1994, **116**, 9620.
38. E. G. Nesterova, T. N. Gribanova, R. M. Minyaev, and V. I. Minkin, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 189 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 195].
39. B. Foresman and A. Frisch, *Exploring Chemistry with Electronic Structure Methods*, Gaussian, Inc., Pittsburgh (PA), 1996.
40. M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, *GAUSSIAN-94*, *Revision B.3*, Gaussian, Inc., Pittsburgh (PA), 1995.
41. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su, L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.*, 1993, **14**, 1347.
42. D. B. Cook, T. L. Sordo, and J. A. Sordo, *J. Chem. Soc., Chem. Commun.*, 1990, 185.
43. P. Valiron, A. Vibok, and I. Mayer, *J. Comput. Chem.*, 1993, **14**, 401.
44. P. Pyykkö, *Chem. Rev.*, 1997, **97**, 597.
45. S. Sheiner, *Acc. Chem. Res.*, 1994, **27**, 402.
46. M. S. Gordon and J. H. Jensen, *Acc. Chem. Res.*, 1996, **29**, 536.
47. W. Nakanishi, S. Hayashi, A. Sakaue, G. Ono, and Y. Kawada, *J. Am. Chem. Soc.*, 1998, **120**, 3635.
48. B. M. Gimarc and M Zhao, *Coord. Chem. Rev.*, 1997, **158**, 385.
49. M. R. Detty, B. J. Murray, D. L. Smith, and J. Zumbulyadis, *J. Am. Chem. Soc.*, 1983, **105**, 875.
50. G. M. Landrum, N. Goldberg, R. Hoffmann, and R. M. Minyaev, *New J. Chem.*, 1998, 883.
51. J. J. Dannenberg and R. Rios, *J. Phys. Chem.*, 1994, **98**, 6714.
52. R. M. Minyaev and V. I. Minkin, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 1246 [*Russ. Chem. Bull.*, 1999, **48**, 1234 (Engl. Transl.)].
53. J. G. Fowler and H. F. Schaefer, III, *J. Am. Chem. Soc.*, 1994, **116**, 9596.
54. E. F. Perozzi, J. C. Martin, and I. C. Paul, *J. Am. Chem. Soc.*, 1974, **96**, 6735.

Received January 22, 2001,
in revised form April 27, 2001