Inversion of Pyramidal Configuration of Pnictogenic Center in Diazapnictolenes
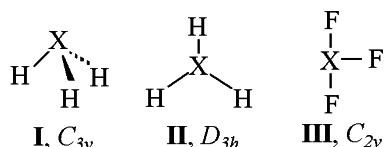
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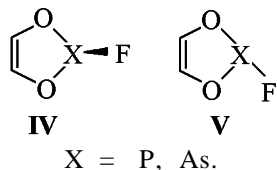*e-mail: minyaev@ipoc.rsu.ru*

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Abstract—The possibility of pyramidal inversion in diazapnictolenes was investigated by methods *ab initio* MP2(full)/6-31G** and density functional theory B3LYP/6-31G**. The inversion of tricoordinate phosphorus in 2-fluoro-1,3,2-diazaphospholene and of arsenic in 2-fluoro-1,3,2-diazaarsolene requires low activation barriers (<15 kcal mol^{-1}) corresponding to the time scale of the NMR method.

According to experimental and theoretical data [1–3] the inversion of tricoordinate pyramidal hydrides XH_3 (X = N, P, As, Sb, and Bi) (**I**) occurs via a planar transition state (**II**) of D_{3h} symmetry, and the barrier to inversion grows in the series N, P, As, Sb, and Bi from 5.3 kcal mol^{-1} for ammonia to 42 kcal mol^{-1} for bismuthine. Replacement hydrogens for fluorine in hydrides (**I**) considerably increases the barriers to inversion, and with X = p, As, Sb the mechanism of conversion is changed [4]. Thus with trifluorides of phosphorus, arsenic, and antimony the inversion occurs unlike that of trihydrides not through the transition state of D_{3h} symmetry but trough a T-form structure **III** of C_{2v} symmetry.

I, C_{3v} **II**, D_{3h} **III**, C_{2v}

Including of a tricoordinate pnictogenic center into a ring of 2-fluoro-1,3,2-dioxapnictolene (**IV**) with X = P, As results in formation of 6π-electron aromatic system in the planar transition structure **V** and consequently leads to significant diminishing of barriers to inversion.

IV   **V**

X = P, As.

For instance, according to calculations performed by methods *ab initio* and DFT [5], the value of the energy barrier for 2-fluoro-1,3,2-dioxaphospholene amounts to ~31 kcal mol^{-1}, and for 2-fluoro-1,3,2-dioxaarsolene it is mere ~22 kcal mol^{-1}. These values suggest a possibility to observe the inversion process in the systems by means of NMR spectroscopy.

It is interesting to reveal the influence on the inversion of replacing the oxygen atoms in system **IV** by less electronegative nitrogen whose unshared electron pairs are prone to stronger delocalization along the conjugation chain.
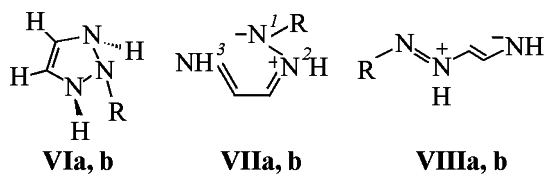
Calculation procedure. The calculations were performed by nonempirical Hartree-Fock method (RHF) with accounting for correlation of valence and core electrons by Møller–Plesset perturbation theory of the second order MP2(full) and by density functional method Becke3LYP (DFT) in the valence-split basis 6-31G** with the use of software packages Gaussian-98 [7] and Gamess [8]. Full optimization of molecular geometry corresponding to energy minima (λ = 0, where λ is a number of negative eigenvalues of Hesse matrix at a given stationary point [9]) and saddle points (λ = 1) on the potential energy surface (PES) was carried out in "tight" mode for Gaussian routine and till gradient value of 10^{-5} hartree/bohr for GAMESS program. Molecular structures on the figures are carried out in PLUTO form [10].

1,2,3-Triazoline and 2-fluoro-1,2,3-triazoline. Structures **VI–VIII** as showed the calculations correspond to energy minima (λ = 0) on the PES of systems $N_3C_2H_5$ and $N_3C_2FH_4$. In both systems the structures with pyramidal centers **VIa, b** are slightly more energetically stable: at R=H by 1.4 (MP2), 1.2 (B3LYP) kcal mol^{-1}, at R = F by 10.8 (MP2), 9.9 (B3LYP) kcal mol^{-1} than polyene structures **VIIa, b**.

Table 1. Results of calculation of structures **VI**–**XV** by methods *ab initio* (MP2(full)/G**) and DFT (B3LYP/6-31G**)[a]

Structure	X/R	Method	λ	E_{tot}, au	ΔE kcal mol^{-1}	ZPE, au	ΔE_{ZPE}, kcal mol^{-1}	ΔH, kcal mol^{-1}	ω, cm^{-1}
VIa		MP2	0	−242.682144	−1.4	0.084103	0.1	−0.5	333.6
		B3LYP	0	−243.380060	−1.2	0.082443	0.1	−0.5	323.1
VIIa	N/H	MP2	0	−242.679906	0	0.081662	0	0	191.4
		B3LYP	0	−243.378202	0	0.080441	0	0	197.8
VIIIa		MP2	0	−242.692961	−8.2	0.081924	−8.0	−8.0	150.6
		B3LYP	0	−243.391942	−8.7	0.080654	−8.6	−8.5	164.6
VIb		MP2	0	−341.660259	−10.8	0.073959	−9.8	−10.3	213.3
		B3LYP	0	−342.578373	−9.9	0.072820	−8.9	−9.3	213.7
VIIb	N/F	MP2	0	−341.643047	0	0.072407	0	0	130.4
		B3LYP	0	−342.562609	0	0.071213	0	0	135.4
VIIIb		MP2	0	−341.650050	−4.4	0.072993	−4.0	−4.1	147.5
		B3LYP	0	−342.571056	−5.3	0.071756	−5.0	−5.0	163.2
IXa		MP2	0	−528.985538	−20.9	0.077244	−20.1	−20.6	283.6
		B3LYP	0	−530.052933	−18.3	0.075327	−17.9	−18.3	264.3
Xa	P/H	MP2	0	−528.952247	0	0.076028	0	0	143.8
		B3LYP	0	−530.023770	0	0.074676	0	0	148.7
XIa		MP2	0	−528.942258	6.3	0.075307	5.8	6.0	131.3
		B3LYP	0	−530.021607	1.4	0.074155	1.1	1.3	142.1
IXb		MP2	0	−628.067245	−13.4	0.070290	−13.8	−13.1	162.1
		B3LYP	0	−629.344579	−14.2	0.068801	−14.6	−13.9	162.3
Xb	P/F	MP2	1	−628.045954	0	0.070879	0	0	i18.8
		B3LYP	1	−629.322019	0	0.069486	0	0	i53.2
XIb		MP2	0	−627.990690	34.7	0.069107	33.6	34.6	129.1
		B3LYP	0	−629.281318	25.5	0.068290	24.7	25.8	128.4
XIIa		MP2	0	−2420.304649	−14.6	0.075513	−13.9	−15.3	239.0
		B3LYP	0	−2422.457125	−12.5	0.073751	−12.2	−12.2	220.9
XIIIa	As/H	MP2	0	−2420.281345	0	0.074464	0	0	187.5
		B3LYP	0	−2422.437180	0	0.073296	0	0	152.9
XIVa		MP2	0	−2420.230504	31.9	0.073949	31.6	31.8	130.4
		B3LYP	0	−2422.429461	4.9	0.073053	4.7	5.0	136.4
XIIb		MP2	0	−2519.380114	−5.2	0.068278	−6.1	−5.9	143.1
		B3LYP	0	−2521.742545	−6.5	0.067175	−7.2	7.0	153.7
XIIIb		MP2	0	−2519.371832	0	0.069814	0	0	78.8
	As/F	B3LYP	0	−2521.732212	0	0.068290	0	0	75.1
XIVb		MP2	0	−2519.277714	59.1	0.068090	58.0	58.5	121.4
		B3LYP	0	−2521.689594	26.7	0.067530	26.2	26.7	128.4
XV		MP2	1	−2519.367729	2.6	0.068985	2.1	1.6	i130.4
		B3LYP	1	−2521.730520	1.1	0.067771	0.9	0.9	i87.2

[a] λ is a number of negative eigenvalues of Hesse matrix at a given stationary point; E_{tot} and ΔE are total and relative energies (1 au = 627.5095 kcal mol^{-1}); ZPE is the energy of zero harmonic oscillations; ΔE_{ZPE} is relative energy corrected for the energy of zero harmonic oscillations; ΔH is relative enthalpy; ω_I is the least or imaginary harmonic frequencies.

VIa, b   **VIIa, b**   **VIIIa, b**

VI–**VIII**, R = H (**a**), F (**b**).

The calculated geometry and energy characteristics of structures **VI**–**VIII** are presented on Fig. 1 and in Table 1.

The difference between total energies of *trans-s-trans* and the corresponding *cis-s-cis* structures (Table 1) evidence that in the latter the $N^1 \cdots N^3$ inter-
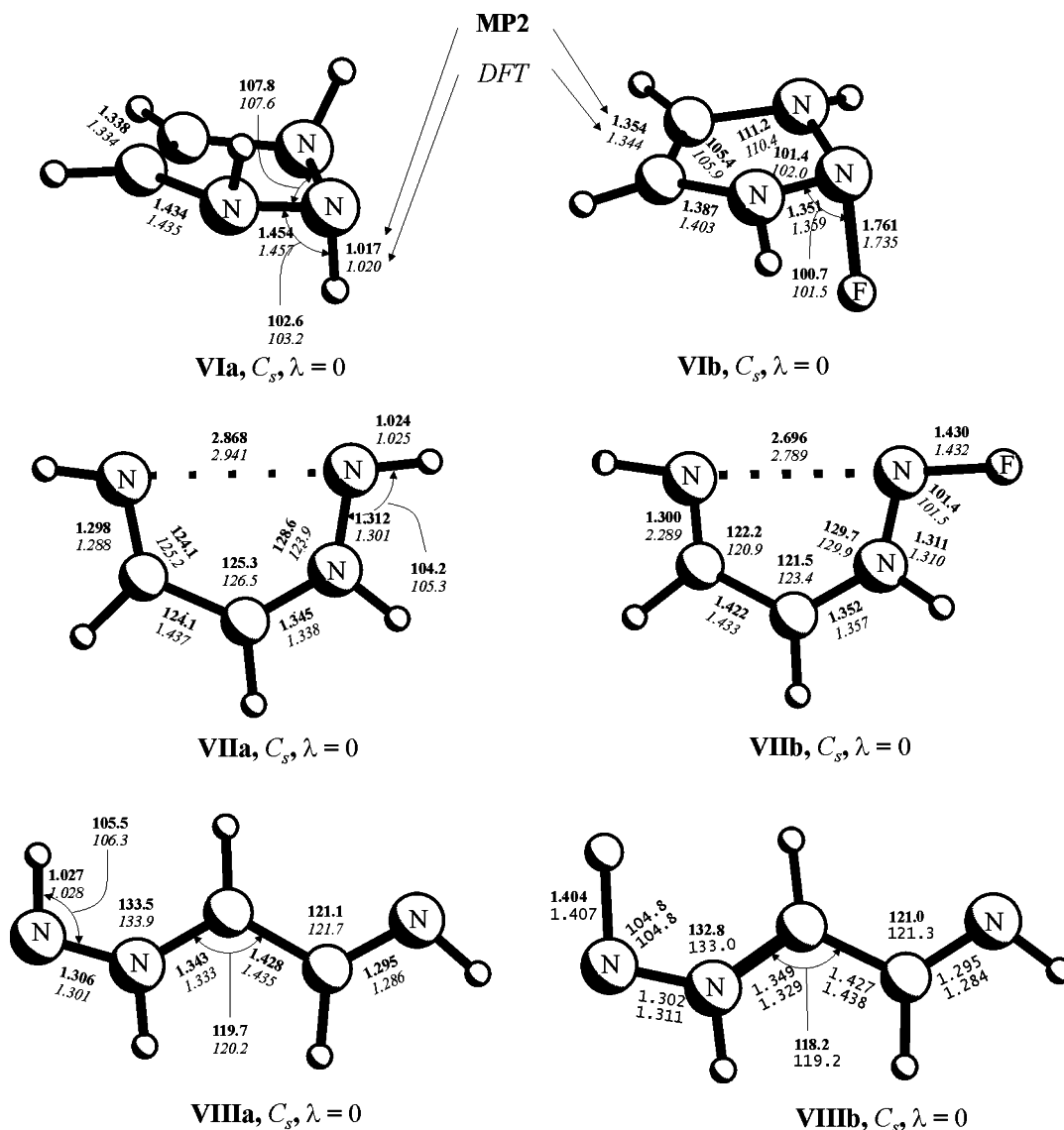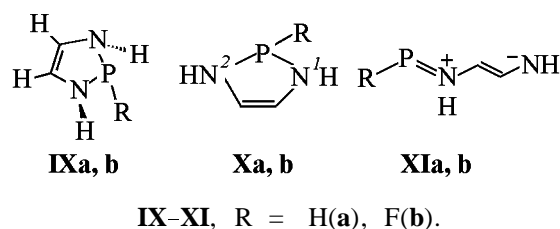
Fig. 1. Geometry characteristics of structures **VIa–VIIIa, VIb–VIIIb**, calculated by methods MP2/6-31G** (bold numbers), DFT/6-31G** (italic numbers). Bond lengths, Å; bond angles, deg.

action is repulsive; therewith the presence of an electronegative substitutent (R = F) at nitrogen reduces this interaction approximately by half. A similar effect of an electronegative substituent at X atom on the length and energy of intramolecular co-ordination bonds X···O was observed before [12].

The replacement of a hydrogen by a fluorine in the pyramidal structure **VI** results in a less pronounced pyramidal form of the NH bonds and in equalization of bond lengths (NN and CN bonds get shorter, CC bond gets longer) in **VIb** structure as compared with **VIa** structure indicating that in the former a stronger conjugation in the π-electron system occurs.

1,3,2-Diazaphospholene and 2-fluoro-1,3,2-di-azaphospholene. For the molecule of 1,3,2-diaza-

phospholene same as for 1,2,3-triazoline **VIa** both planar **Xa** and pyramidal **IXa** structures correspond to minima (λ = 0) on the PES of the system $PN_2C_2H_5$. Therewith the pyramidal structure **IXa** by 20.9 (MP2), 18.3 (B3LYP) kcal mol^{-1} is more energetically stable than the planar **Xa**. For 2-fluoro-1,3,2-di-azaphospholene the planar structure **Xb** corresponds to the transition state of the inversion process
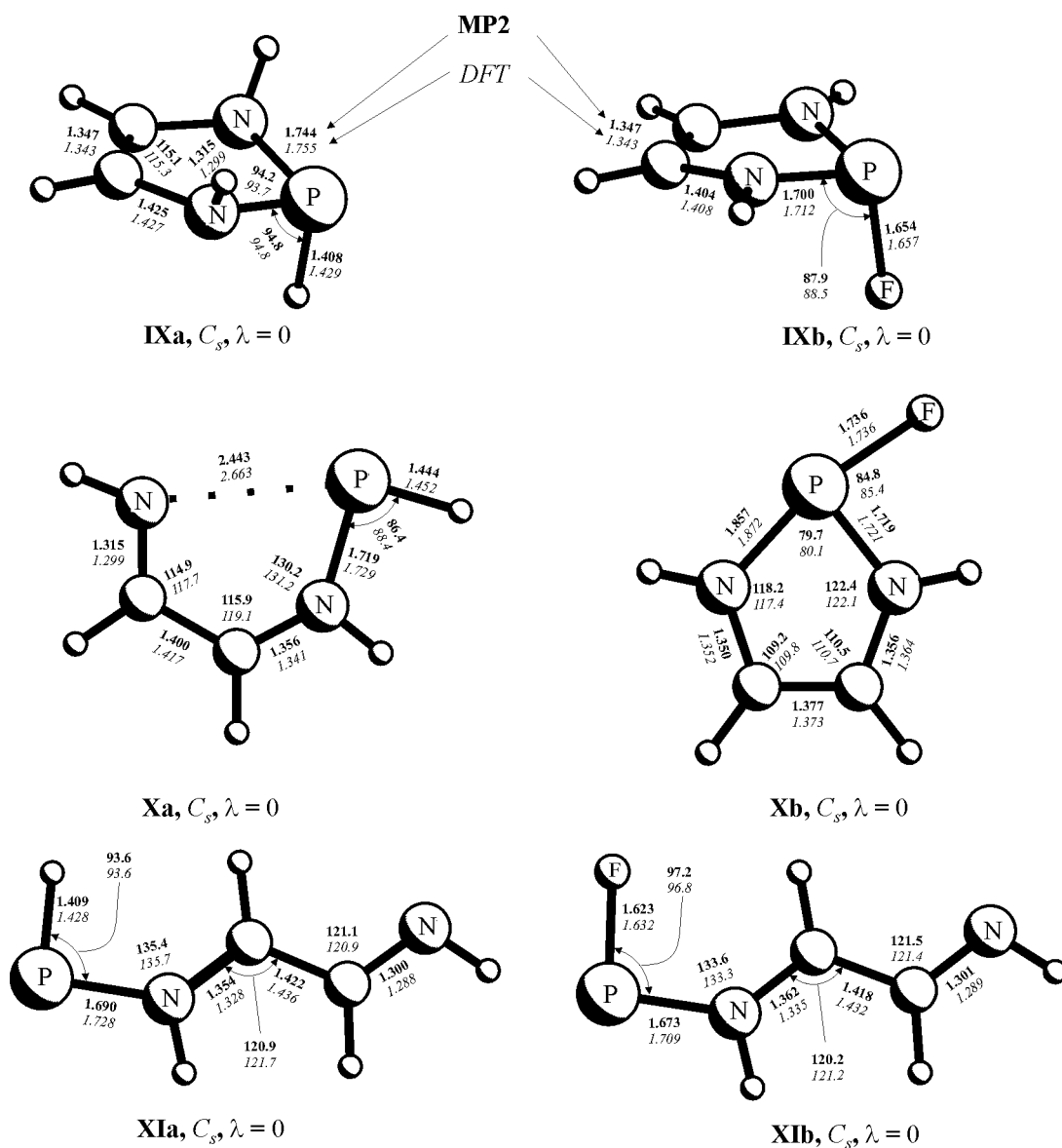

IXa, b   **Xa, b**   **XIa, b**

IX–XI, R = H(**a**), F(**b**).

Fig. 2. Geometry characteristics of structures **IXa–XIa, IXb–XIb,** calculated by methods MP2/6-31G** (bold numbers), DFT/6-31G** (italic numbers). Bond lengths, Å; bond angles, deg.

IXb ⇄ Xb ⇄ IXb', and its barrier amounts only to 13.4 (MP2), 14.2 (B3LYP) kcal mol⁻¹.

Note that in **Xa** structure the contact P⋯N¹ is a short covalent bond, and the contact P⋯N² is a long secondary bond of a donor–acceptor type. The calculated distance P⋯N² in **Xa** is significantly less (2.443 Å, MP2; 2.663 Å, B3LYP) than the sum of van der Waals radii of phosphorus and nitrogen (3.4 Å) [1]. The attraction energy P⋯N² calculated as the energy difference between the *cis-s-cis* (**Xa**) and *trans-s-trans* (**XIa**) structures is 6.3 (MP2), 1.4 (B3LYP) kcal mol⁻¹.
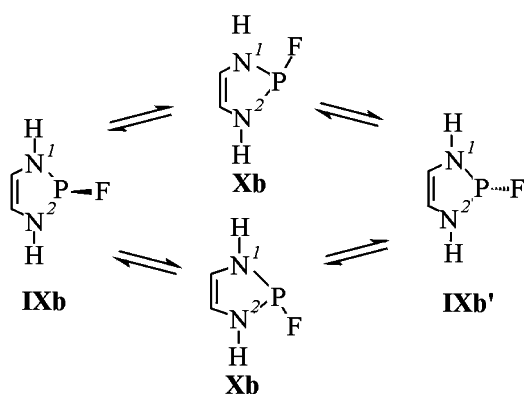
The replacement of hydrogen at phosphorus in **Xa** for more electronegative fluorine results in trans-

formation of noncovalent contact P⋯N² into a covalent bond PN² which is a little longer than an ordinary bond P⋯N² that can be rationalized as a consequence of a polarity rule [13]. The bond energy of PN² calculated as the difference between total energies of structures **Xb** and **XIb** equals to 34.7 (MP2), 25.5 (B3LYP) kcal mol⁻¹.

The calculated geometry and energy characteristics of structures **IX–XI** are presented on Fig. 2 and in Table 1.

The stabilization of planar structures **Xa** and **Xb** beside the attraction P⋯N is supported by the existence of an aromatic π-electron sextet, i.e., in this system only three occupied π-orbitals are present.

Scheme 1.

The forms of the three occupied and of the lowest unoccupied π-orbital of **Xa** structure are shown on Fig. 3.

The presence of two nonequivalent PN bonds in the transition state **Xb** (see Fig. 2) as was mentioned before [5] evidences the existence of two mirror-like inversion paths: **IXb** ⇄ **Xb** ⇄ **IXb**′ and **IXb** ⇄ **Xb**′ ⇄ **IXb**′ (see Scheme 1).

The replacement of hydrogen attached to **X** atom in compound **IXb** for more electronegative fluorine as in compound **VIb** results in stabilization of the pyramidal structure as compared with *trans-s-trans* one. However in compound **IXb** the shortening of bonds XN is notably less (0.5 Å) than in compound **VIb** (1.0 Å).

1,3,2-Diazaarsolene and 2-fluoro-1,3,2-diaza-arsolene. The trend to greater energetical stability of pyramidal compared to planar structure is conserved also in the arsenic-containing compounds. Pyramidal (**XIIa, b**) and planar (**XIIIa, b**) structures of 1,3,2-diazaarsolene and 2-fluoro-1,3,2-diazaarsolene correspond to the energy minima on the PES of systems $AsN_2C_2H_5$ and AsC_2FH_4. However it should be stressed that unlike the phosphorus structures where structure **Xa** corresponding to a minimum is a polyene, and cyclic structure **Xb** corresponds to the transition state, the arsenic systems **XIIIa, b** are cyclic with AsN bonds of different length and correspond to minima.

Pyramidal structures **XII** are energetically more stable than the corresponding planar forms **XIII**: at
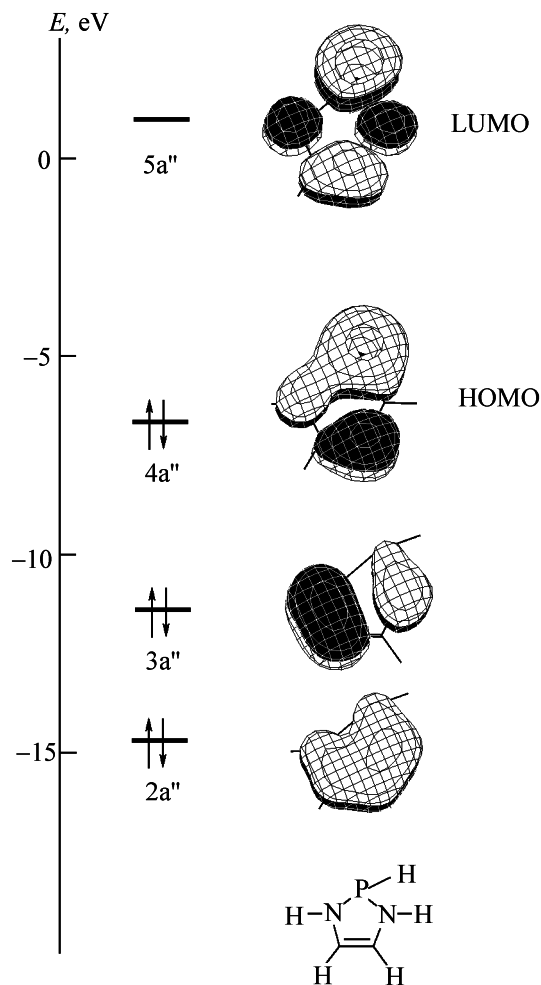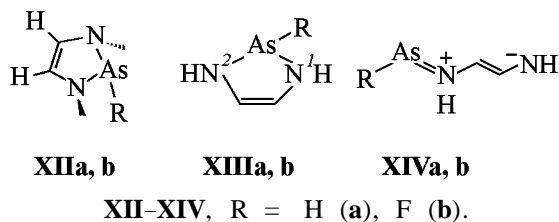

XIIa, b   **XIIIa, b**   **XIVa, b**

XII–XIV, R = H (**a**), F (**b**).

Fig. 3. Forms of occupied π-orbitals of the molecule of 1,3,2-diazaphospholene **Xa.**

R = H by 14.6 (MP2), 12.5 (B3LYP) kcal mol^{-1}, and at R = F by 5.2 (MP2), 6.5 (B3LYP) kcal mol^{-1}.

The change of hydrogen for fluorine at the arsenic in compound **XIIIa** results in sharp reduction in the length of As–N^2 bond, by 0.35 Å (MP2), 0.52 Å (B3LYP) due to additional interaction between the unshared electron pair of fluorine with the σ^*-orbital of the As–N^2 bond.

The difference between the total energies of the corresponding *cis-s-cis* and *trans-s-trans* structures alongside the energy of the As–N^2 bond contains also the energy of the π-electron delocalization that amounts respectively to 31.9 (MP2), 4.9 (B3LYP) kcal mol^{-1} for compound **XIIIa** and 59.1 (MP2), 26.7 (B3LYP) kcal mol^{-1} for **XIIIb**. Note here large difference between the values of relative energies calculated by methods MP2 and B3LYP apparently due to insufficiently precise three-parameter potential in the B3LYP method.
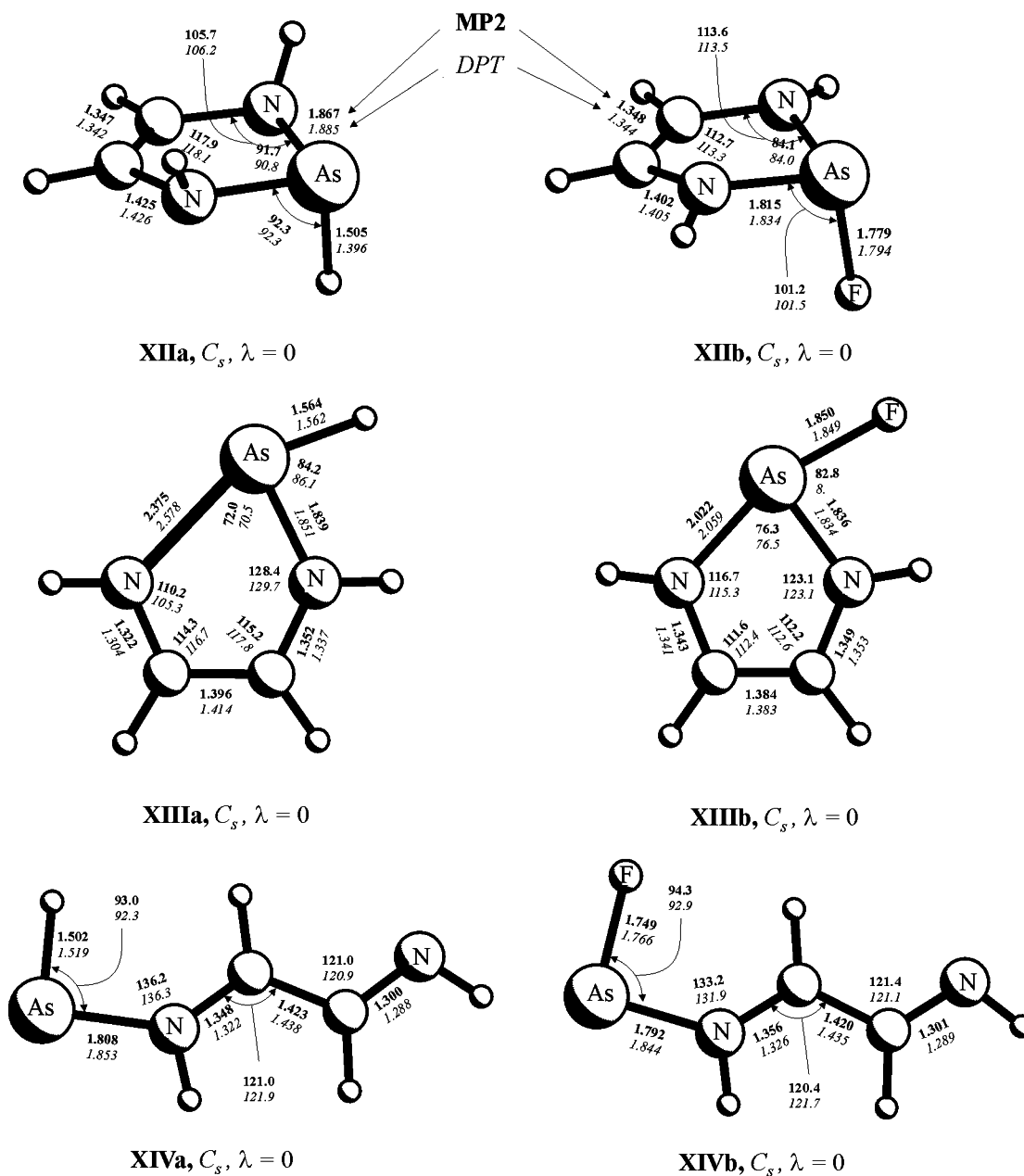
Fig. 4. Geometry characteristics of structures **XIIa–XIVa, XIIb–XIVb**, calculated by methods MP2/6-31G** (bold numbers), DFT/6-31G** (italic numbers). Bond lengths, Å; bond angles, deg.
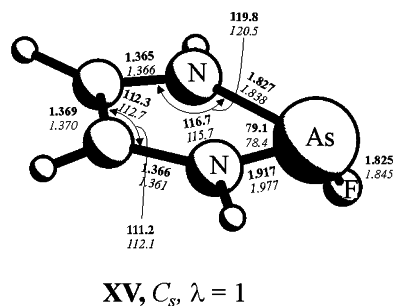

Fig. 5. Geometry characteristics of structures **XV**, calculated by methods MP2/6-31G** (bold numbers), DFT/6-31G** (italic numbers). Bond lengths, Å; bond angles, deg.
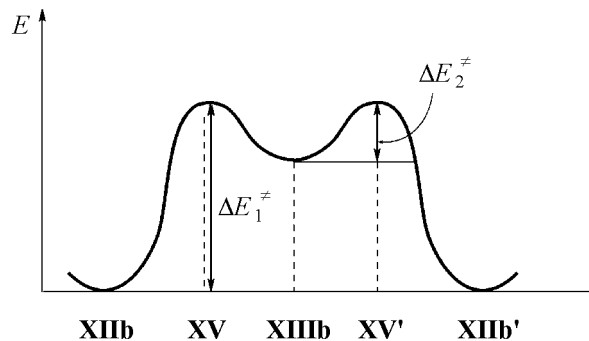
Fig. 6. Energy profile of inversion $(\mathbf{XIIb}) \rightleftarrows (\mathbf{XIIb'})$.

The calculated geometry and energy characteristics of structures **XII–XIV** are presented on Fig. 4 and in Table 1.

For 2-fluoro-1,3,2-diazaarsolene structure **XIIIb** corresponds to a shallow minimum (intermediate) as indicated by low frequency value of the first harmonic oscillation (see Table 1). Structure **XV** (see Fig. 5) is a transition state between the planar structure **XIIIb** and pyramidal form **XIIb** (Fig. 6). The energy barrier for this conversion $\Delta E_1^{\neq}$ is 2.6 (MP2), 1.1 (B3LYP) kcal mol^{-1}, and the barrier to inversion is $\Delta E_1^{\neq}$ 7.8 (MP2), 7.6 (B3LYP) kcal mol^{-1}.

Thus the calculations performed show that introduction of nitrogen into the five-membered ring of diazapnictolenes strongly stabilizes the planar structure and sharply reduces the barrier to pyramidal inversion of the bonds at the pnictogenic center. Therewith both the height of the barrier and the inversion mechanism depend on the nature of the pnictogenic center and on the electronegativity of a substituent attached thereto: the height of the barrier diminishes in the series N, P, As, and also in going from R = H to R = F, and the least value for 2-fluoro-1,3,2-diazaarsolene amounts to ~8 kcal mol^{-1}. The inversion process for 2-fluoro-1,3,2-diazaphospholene and 2-fluoro-1,3,2-diazaarsolene includes two mirror-like reaction paths through a structure of transition state (or intermediate) with the T-configuration of bonds at the pnictogenic center.

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