Structure and isomerization of heterapentalene compounds containing hypervalent bonds with central nitrogen, phosphorus, or arsenic atom

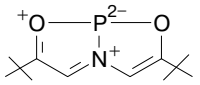
E. G. Nesterova, T. N. Gribanova, R. M. Minyaev, and V. I. Minkin*

Institute of Physical and Organic Chemistry at Rostov State University, 194/2 prosp. Stachki, 344090 Rostov-on-Don, Russian Federation. Fax: +7 (863 2) 28 5667. E-mail: minyaev@ipoc.rsu.ru

The possibility for a specific type of isomerization (electromorphism) to occur in conjugated bicyclic organic compounds containing Group V elements was studied by the *ab initio* (RHF/6-31G**, MP2(full)/6-31G**), and DFT (B3LYP/6-31G**) methods. Compounds **2** (X = N, P, As) were found to exist in a monocyclic planar form with intramolecular donor-acceptor N...O coordination (X = N) and as aromatic heterapentalene structures with hypervalent O—X—O bonds (X = P, As). According to calculations, no isomerization of planar heteroaromatic structures into pyramidal ones occurs. The strength of the O—X—O hypervalent bond and the aromaticity of heterapentalene structures **2** with ten π-electrons increase on going from X = N to X = P. Correct estimation of these effects requires the inclusion of electron correlation.

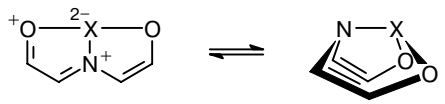
Key words: *ab initio* quantum-chemical calculations, heterapentalene structures, hypervalent bond.

X-Ray studies of 3,7-di(*tert*-butyl)-5-aza-2,8-dioxa-1-(10-P-3)-phosphabicyclo[3.3.0]octa-2,4,6-triene (**1**), which was first synthesized in 1983, revealed its unusual planar pentalene-type structure with a T-shaped bonding at the P atom.[1]



1

It is well known[2—5] that the barriers to inversion of ticoordinated hydrides XH_3 (X = N, P, As, Sb) increase from 5.3 kcal mol^{-1} (X = N)[3,4] to ~40—44 kcal mol^{-1} (X = As, Sb).[5] The reverse tendency is observed for trifluorides, XF_3, of the same elements; however, the barrier heights remain greater than 50 kcal mol^{-1}.[5]



2: X = N, P, As

3

Each of the two ticoordinated centers in compound **1** prefers pyramidal bonding. Therefore, judging from the "overall" effect, the pyramidal structure **3** must be at least 50 kcal mol^{-1} more energetically favorable than the planar structure. Pioneering *ab initio* RHF/6-31G** calculations of unsubstituted compounds **2** and **3** (X = P) showed[1] that planar structure **2** is 9.9 kcal mol^{-1} less energetically favorable than pyramidal structure **3**. Later, MP2 calculations with inclusion of electron correlation revealed a higher stability for the planar structure; on the other hand, it was confirmed that the pyramidal structure corresponds to a local minimum on the potential energy surface (PES) of this compound. Based on the results of the above-mentioned calculations, it was assumed[1] that the structures **2** and **3** (X = P) can have close thermodynamic stabilities. This allows the possibility for isomerization **2** ⇌ **3**, which was called electromorphism,[1] to occur. However, the kinetic stability of structure **3** (X = P), which is determined by the activation barrier to the reaction **2** ⇌ **3**, was not studied. Therefore, the question whether the pyramidal structure is a kinetically stable system or it is a short-lived intermediate on the valence isomerization pathway is still an open question.

In order to study a hypothetical new phenomenon, electromorphism, in this work we carried out *ab initio* calculations of the pathway of the isomerization **2** ⇌ **3** and its transition state (TS) for organophosphorus compounds. To reveal possible trends in the series of compounds with X = N, P, As, we also performed calculations for related structures with X = N and As.

Calculation Procedure

Calculations were carried out (i) by the *ab initio* Hartree—Fock (RHF) method, (ii) with inclusion of correlation of valence and core electrons at the second-order level of Møller—Plesset perturbation theory (MP2), and (iii) using density functional theory (DFT) with the B3LYP density functional in the 6-31G** split-valence basis set using the GAUSSIAN-94 [6] and GAMESS [7] program packages on RISC-6000, DEC Alpha-station 500, and Duranga workstations. Full optimization

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of the geometry of the molecular structures corresponding to the saddle points ($\lambda = 1$, where λ is the number of negative eigenvalues of the Hesse matrix[8]) and to the energy minima ($\lambda = 0$) on the PES was carried out up to the gradient magnitude of 10^{-5} hartree bohr^{-1} (the GAUSSIAN-94 program package running in the "tight" mode). The molecular structures shown in Figs. 1, 3, and 5 were obtained using the PD program (the PLUTO mode) incorporated into PCMODEL program package.[9]

Results and Discussion

Isomerization of 2-(1,2,3-oxadiazol-3-onia-3-yl)ethen-1-olate. Four stationary points corresponding to the structures **4—6**, and **8** (Fig. 1) were localized on the PES of 1,2,3-oxadiazolo-3-ylidenacetaldehyde.

Structures **4** and **8** correspond to the energy minima ($\lambda = 0$) while structures **5** and **6** correspond to the TS of isomerization ($\lambda = 1$). Cyclic structure **4** has one covalent N—O bond of length 1.410 (B3LYP), 1.398 (MP2), and 1.362 Å (RHF) and a short intramolecular N...O contact (2.766, 2.686, and 2.792 Å according to B3LYP, MP2, and RHF calculations, respectively), which is much shorter than the sum of the van der Waals radii of N (1.5 Å) and O (1.4—1.6 Å) atoms.[10] This is an additional argument in favor of the existence of attractive N...O interaction. The van der Waals radius of

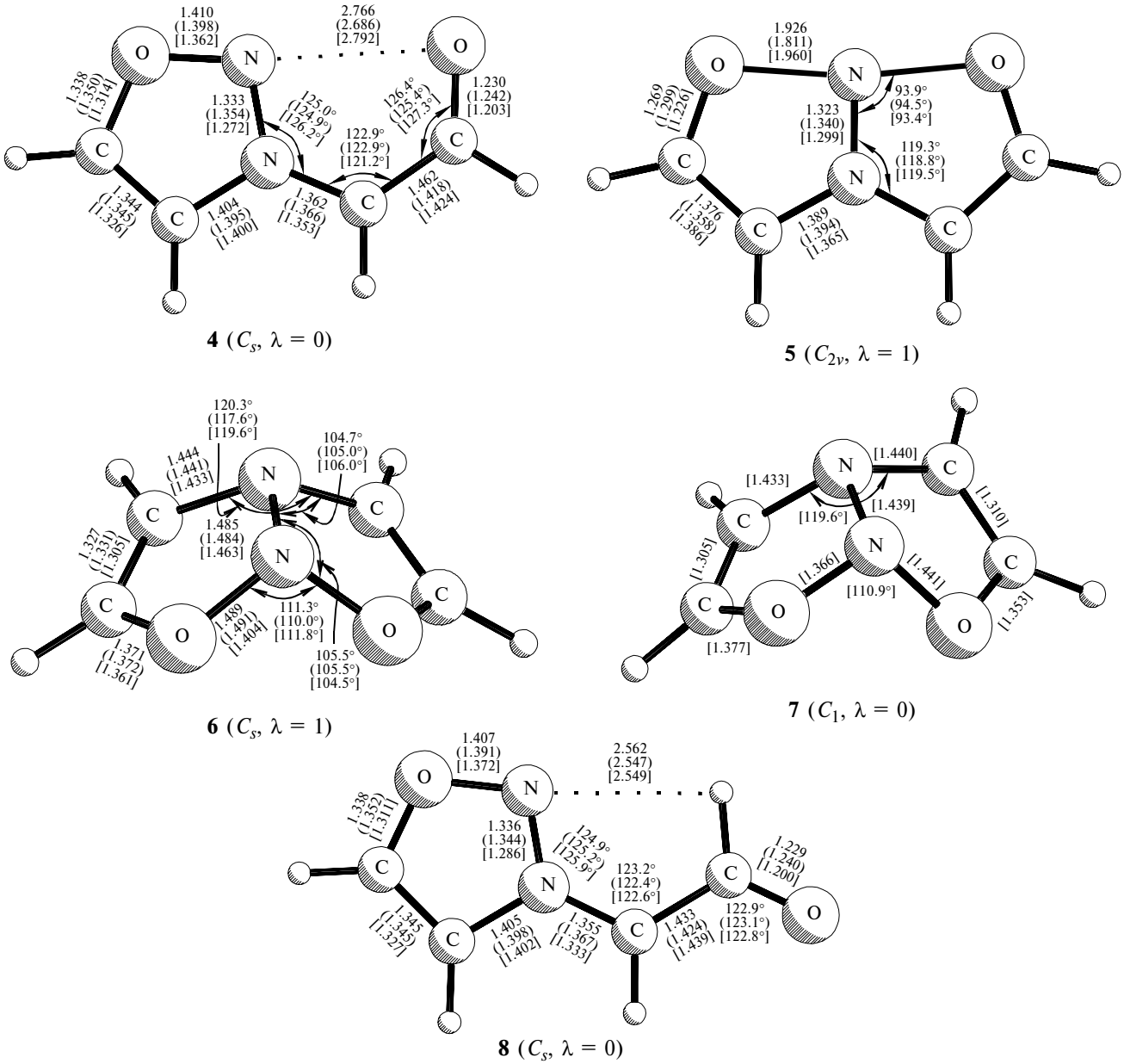


Fig. 1. Geometric parameters of structures **4—8** (X = N), obtained from the DFT (B3LYP), MP2 (figures in parentheses), and RHF (figures in brackets) calculations. Here and in Fig. 3 and Fig. 5 shown are bond lengths (in Å) and the bond angles.

Table 1. Results of the *ab initio* and DFT calculations of heterapentalene structures with X = N, P, and As

Structure	Method	λ	E_{tot}/au	ΔE /kcal mol^{-1}	ZPE/au	ΔE_{ZPE} kcal mol^{-1}	ΔH kcal mol^{-1}	(ω/*i*ω)/cm^{-1}
				X = N				
4	RHF	0	−412.249801	0	0.090321	0	0	98
	MP2	0	−413.518996	0	0.084039	0	0	79
	B3LYP	0	−414.644176	0	0.083002	0	0	94
5	RHF	1	−412.187043	39.4	0.086498	35.1	36.8	*i*701
	MP2	1	−413.481680	23.4	0.082763	22.6	22.2	*i*711
	B3LYP	1	−414.616099	17.6	0.081061	16.4	16.1	*i*346
6	RHF	1	−412.192018	36.3	0.091107	34.9	35.8	*i*130
	MP2	1	−413.440880	49.0	0.082252	47.9	47.1	*i*176
	B3LYP	1	−414.572686	44.8	0.081448	43.9	43.2	*i*171
7	RHF	0	−412.194893	34.5	0.091625	33.4	34.6	175
8	RHF	0	−412.250418	−0.4	0.090125	−2.4	0	111
	MP2	0	−413.516274	1.7	0.084012	1.7	1.8	51
	B3LYP	0	−414.643992	0.1	0.082890	0	0.2	87
				X = P				
11	RHF	0	−698.649378	0	0.087699	0	0	142
	MP2	0	−699.886027	0	0.082368	0	0	151
	B3LYP	0	−701.373244	0	0.081173	0	0	158
12	RHF	0	−698.664577	−9.5	0.087621	−9.55	−9.6	79
	MP2	0	−699.859543	16.6	0.081341	16.0	16.1	119
13	RHF	1	−698.643718	3.6	0.087291	3.3	2.9	*i*196
	MP2	1	−699.859098	16.9	0.081089	16.1	15.7	*i*146
14	RHF	0	−698.612397	23.2	0.085867	22.1	22.7	91
	MP2	1	−699.830617	34.8	0.080412	26.5	33.7	*i*45
	B3LYP	0	−701.329622	27.4	0.079454	26.3	26.8	73
				X = As				
15	RHF	0	−2589.924653	0	0.086391	0	0	150
	MP2	0	−2589.988590	0	0.080910	0	0	142
	B3LYP	0	−2593.791721	0	0.080206	0	0	152
16	RHF	0	−2589.925610	−0.6	0.086448	−0.56	−0.6	102
17	RHF	0	−2589.887788	23.1	0.085163	22.4	22.4	93
	MP2	0	−2589.944544	27.6	0.079034	26.5	26.5	34
	B3LYP	0	−2593.743230	30.4	0.078668	29.5	29.5	81

Note: calculations were carried out with the 6-31G** basis set; E_{tot} is the total energy (1 au = 627.5095 kcal mol^{-1}); λ is the number of negative eigenvalues of the Hesse matrix; ΔE is the relative energy; ZPE is the zero-point vibrational energy correction; ΔE_{ZPE} is the relative energy with inclusion of zero-point vibrational energy correction; ΔH is the relative enthalpy under standard conditions (p = 1 atm, T = 298.15 K); and ω is the lowest or imaginary harmonic frequency.

O atom (1.29 Å, see review[11]) seems to be too underestimated. The energy of intramolecular, donor-acceptor N...O interaction can be roughly estimated as the difference between the total energies of structures **4** and **8** (Table 1). Structure **8** was so chosen that the N...O interaction is excluded, but conjugation effects are retained. The calculated energy of the N...O interaction was found to be 0.1 (B3LYP) and 1.7 (MP2) kcal mol^{-1}. On the other hand, RHF calculations do not predict the existence of attractive N...O interaction (ΔE = −0.4 kcal mol^{-1}). In line with the conclusions drawn earlier,[12,13] this indicates that a correct estimate of the energy of this interaction requires the inclusion of electron correlation. The approach of the N and O atoms in system **4** is due to the interaction between the lone electron pair orbital of the O atom and the vacant σ*-orbital localized on the N atom. The pattern of the resultant MO (23a′), which describes this donor-acceptor interaction, is shown in Fig. 2.

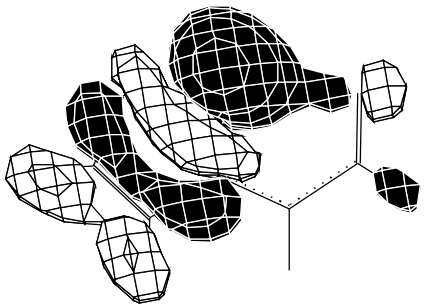
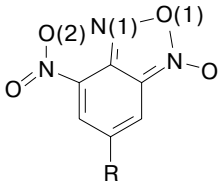


Fig. 2. Pattern of the 23a′ MO describing the N...O donor-acceptor interaction.

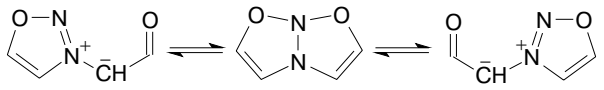
Experimental[14] and theoretical[15] studies of the benzannelated substituted systems **9**, which are best suited to simulation of heterocyclic pentalene **4**, showed that they do exist in open forms and their structural characteristics are in good agreement with the results obtained in this work. For instance, the N(1)—O(1) and N(1)—O(2) bond lengths in 4,6-dinitrobenzofuroxan (system **9**, R = NO_2) are 1.42 and 2.63 Å, respectively.



9

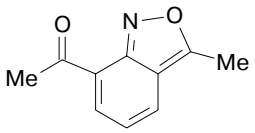
Mention may be made of a small deviation of the calculated C=C, C—N, and C—O bond lengths (see Fig. 1) from the values typical of conjugated systems (1.335,[10] 1.430, and 1.360 Å) toward their delocalization.

According to calculations, structure **5** ($\lambda = 1$) is a TS of the isomerization **4a** ⇌ **5** ⇌ **4b**, which proceeds by the mechanism of intramolecular nucleophilic substitution at the dicoordinated N atom. The activation barrier was found to be dependent on the computational method employed, namely, 39.4 (RHF), 23.4 (MP2) and 17.6 kcal mol^{-1} (DFT). The strong decrease in the activation barrier observed on going from the RHF to MP2 calculations indicates that correlation effects make an appreciable contribution (nearly 50%) to the barrier height.



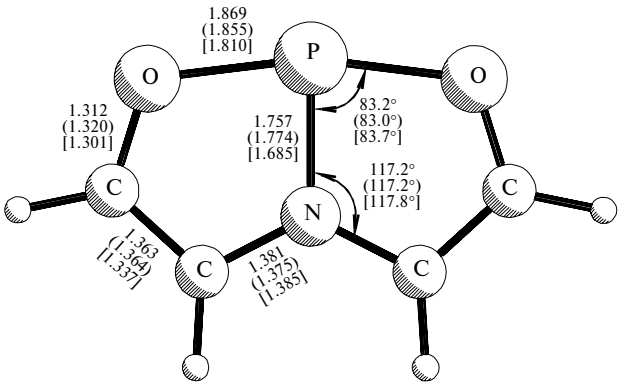
4a **5** **4b**

Previously, a similar intramolecular nucleophilic substitution proceeding by the mechanism of the Boulton—Katritzky rearrangement has been studied experimentally[16,17] and theoretically[15] taking 7-acetyl-3-methylanthranil (**10**) and 4-nitrobenzofuroxan (system **9**, R = H) as respective examples.

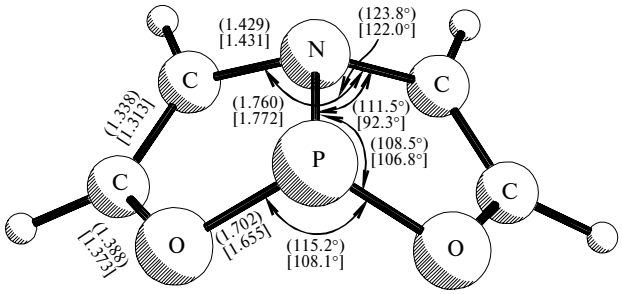


10

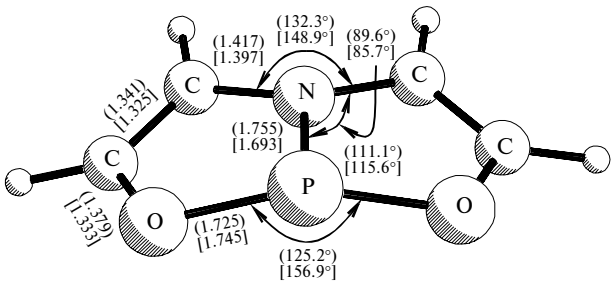
NMR studies[16] of system **10** showed that the activation barrier to the O—N...O ⇌ O...N—O bond migration lies between 23.0 and 23.5 kcal mol^{-1}. This is in good agreement with the results of our calculations.



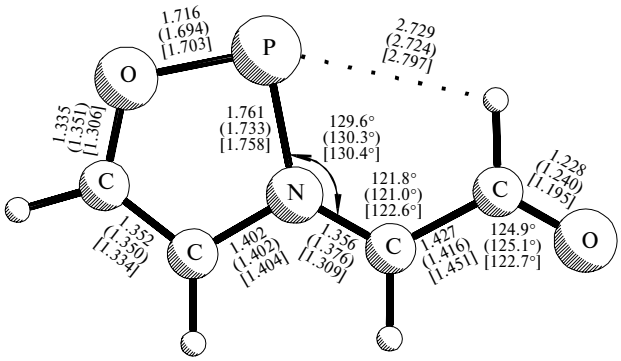
11 (C_{2v}, $\lambda = 0$)



12 (C_s, $\lambda = 0$)



13 (C_s, $\lambda = 1$)

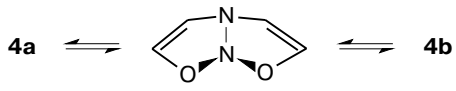


14 (C_s, $\lambda = 0$)

Fig. 3. Geometric parameters of structures **11—14** (X = P), obtained from the DFT (B3LYP), MP2 (figures in parentheses), and RHF calculations (figures in brackets).

Nonempirical calculations[15] of the isomerization of 4-nitrobenzofuroxan showed that the height of the activation barrier to the O—N...O ⇌ O...N—O bond migration is strongly dependent on the computational method employed and lies between 21.5 and 43.5 kcal mol^{-1}. The difference between these values and the results obtained in our studies is likely due to the fact that the bond migration in 4-nitrobenzofuroxan occurs between nitro groups, whereas in our case this occurs between carbonyl groups.

According to calculations, the isomerization **4a** ⇌ **4b** can also follow the pathway **4a** ⇌ **6** ⇌ **4b** passing through a "pyramidal" TS **6** with an energy barrier of 49.0 (MP2) and 44.8 kcal mol^{-1} (DFT), which is much higher than the barrier to the isomerization **4a** ⇌ **5** ⇌ **4b**.



6

RHF calculations predict the existence of intermediate **7** ($\lambda = 0$) of the isomerization **4a** ⇌ **6** ⇌ **4b**, with a slightly distorted pyramidal structure with C_1 symmetry (see Fig. 1). However, calculations at the MP2 level of theory with inclusion of electron correlation show that structure **7** is not a stationary point.

Therefore, despite the fact that the pyramidal structure **6** corresponds to a stationary point on the PES of 1,2,3-oxadiazolo-3-ylidenacetaldehyde, it is unstable (a TS, in the framework of this approximation). Thus, no electromorphism occurs in system **4**.

Isomerization of 5-aza-2,8-dioxa-1-(10-P-3)-phosphabicyclo[3.3.0]octa-2,4,6-triene. According to our calculations, the molecule **2** (X = P) can adopt two conformations, a planar conformation **11** and a pyramidal conformation **12**. The calculated structural and energy characteristics of the conformations are presented in Fig. 3 and listed in Table 1, respectively.

Planar bicyclic structure **11** has a C_{2v} symmetry. The calculated P—O bond length is 1.869 (DFT), 1.855 (MP2), and 1.810 Å (RHF). The P—O interaction in 5-aza-2,8-dioxa-1-(10-P-3)-phosphabicyclo[3.3.0]octa-2,4,6-triene **11** is much stronger than the N—O interaction in compound **4** and leads to the formation of a rather strong O—P—O triad with a hypervalent bond.

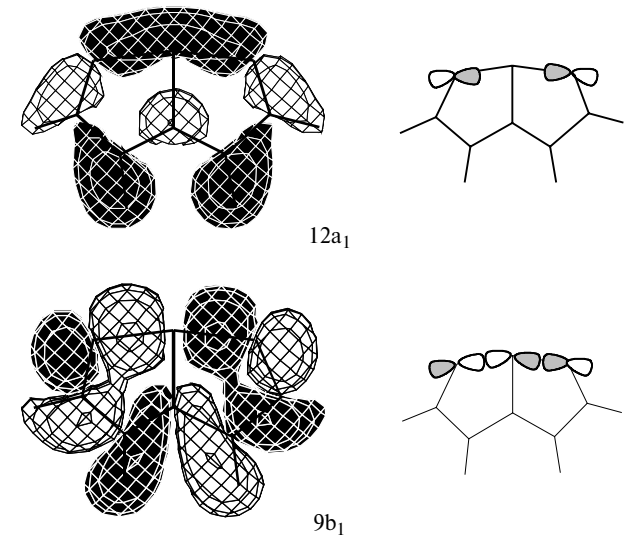
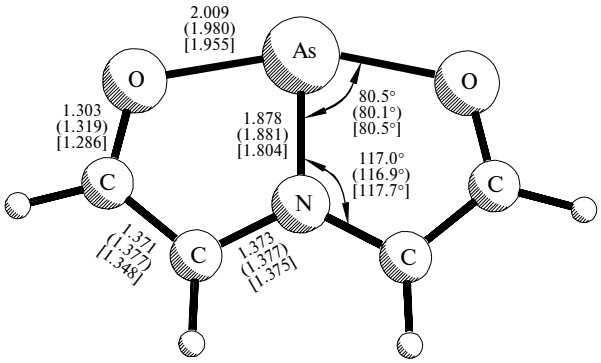
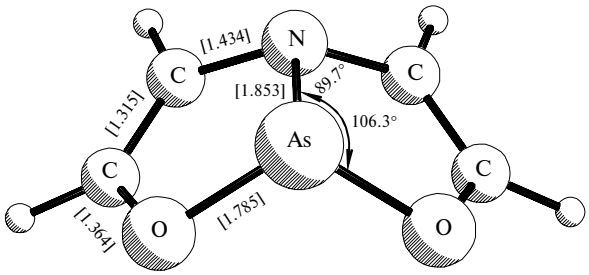


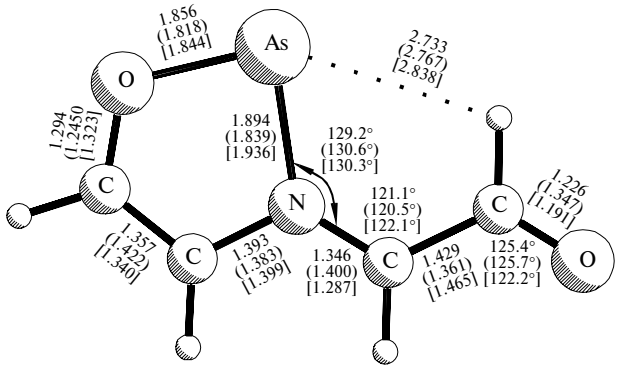
Fig. 4. Patterns of the $12a_1$ and $9b_1$ orbitals describing the O—P—O hypervalent interaction.



15 (C_{2v}, $\lambda = 0$)



16 (C_s, $\lambda = 0$)



17 (C_s, $\lambda = 0$)

Fig. 5. Geometric parameters of structures **15—17** (X = As), obtained from the DFT (B3LYP), MP2 (figures in parentheses), and RHF calculations (figures in brackets).

The orbital patterns for this bond are presented in Fig. 4. The energy of the hypervalent bond and the contribution of "aromaticity" to structure **11** estimated as the differences between the total energies of structures **11** and **14** are 27.4 (DFT), 34.8 (MP2) and 23.2 kcal mol^{-1} (RHF). These values must be even somewhat increased owing to relaxation of the strain in structure **11**.

Structural characteristics of planar system **11** calculated in this work are in good agreement with the published results[1] of X-ray study of 3,7-di(*tert*-butyl)-5-aza-2,8-dioxa-1-(10-P-3)-phosphabicyclo[3.3.0]octa-2,4,6-triene **1** in which the bond lengths are 1.835(2) and 1.792(2) Å for P—O, 1.375(3) and 1.382(3) Å for C—N, 1.331(4) and 1.328(4) Å for C—O, and 1.342(4) and 1.337(4) Å for C—C.

The calculated relative energy of structure **12** (see Table 1) is −9.5 (RHF) and 16.6 kcal mol^{-1} (MP2). According to RHF calculations, the pyramidal structure is more thermodynamically stable, whereas the reverse is predicted at the MP2 level of theory with inclusion of electron correlation. On the other hand, density functional approach, which is known to be well suited to

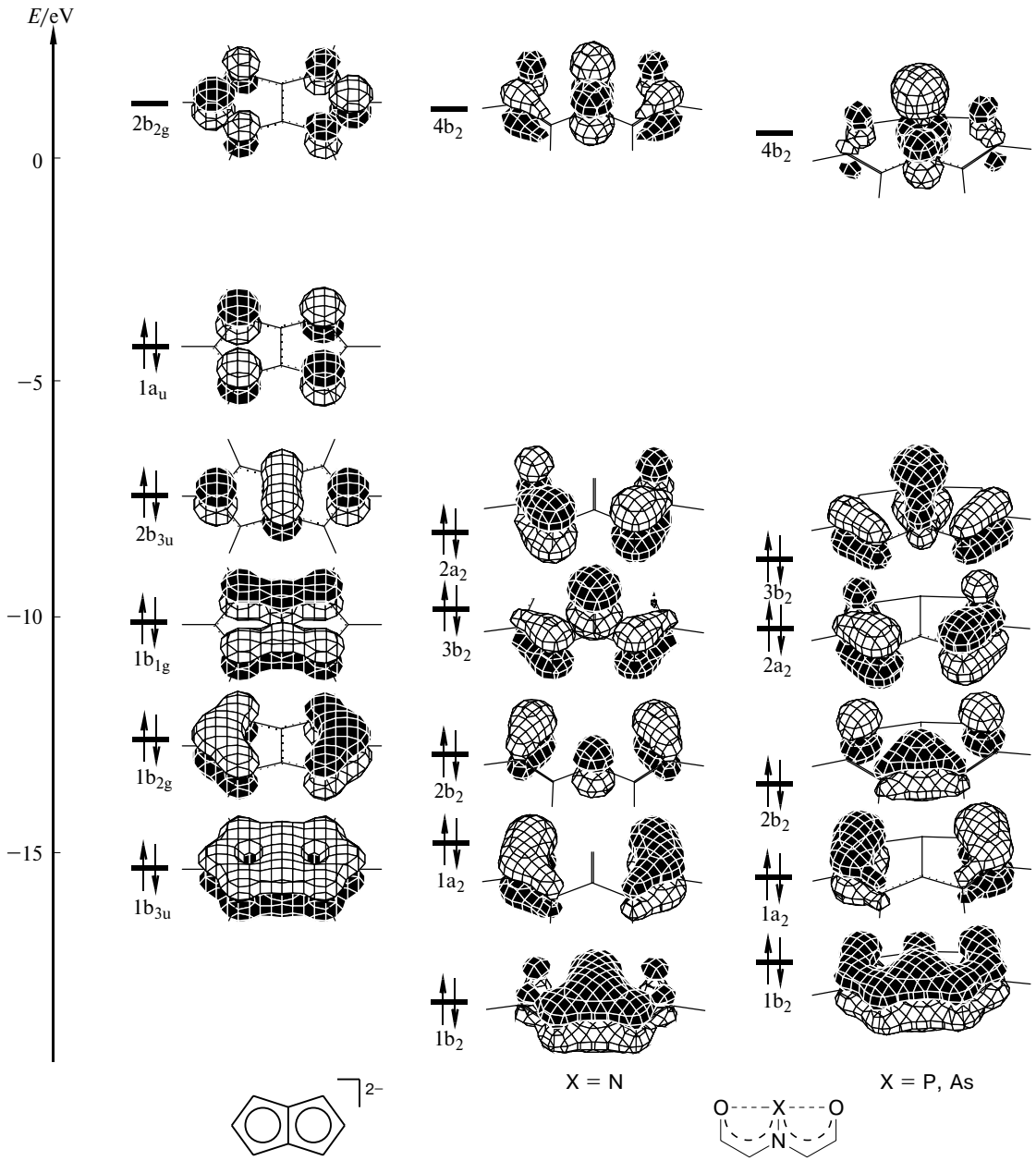
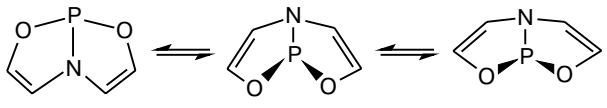


Fig. 6. Correlation of the π-orbitals of the pentalene dianion and planar structure **2** with ten π-electrons.

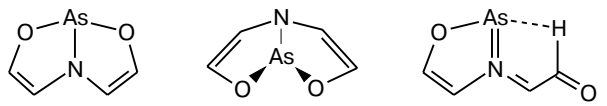
description of hypervalent interactions,[18] does not predict the existence of pyramidal structures of the types **12** and **13**.



11 **13** **12**

According to calculations (see Table 1), the kinetic stability of structure **12** is low (the energy barrier to the reaction **12** → **11** does not exceed 0.3 kcal mol^{-1}). This suggests that the isomerization of the type **11** ⇌ **12** (electromorphism) in 5-aza-2,8-dioxa-1-(10-P-3)-phosphabicyclo[3.3.0]octa-2,4,6-triene and its derivatives is purely hypothetical.

Isomerization of 5-aza-2,8-dioxa-1-(10-As-3)-arsenabicyclo[3.3.0]octa-2,4,6-triene. As was mentioned above, the barriers to inversion in the arsenic hydride AsH_3 and arsenic fluoride AsF_3 exceed 50 kcal mol^{-1}. Since the covalent radius[19] of As is much larger than that of P (1.21 *vs.* 1.09 Å, respectively), the pentalene-type system **15** is more sterically strained than system **11**. Therefore, one can expect a higher stability of the pyramidal structure as compared to that of the planar structure on going to the As derivative **15**. However, both MP2 and DFT calculations predict the reverse situation, namely, that the molecule of 5-aza-2,8-dioxa-1-(10-As-3)-arsenabicyclo[3.3.0]octa-2,4,6-triene exists only in the aromatic planar form **15**. On the other hand, RHF calculations do predict the existence of pyramidal structure **16**, which in this approximation appears to be 0.6 kcal mol^{-1} more stable than planar form **15**.



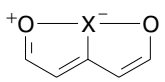
15 **16** **17**

The calculated geometric and energy characteristics of compounds **15**—**17** are shown in Fig. 5 and listed in Table 1, respectively.

On going from the phosphorus to arsenic derivatives, the hypervalent bond is lengthened by ~0.15 Å, which leads to a greater delocalization of the entire structure **15**. As in the case of compound **11**, the As—O bond in structure **15** is hypervalent. Its energy estimated as the difference between the total energies of structures **15** and **17** is 30.4 (DFT), 27.6 (MP2), and 23.1 kcal mol^{-1} (RHF). The energy of the As—O bond in structure **15** is somewhat lower than that of the P—O bond in structure **11**. This weakening of bonding is due to the larger covalent radius of As compared to P, and, hence, to an increase in the steric strain in the pentalene-type structure **15**.

The results of our calculations suggest that, similarly to the nitrogen and phosphorus compounds considered above, no isomerization of the type **15** ⇌ **16** (electromorphism) occurs in system **15**.

In conclusion, mention may be made that the stabilities of bicyclic aromatic structures and the strengths of the three-center O—X—O hypervalent bonds increase with an increase in the number of the central atom, as is the case of recently studied[20] 1,6-dioxa-6a-chalcogenopentalenes **18**, which are isoelectronic analogs of structure **2**. Correct estimates of the role of these effects requires the inclusion of electron correlation.



18: X = S, Se, Te

Our calculations showed that system **2** has only five filled π-orbitals (their patterns are shown in Fig. 6) and is an isoelectronic analog of the aromatic structure of pentalene dianion.

Figure 6 illustrates a similarity between the π-systems of an aromatic pentalene dianion with ten π-electrons and heteropentalene structures, which can be evidence of the 10π-electron aromaticity of the structures under study.

Thus, we found that planar structure **2** with the hypervalent atom X in position 1 is more energetically favorable (by 25.6 kcal mol^{-1} (MP2) for X = N, 16.6 kcal mol^{-1} (MP2) for X = P, and 25.4 kcal mol^{-1} (DFT) for X = As) than the classical structure **3** with two pyramidal pnictogenic atoms. This can be interpreted as a consequence of the 10π-electron aromaticity of the former structure.

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