Cyclic Aromatic Systems with Hypervalent Centers

Vladimir I. Minkin* and Ruslan M. Minyaev

Institute of Physical & Organic Chemistry, Rostov State University, 194/2 Stachka St. 344090 Rostov on Don, Russia

Received August 20, 2000

Contents

I. Introduction

Among the theoretical concepts that constitute the rational basis of modern organic chemistry, the concept of aromaticity is one of the most general but also vaguely defined constructs. Aromaticity is discussed in terms of structural (bond length alternation, planarity), magnetic (anisotropy and exaltation of magnetic susceptibility, ^{1}H NMR and nuclear independent chemical shifts−NICS), and energetic (stabilization energies) criteria.[1−6] Additional stabilization caused by the cyclic electron delocalization represents the most important feature of the aromatic character of a compound. Such an effect manifests itself in a broad variety of π-conjugated organic and organometallic ring systems, for which reason aromaticity as a theoretical concept and the terms “aromaticity” and “aromatic” appeared to be among the most often used in organic chemistry.[6] While being introduced for the description of specific chemical, structural, and magnetic properties of conjugated hydrocarbons, before long the concept of aromaticity was extended to various other types of compounds, first of all to conjugated heterocycles displaying cyclic electron delocalization.[3,7−9] By substituting CH (CR) units in a conjugated cyclic hydrocarbon by heteroatoms divided into three main types X, Y, and Z depending on the number of electrons in

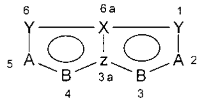
Vladimir Minkin received his Candidate and Doctor of Sciences (Chemistry) degrees from Rostov State University in 1959 and 1966, respectively. In 1967 he was appointed Professor at the same university, and since 1981 he has held the position of Head of the Institute of Physical and Organic Chemistry. He was a visiting professor or visiting scientist at the Havana, Queens, Strathclyde, Cornell, and Humboldt Universities, received his Dr. h.c. degree from the University of Aix-Marseille, and was elected a member of Russian Academy of Sciences. His research interests include applied quantum chemistry, stereodynamics of metal coordination compounds, photochromism, tautomerism, and organotellurium chemistry.

Ruslan M. Minyaev was born in Semipalatinsk (USSR) in 1943. He received his B.S. degree (in Physics) in 1969 at the Rostov State University, Rostov on Don, Ph.D. degree in 1974 with V. I. Minkin at Rostov State University, and Doctor of Science degree in 1985 (in Physical and Organic Chemistry) at the Rostov State University. After passing all researcher positions from junior to main researcher, he assumed his current position as head of the laboratory (1992) at the Institute of Physical and Organic Chemistry of Rostov State University. He was visiting scientist at the Chemistry Department of Cornell University (1989–1990), the University Chemical Laboratories at Cambridge University (1993, 1996), and Emerson Center of Chemistry Department at Emory University (1997). His current research interests focus on the topology of potential-energy surface, chemical valence and bonding, nonclassical molecular structure of organic and main-group metal-containing organic compounds, low-barrier isomerization, reaction mechanisms of intramolecular rearrangements, hydrogen and donor–acceptor bonding, and cooperative processes in molecules and their clusters.

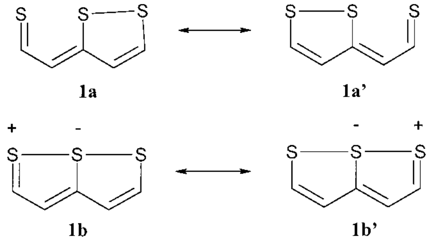
10.1021/cr990358h CCC: $36.00

the p_z orbital of the sp^2-hybridized atom and by applying, along with the general ($4n + 2$) rule, the so-called semiempirical aromatic electronegativity constants attributed to each particular center,[10] one can derive a reasonably good approach to prediction of the aromatic (or antiaromatic) character of a given heterocycle.

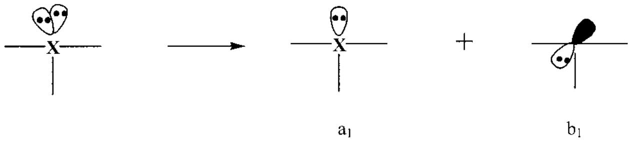
This approach does not, however, account for a special type of heteroatoms that possesses expanded valence electron shells, i.e., those in their hypervalent state. A long-known and amply discussed[11−14] example of the heteroaromatic compounds containing such a heteroatom is given by 1,6,6aλ^4-trithiapentalene and related compounds **1**. The structures of the parent trithiapentalene **1** (X = Y = S, A = B = CH, Z = C) and its symmetrically substituted derivatives and analogues have C_{2v} symmetry. Therefore, they cannot be represented by a single Lewis structure and have to be treated as either no bond resonance **1a** ↔ **1a′** or resonance of the two forms **1b** ↔ **1b′** containing three-center, four-electron Y−X−Y bonds.



1 X=S, Se, Te, NR, PR, AsR, SbR, BiR; Y=O, S, Se, NR; A=B=C(R), N; Z=N, C



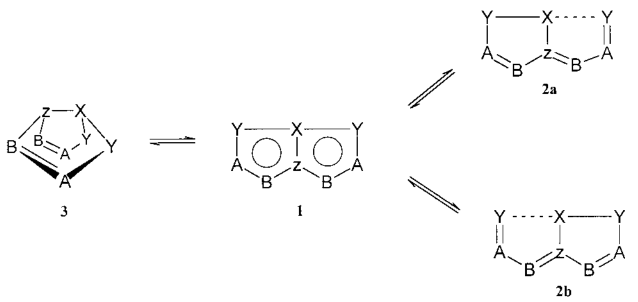
The bonding type realized in the latter case implies formation of familiar σ-orbitals of the hypervalent (i.e., expanding its valence shell beyond the limits of the Lewis octet rule) T-shaped electron-rich center also bearing two lone pairs that can be presented as their symmetry-adapted MO equivalents.[15−17] The b_1 lone pair contributes to the formation of the aromatic decet of the bicyclic species **1b**, thus providing for the extra stability of its C_{2v} structure.



X = F, Cl, Br, I, S$^-$, Se$^-$, Te$^-$, P^{2-}, As^{2-}, Sb^{2-}, Bi^{2-}

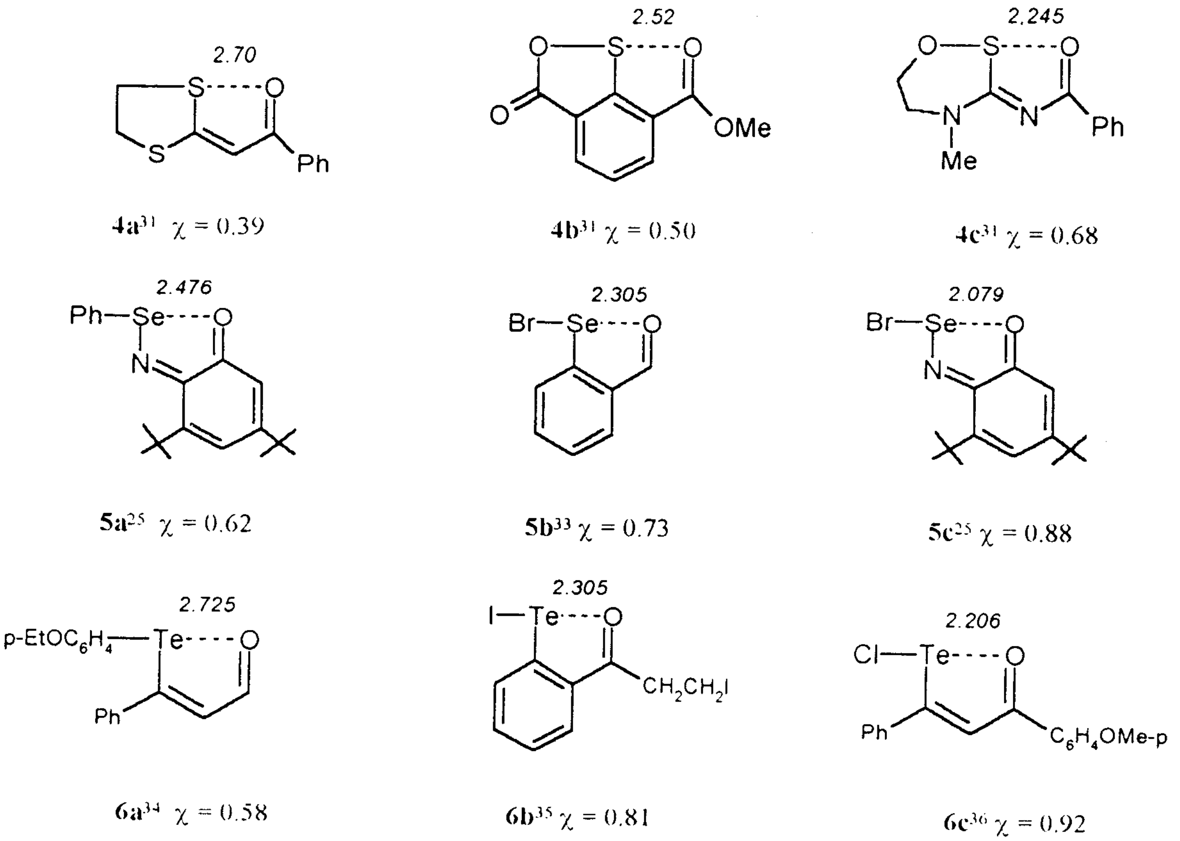
Depending on the nature of the central atom X and ring centers Y and Z, the molecules **1** may undergo deformations of two types, each resulting in destroying the aromatic electron configuration (Scheme 1). The energy released upon the isomerization **1** ⇌ **3** due to folding along the X−Z bond may serve as a measure of aromaticity of the planar structure **1**, even though corrections are to be made as to conversion of one three-center, four-electron Y−X−Y bond to two covalent X−Y bonds. Conformational rearrangement of this type associated with the phenomenon of “electromorphism”[18,19] was considered as characteristic for the tricoordinated hypervalent pnictogen (X = P, As, Sb; Z = N) compounds. It was well documented for derivatives of 5-aza-2,8-dioxa-1-phosphabicyclo[3.3.0]octa-2,4,6-triene **3** (X = P, Y = O, Z = N, A = B = CH).[18−20] No such distortion has so far been registered for the isoelectronic dioxachalcapentalenes **1** (X = S, Se, Te, Y = O, A = B = CH, Z = C) because it requires separation of charges along the X−Z bond in the isomer **3** (e.g., $S^+{-}C^-$ in 1,6-dioxa-6a-thiapentalene). Instead of this, the type **1** compounds with tricoordinated chalcogen centers X are known to be influenced by the tendency for lateral distortions **1** ⇌ **2**. Extensive X-ray crystallography studies have shown that the two X−Y distances in all unsymmetrically substituted trithiapentalenes, 1,6-dioxa-6a-chalcapentalenes and their analogues (X = Chalc, Y = O, Chalc, NR) differ in their length, one of them being significantly elongated compared to the standard covalent X−Y bond.[12,21,22] At the same time, these molecules retain the sterically strained C_s-symmetric structure **2** with *cis*-configuration about the Z=B bond, which ensures strong attractive intramolecular interaction between the formally nonbonded closed electron-shell centers X and Y.

Scheme 1



The nature and chemical and structural consequences of the X···Y interactions of this type occurring between two electron-abundant main-group 15−17 (VA−VIIA) element centers within a molecule have drawn special attention of both experimentalists and theorists and are a topic of rapidly growing interest.[21−30] An important feature of the X···Y bonds is strong dependence of their strength and lengths on the nature of the interacting centers and the electronegativity of the attached substituents. By varying these factors in a series of compounds with similar molecular frameworks, it is possible to cover a wide range of intramolecular distances, from those approaching values characteristic of covalent X−Y bonds to those close to van der Waals (vdW) contacts. This trend is illustrated by an excerpt of X-ray structural data for the organochalcogen (X = Chalc) compounds with conjugated five-membered chelate rings, which are the fragments of structure **2** (Figure 1).

On the basis of the theoretical work performed at the HF level with basis sets STO-3G, 3-21G, and 3-21G*, it was concluded that the principal factor that accounts for this tendency and, in general, for the strength of a X···Y bond is donation of an electron



4a[31] $\chi = 0.39$ **4b**[31] $\chi = 0.50$ **4c**[31] $\chi = 0.68$

5a[25] $\chi = 0.62$ **5b**[33] $\chi = 0.73$ **5c**[25] $\chi = 0.88$

6a[34] $\chi = 0.58$ **6b**[35] $\chi = 0.81$ **6c**[36] $\chi = 0.92$

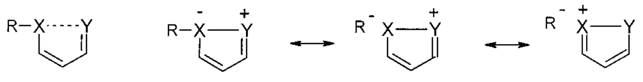
Figure 1. X-ray structural data (Chalcogen···O bond length, d in Å) and the covalency ratio factors, χ, calculated on the basis of Bondi[37] covalent and van der Waals radii. ΣR_{vdW} (S, O) = 3.30 Å, ΣR_{vdW} (Se, O) = 3.40 Å, ΣR_{vdW} (Te, O) = 3.60 Å.

pair from the highest π or n orbitals of Y to the lowest lying σ^* orbital of the neighboring center X. This interaction, which corresponds to the $n_O-\sigma^*_{Ch-R}$ type (negative hyperconjugation) in compounds **4**–**6**, leads to expansion of the valence shell of the chalcogen atoms, for which reason bonds of this type were suggested to be qualified as "premature hypervalent bonds".[24] The degree of this expansion may be characterized by the so-called covalency ratio factor χ introduced by Weinhold and co-workers[38]

$$\chi = \frac{(R_X + R_Y) - d_{XY}}{(R_X + R_Y) - (r_X + r_Y)} \qquad (1)$$

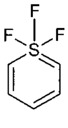
where R_X and R_Y stand for van der Waals and r_X and r_Y for covalent radii of the interacting centers, d_{XY} being the experimentally determined (or calculated) contact.

As seen from the experimental data on the Chalc···O distances shown in Figure 1 and the corresponding χ values calculated based on these data, the secondary Chalc···O bonds in all the compounds are much shorter than the sum of the van der Waals radii of respective atoms and in some of the compounds, e.g., **5b**, **6b**, **6c**, are almost indistinguishable in their lengths from the corresponding covalent two-center, two-electron bonds. At the same time, the R–Chalc bonds in compounds **4**–**6** are significantly elongated. Owing to very short ClTe···O and ClSe···O contacts in derivatives of β-chalcovinylaldehydes **7** (X = S, Se, Te; Y = O), these compounds are considered, indeed, as the true heterocycles, respectively, 1,2-oxatellurolyl-1-ium and 1,2-oxaselenolyl-1-ium chlorides.[36,39,40] Their electronic structure can, therefore, be described as the resonance hybrid of the structures with six-electron delocalized π-systems. The chemical behavior of compounds **7** (retention of the structural type in reactions with electrophiles, readiness to ionization of the R–X bond under treatment with supernucleophiles) well corresponds to the aromatic **7a** ↔ **7a′** ↔ **7a″** but not to the heterodiene structure of the type **7**.[27,41,42]

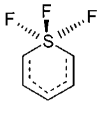


7 7a 7a' 7a''

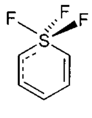
High values of the covalency ratio factors for compounds **4**–**6** are in line with the results of calculations, e.g.,[25,43] employing the theory of atoms in molecules (AIM),[44] which point to the existence of a chemical bond between formally nonbonded chalcogen and oxygen atoms involved into the conjugated five-membered rings **7**. These findings justify the attribution of a broad variety of type **7** compounds to the pseudo-heterocycles containing π-electron sextets in the ring and, therefore, acquiring substantial aromatic character. On the contrary, in this review paper we do not assign to aromatics such compounds as thiazole and thiadiazole-1 of 1-dioxides[45] or 1,1,1-trifluorothiabenzene[46] **8**, in which no vacant or a lone electron pair orbital of π-symmetry is located at the hypervalent center incorporated into the unsaturated ring. Although the RHF (DZ + P) calculations[46] addressed the question “whether an intimate fusion of aromaticity with hypervalency is possible”, it was found that the C_s ring structure **8a** is consistent with aromaticity (notable equalization of the CC distances in the ring); it does not correspond to a minimum on the PES. For the stable C_s structure **8b**, the calculations[46] revealed significant alternation of the CC bond lengths. The lack of the aromatic character in **8** and other compounds of similar type is in accord with recent theoretical analyses[47−49] which showed that multiply bonded molecules of main-group 15−17 elements, traditionally treated as hypervalent, are better described in terms of the ionic structures. No evidence was found for double bonding at four- and higher-coordinated sulfur or selenium atoms, which for a long time has been a conventional way to describe the structure of the molecules they form.



8



8a

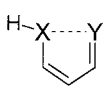


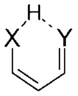
8b

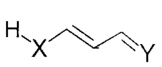
II. Five-Membered Rings with the Intramolecular Coordination X←Y Bonds (X = Chalc, Pnict, Hal; Y = O, NR, S)

II.1. β-Chalcovinylaldehydes and Derivatives

A particular class of compounds **7** exhibiting the shortest X···Y nonbonded contacts is β-chalcovinylaldehydes **7** (X = S, Se, Te; Y = O) and their imines (Y = NR). The high strength of the Chalc···Y (O, S, NR) interaction in these compounds is elucidated by the computational findings[24,50,51] which showed that the *trans-cis-cis* conformations **7** (R = H) with the tricoordinated T-shaped chalcogen centers are roughly energy equivalent to both *cis-cis-cis* conformations **7a**, ensuring formation of the intramolecular hydrogen bonds (like that in the most stable conformation of its oxygen analogue **7** (X = Y = O)), and the unstrained *trans-trans-trans* conformations **7b**.







		7 (R=H)	7a (R=H)	7b (R=H)
X=Y=O	E_{rel} (kcal mol^{-1})[a]	12.7	0	5.7
X=S, Y=O		0.3	0	1.0
X=Y=S		0		0.9

[a] MP2(full)/6-31G** computed values[50,51]. There is no local minimum on the PES for the planar structure 7a (X=Y=S).

The calculations[24,29,30,50,51] performed at various levels of approximation predict that molecules of all parent β-chalcovinylaldehydes and their imines, **7**, are planar with the Chalc···Y(O, NH) distances significantly shortened compared to respective vdW contacts. In accordance with the experimental data (Figure 1), the degree of this shortening and, thus, the strength of the intramolecular coordination Chalc←Y(O, NH) bonds are strongly affected by the electronegativity of the group R attached to the chalcogen atom. As seen from Figure 2, which shows the optimized geometries of β-chalcovinylaldehydes, the Chalc···O distance in **7** (Y = O) decreases by about 0.5 Å when the substituent R = H is replaced by the more electronegative chlorine atom, R = Cl. In the tellurium compounds **7** (X = Te, R = Cl, Y = O, NH), the calculated Te···O distances (2.202 and 2.206 Å, respectively) almost approach the length of a normal covalent Te−O bond (2.03−2.15 Å), whereas for the sulfur analogues **7** (X = S, R = Cl, Y = O, NH), the difference between the calculated S···O contacts and the length of a covalent S−O bond is substantially larger (0.5−1.0 Å depending on the approximation).

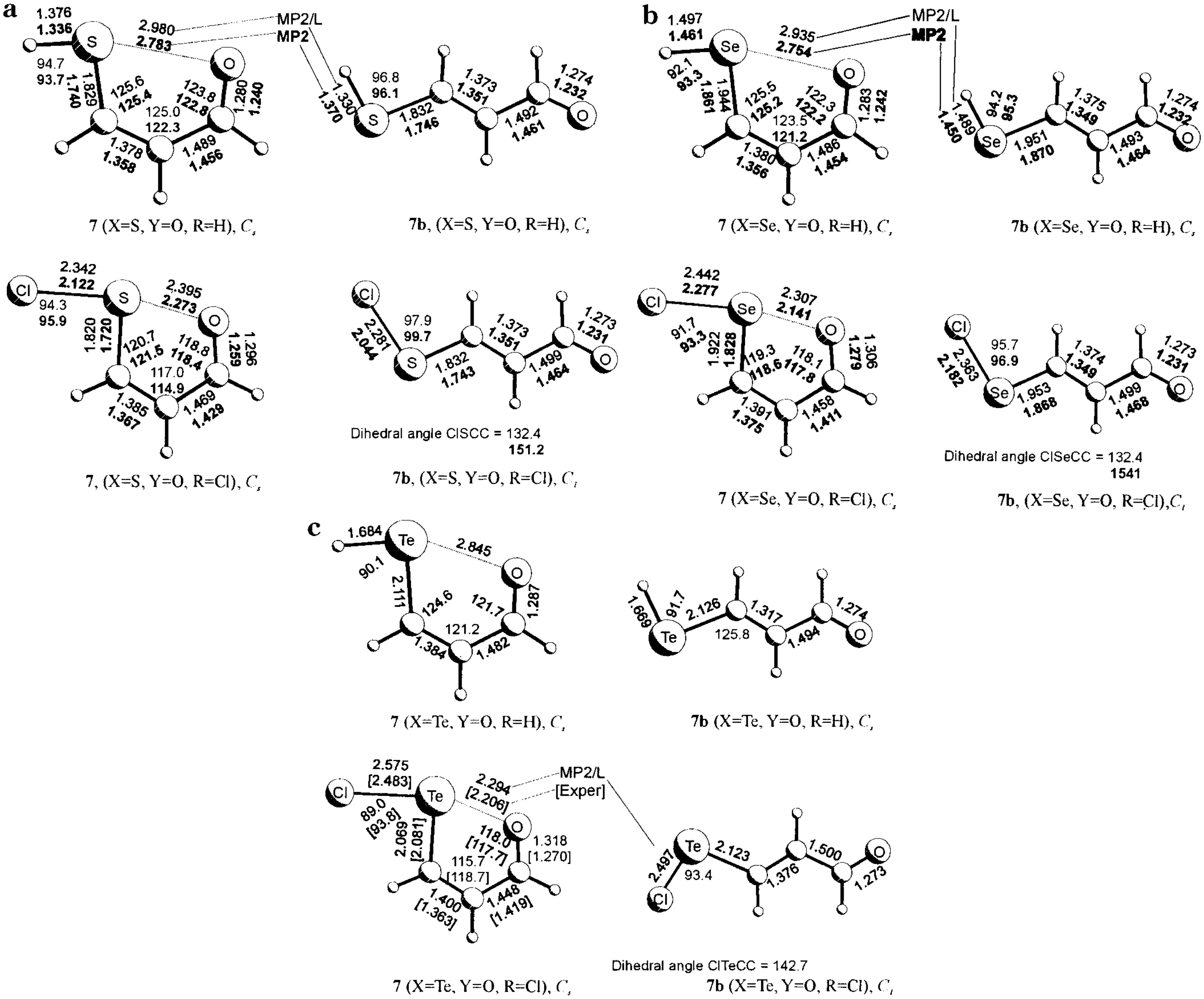
Table 1. Homodesmotic Stabilization Energies (HSE) of β-Chalcovinylaldehydes and Their Imines 7, Energy Differences (Δ*E*) between the Ring-Closed and Chain (7b) Isomers, and Energies of Stabilization (E_{stab}) of the Bimolecular Complexes 9 (in kcal mol^{-1}) as Calculated by MP2/LanL2DZ Method[29,50]

X/R	Y	**7**, $d_{X\cdots Y}$[a]	Δ*E* (**7** − **7b**)	**9**,[b] $d_{X\cdots Y}$[a]	**9**, E_{stab}	HSE
S/H	O	2.980 (2.780[c])	−3.6[d] (0.7[c])	3.465	0.7	2.0
S/H	NH	2.974	−1.4	3.707	1.4	1.1
S/Cl	O	2.395 (2.246[c])	5.0 (6.5[c])	2.833	4.1	2.6
S/Cl	NH	2.041	17.0	2.640	4.7	14.7
Se/H	O	2.935	0.9	3.402	1.2	3.6
Se/H	NH	2.855	1.5	3.506	3.2	2.8
Se/Cl	O	2.397	10.5	2.817	5.2	6.9
Se/Cl	NH	2.089	23.7	2.557	8.0	18.7
Te/H	O	2.845	3.8	3.409	1.8	5.6
Te/H	NH	2.693	6.0	3.730	4.0	6.7
Te/Cl	O	2.294	16.5	2.568	6.3	12.5
Te/Cl	NH	2.202	30.1	2.614	11.6	21.9

[a] The distances X···Y in **7** and **9** ($d_{X\cdots Y}$) are given in Å. [b] Structures **9** were constrained in a geometry similar to the structure of the coordination sites of **7** (angles O···X−CH_3 and X···O=C are about 90° and 120°, respectively, all other structural parameters being optimized). [c] MP2(full)/6-31G**. [d] From this point on, positive and negative signs at energy values signify stabilization and destabilization, respectively.

The total gain in energy due to formation of the secondary Chalc···Y bond of the hypervalent type in the compounds **7** can be evaluated as the energy difference (Δ*E*) between the ring-closed and chain isomers, respectively, **7** and **7b**. According to ab initio (MP2/6-31G** and MP2/LanL2DZ) calculations,[29] the attractive interaction increases along the sequence S, Se, Te and with an increase in the electronegativity of the substituent R attached to the chalcogen center. Whereas the isomers **7** (X = S, R = H, Y = O, NH) at various levels of approximation, up to MP2/6-31+G**, are less stable than their unstrained isomers **7b**, for the tellurium (X = Te) analogues, isomers **7** are energy preferable to **7b**, even at the RHF level of approximation. Replacement of the hydrogen atom R = H in **7** (X = Te, Y = O, NH) by the more electronegative chlorine atom results in an increase in the energy of the Te···O bond up to 16.5−30 kcal mol^{-1} (Table 1).

To evaluate the contribution of the aromatic stabilization of the five-membered rings in compounds **7**, an approach has been employed[50] based on the



7 (X=S, Y=O, R=H), C_s 7b, (X=S, Y=O, R=H), C_s 7 (X=Se, Y=O, R=H), C_s 7b (X=Se, Y=O, R=H), C_s

Dihedral angle ClSCC = 132.4 151.2

Dihedral angle ClSeCC = 132.4 1541

7, (X=S, Y=O, R=Cl), C_s 7b, (X=S, Y=O, R=Cl), C_1 7 (X=Se, Y=O, R=Cl), C_s 7b, (X=Se, Y=O, R=Cl), C_1

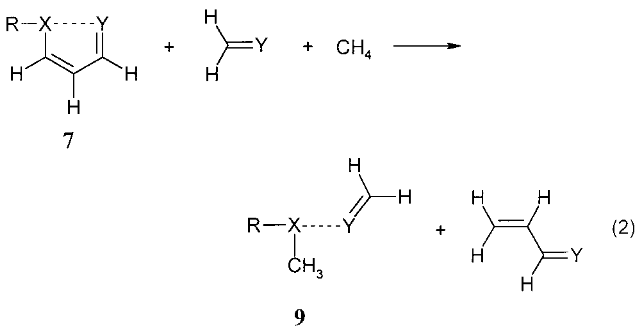
7 (X=Te, Y=O, R=H), C_s 7b (X=Te, Y=O, R=H), C_s

Dihedral angle ClTeCC = 142.7

7 (X=Te, Y=O, R=Cl), C_s 7b (X=Te, Y=O, R=Cl), C_1

Figure 2. MP2(fc)/6-31+G** (MP2) and MP2/LanL2DZ (MP2/L) optimized geometries (distances in angstroms and angles in degrees) for *cis-s-cis* and *trans-s-trans* isomers of β-chalcovinylaldehydes **7**:[29] (a) thiovinylaldehydes, (b) selenovinylaldehydes, (c) tellurovinyl-aldehydes. Experimental data are given for compound **6c** (Figure 1).

concept of homodesmotic reactions designed to single out that part of the stabilization which is caused by the π-electron cyclic delocalization.[52-54] Although no precise homodesmotic reaction (in which the number of bonds of each formal type is retained in both reactants and products) can be designed for compounds such as **7**, the reaction described by eq 2, in which the bimolecular complexes **9** are the adducts stabilized by the $n_X \rightarrow \sigma^*_{X-R}$ interaction,[29,50] serves as a sufficiently good approximation. The only deviation from this demandable condition is the difference in the number of $C_{sp3}-H$ and $C_{sp2}-H$ bonds in reactants (4 and 5, correspondingly) and products (3 and 6). However, a small difference in energy between a $C_{sp3}-H$ and a $C_{sp2}-H$ bond is included into the HSE values of all the compounds **7** under consideration and does not, therefore, affect the principal conclusions.



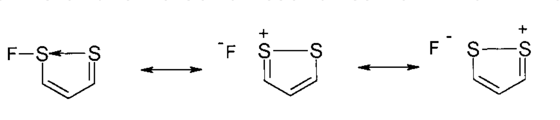
The HSE values for β-chalcovinylaldehydes and their imines **7** are listed in Table 1 together with the computed Chalc···O(NH) distances in **7** and complexes **9**. The energy of stabilization for a bimolecular complex **9** is defined as the difference between the total energy of the dimer and the combined energy of the separated monomers. Aromaticity of the cyclic structure **7**, as defined by the HSE value, plays an important role in stabilization of the ring-closed form. Its relative contribution increases with an increase in the covalency ratio factor of the secondary bond, i.e., as the electronic structure of a compound approaches the **7a** ↔ **7b** ↔ **7c** description. The HSE values of the pseudo-heterocycles **7** listed in Table 1 constitute 10−40% of the HSE value of the prototype aromatic system of benzene (28.9 kcal mol^{-1})[4,6] calculated at a similar level of approximation.

An important sign of the partial aromatic character of β-chalcovinylaldehydes and their imines **7** is significant equalization of lengths of the two carbon−carbon bonds in the CH−CH=CH triad. As seen from Figure 2, in the cyclic conformation of the chalcogenyl chlorides **7** (X = Chalc, R = Cl), the difference between the lengths of the two CC bonds, Δl, is 0.05−0.09 Å, the minimal value corresponding to the more aromatic β-chlorotellurovinylaldehyde. For the less aromatic parent compounds **7** (R = H), the values Δl = 0.09−0.11 Å. At the same time, for the open isomers **7b**, the alternation is much larger (0.11−0.16 Å) and in contrast with **7** it is virtually unaffected by the origin of the chalcogen center and the substituent R. These findings lend support to consideration[36] of derivatives of β-chlorochalcovinylaldehydes **7** (X = S, Te, Se, R = Cl) and their imines (Y = NH) as the heterocycles, whose electronic structure is described as the resonance hybrid **7a** ↔ **7a′** ↔ **7a″** of the six-electron delocalized π-systems. Appreciable elongation (about 0.3 Å) of the Chalc−Cl bond and the large positive charge (about +0.5) on the chalcogen center in these compounds are consistent with the significant contribution of the ionic resonance structure **7a″**.

II.2. 3-Thiopropenthiones

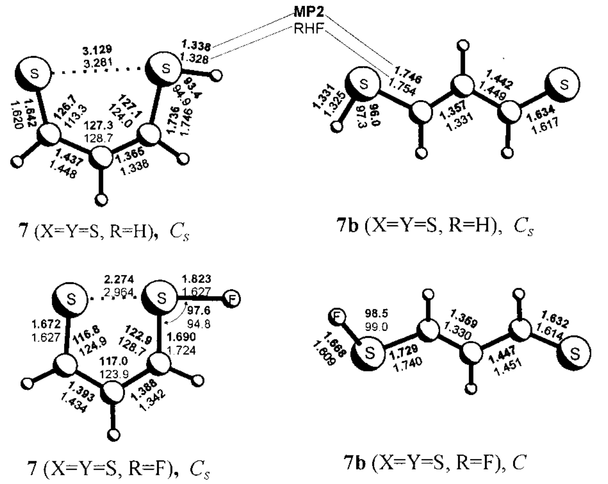
Consideration of electron correlation plays an important role for the correct description of the energetic and geometric parameters of the compounds with the intermolecular or intramolecular attractive nonbonded interactions between the electron-abundant centers.[26,29] Accounting for the electron correlation leads to significant enhancement of the Chalc···O hypervalent interactions in **7** and provides for additional delocalization of the electron density associated with equalization of bond lengths in their molecules. This effect is clearly illustrated by the calculations[51] of structural and energetic characteristics of the ring-closed, **7** (X = Y = S), and ring-open, **7b** (X = Y = S), isomers of 3-thiopropenthione (R = H) and its S-fluoro (R = F) derivative (Figure 3).

The alternation of the CC bonds in the ring-closed structures **7** (X = Y = S) is substantially lower compared to that in their open isomers. This effect is particularly pronounced in the S-fluoro derivative, in which both CC bonds at the MP2(full)/6-31G** level of approximation are predicted to have almost equal lengths and the S···S distance is 1.43 Å shorter (χ = 0.88) than the vdW contact. These features justify presentation of the structure **7** (X = Y = S, R = F) as the 1,2-dithiolium fluoride, i.e., its description in terms of the no bond resonance **7a** ↔ **7a′** ↔ **7a″**.



7 (X=Y=S, R=F)

By using reaction scheme 2, where X = Y = S, R = F, the high HSE value (15.9 kcal mol^{-1}) has been calculated for this compound.



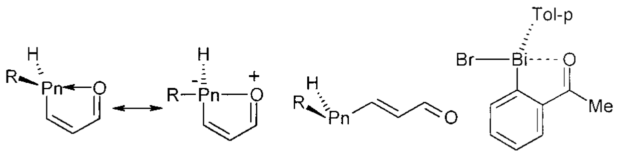
7 (X=Y=S, R=H), C_s **7b** (X=Y=S, R=H), C_s

7 (X=Y=S, R=F), C_s **7b** (X=Y=S, R=F), C

Figure 3. RHF/6-31G** (RHF) and MP2(full)/6-31G** (MP2) optimized geometries (distances in angstroms and angles in degrees) for 3-thiopropenthione and its S-fluoro derivative.[51]

II.3. β-Pnictovinylaldehydes

In contrast with derivatives of β-chalcogenovinylaldehydes **7** (X = S, Se, Te) studied in considerable detail, much less experimental and theoretical attention has been given until recently to the isoelectronic pnictogen (main-group elements N, P, As, Sb, Bi) compounds **10 (7**, X = PnR$_1$**)**, where similar effects of the hypervalent type bonding and aromaticity stabilizing ring-closed conformations may be expected.



10 10a 10b 11

Pn = N, P, As, Sb, Bi

The ability of compounds **10** to form the intramolecular coordination Pn←O bonds is illustrated by the X-ray-determined structure of (2-acetylphenyl)bromo(4-methylphenyl)bismuthane **11**, in which a strong hypervalent O−Bi−Br bond has been found to occur through coordination of the carbonyl oxygen atom to the bismuth center.[55] The intramolecular Bi···O distance (2.519 Å) in **11** is 1.2 Å shorter than the sum of the vdW radii (3.84 Å),[56] which corresponds to a high magnitude of the covalency ratio factor χ = 0.74. On the other hand, the question about the aromatic character of compounds **10** is not so clear. The difference in the electronic structure of derivatives of β-chalcovinylaldehydes **7** (X = Chalc, Y = O) and their pnictogen analogues **10** (Pn = P, As, Sb, Bi) consists of the presence the latter of only one lone electron pair at the accepting center. Orientation of the axis of its orbital dictated by the geometry of the coordination site in compounds **10** does not entirely match the requirement for the optimal overlap of the doubly occupied n_{Pn} orbital with the π-systems of the essentially planar −CH=CH−CH=O moieties of molecules of **10**. From the NBO analysis,[38] it follows that the n_{Pn} orbital has

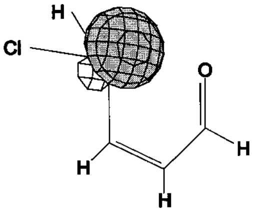


Figure 4. Orientation of the natural hybrid orbital of the lone electron pair at the phosphorus atom in **10** (Pn = P, R = Cl) as found by the RHF/6-31G** calculations.[57]

rather low p character. Its hybridization varies from $sp^{0.6}$ in **10** (Pn = P, R = H) to $sp^{0.2}$ **10** (Pn = Bi, R = Cl), and its axis in compounds **10** (Pn = P, As, Sb, Bi) is not orthogonal to the five-membered ring plane, being declined from the plane on 30–45°. As depicted in Figure 4, the coordination polyhedron of the pnictogen center corresponds to a distorted trigonal bipyramid with the lone pair, as a phantom ligand, taking an equatorial position.

The geometrical parameters for a series of β-pnictovinylaldehydes calculated[57] at various theoretical levels are given in Figure 5.

β-Aminovinylaldehyde **10** (Pn = N, R = H) is the only compound **10** with the completely planar molecular structure ensured by the formation of a strong intramolecular O···HN bond. In all other compounds **10**, even those with R = H, the geometry of the coordination site is primarily determined by the intramolecular coordination of the hypervalent type O···Pn–R, which places the substituent R = Cl, F, H on the line roughly collinear with the O···Pn secondary bond (the O···Pn–R angles are in the range 150–167°, the X-ray determined[55] O···Bi–Br angle in **11** is 160.8°). The heavier the pnictogen atom in **10** and the more electronegative the substituent R, the greater is the O···Pn-R angle.

This geometry of the coordination site shown in Figure 4 is, obviously, less favorable for the cyclic electron delocalization over the ring than that realized in the chalcogen analogues **7,** where two lone electron pairs located on the hypervalent center can adopt the configuration optimal for the formation of the aromatic sextet (see Introduction). The extensive calculations[57] showed, indeed, that contribution of the aromaticity factor to stabilization of the cyclic structures **10** with respect to their open isomers **10b** is virtually absent. Some results of these calculations are collected in Table 2.

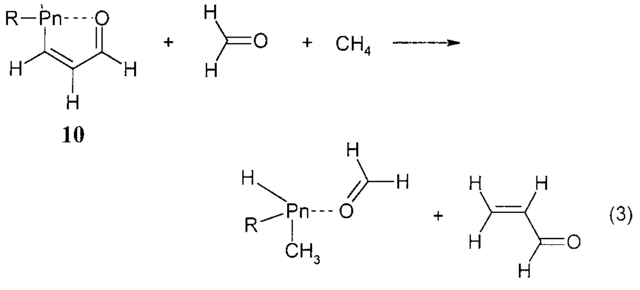
Table 2. Relative Energies (ΔE) of the Ring-Opened Conformations 10b (in kcal mol^{-1}), HSE Values (in kcal mol^{-1}), and Pn···O Distances (in Å) in 10, Energies of Stabilization (E_{Stab}, kcal mol^{-1}) and Pn···O Distances (in Å) in the Dimers 12 Calculated[57] by Various ab Initio Methods Denoted as Follows: MP2-MP2(full)/6-31G, DFT-B3LYP/6-31G**, MP2/L-MP2(fc)/LanL2DZ, DFT/L–B3LYP/6-31G****

PnRH	method	ΔE	**10**, $d_{Pn\cdots O}$[a]	**10**, HSE	**12**, $d_{Pn\cdots O}$[a]	E_{stab}
NH_2	MP2	5.2	2.687	21.2	3.253	0.8
	DFT	5.2	2.693	24.2	3.363	0.3
NHCl	MP2	4.9	2.655	12.8	3.047	2.2
	DFT	5.7	2.630	14.7	3.132	1.6
PH_2	MP2	1.1	2.818	3.7	3.360	1.8
	DFT	0.9	2.865	2.7	3.532	1.0
PHF	MP2	5.6	2.426	0.0	2.426	3.6
	DFT	5.9	2.417	−0.2	3.121	2.5
PHCl	MP2	4.1	2.487	4.1	3.147	3.3
	DFT	4.5	2.431	3.1	3.103	2.9
AsH_2	MP2	2.2	2.793	2.4	3.206	3.8
	DFT	1.6	2.845	−1.0	3.207	5.1
	MP2/L	0.1	3.012	2.3	3.584	1.0
	DFT/L	0.8	2.942	0.8	3.704	0.5
AsHF	MP2	9.6	2.508	−3.9	2.860	7.2
	DFT	8.6	2.559	−4.2	2.921	6.1
AsHCl	MP2	8.0	2.414	0.3	2.916	7.1
	DFT	7.9	2.427	1.0	2.897	7.9
	MP2/L	5.2	2.559	−2.7	2.945	4.5
	DFT/L	7.1	2.440	3.5	2.903	3.4
SbH_2	MP2/L	0.7	2.954	2.2	3.613	1.3
	DFT/L	2.2	2.856	0.6	3.653	0.7
SbHCl	MP2/L	8.4	2.719	−3.1	2.989	5.3
	DFT/L	10.4	2.680	−5.1	2.962	4.8
BiH_2	MP2/L	1.4	2.965	2.3	3.532	1.7
	DFT/L	2.1	2.882	0.6	3.535	1.1
BiHCl	MP2/L	9.5	2.819	−3.8	2.945	6.4
	DFT/L	11.3	2.800	−5.7	2.926	5.8

[a] Structures **12** were constrained in a geometry similar to the structure of the coordination sites of **10** (angles O···Pn–CH_3 and Pn···O=C are about 90° and 120°, respectively, all other structural parameters being optimized). The vdW contacts[56] are as follows: N···O 2.0 Å, P···O 2.34 Å, As···O 3.44 Å, Sb···O 3.64 Å, Bi···O 3.84 Å.

Although the positive ΔE values definitely indicate considerable stabilization of the conformation **10** of β-pnictovinylaldehydes relative to their sterically unstrained *trans-s-trans* conformation **10b,** one may conclude that this stabilization is almost exclusively caused by the factors (electrostatic and $n_O \rightarrow \sigma^*_{Pn-R}$ orbital interaction) responsible for the formation of the secondary Pn···O bond. This conclusion follows from the data on HSE values computed for **10** on the basis of the homodesmotic reaction 3, similar to that (eq 2) applied for evaluation of the aromatic stabilization of β-chalcovinylaldehydes and their imines **7**.

As seen from the data of Table 2, for most of compounds **10** the HSE values are varied in the range of 0 ± 3 kcal mol^{-1}, which reflects merely the accuracy of the approach employed for their estimation. The lack of aromaticity for the heavier main-group 15 (Pn = As, Sb, Bi) β-pnictovinylaldehydes also shows itself in that, unlike their chalcogen analogues **7**, alternation of the CC bonds in the CH–CH=CH triad is almost the same in the chelated, **10**, and open, **10b**, conformations (Figure 5, Table 3). A notable exclusion is β-amino- and β-*N*-(chloro)aminovinylaldehydes **10** (Pn = N). Because of the planarity of their molecules (the sum of the valence angles at the nitrogen is 360° and 351°, respectively), in both compounds the axis of the lone electron pair at the nitrogen is precisely orthogonal to the plane



(3)

12

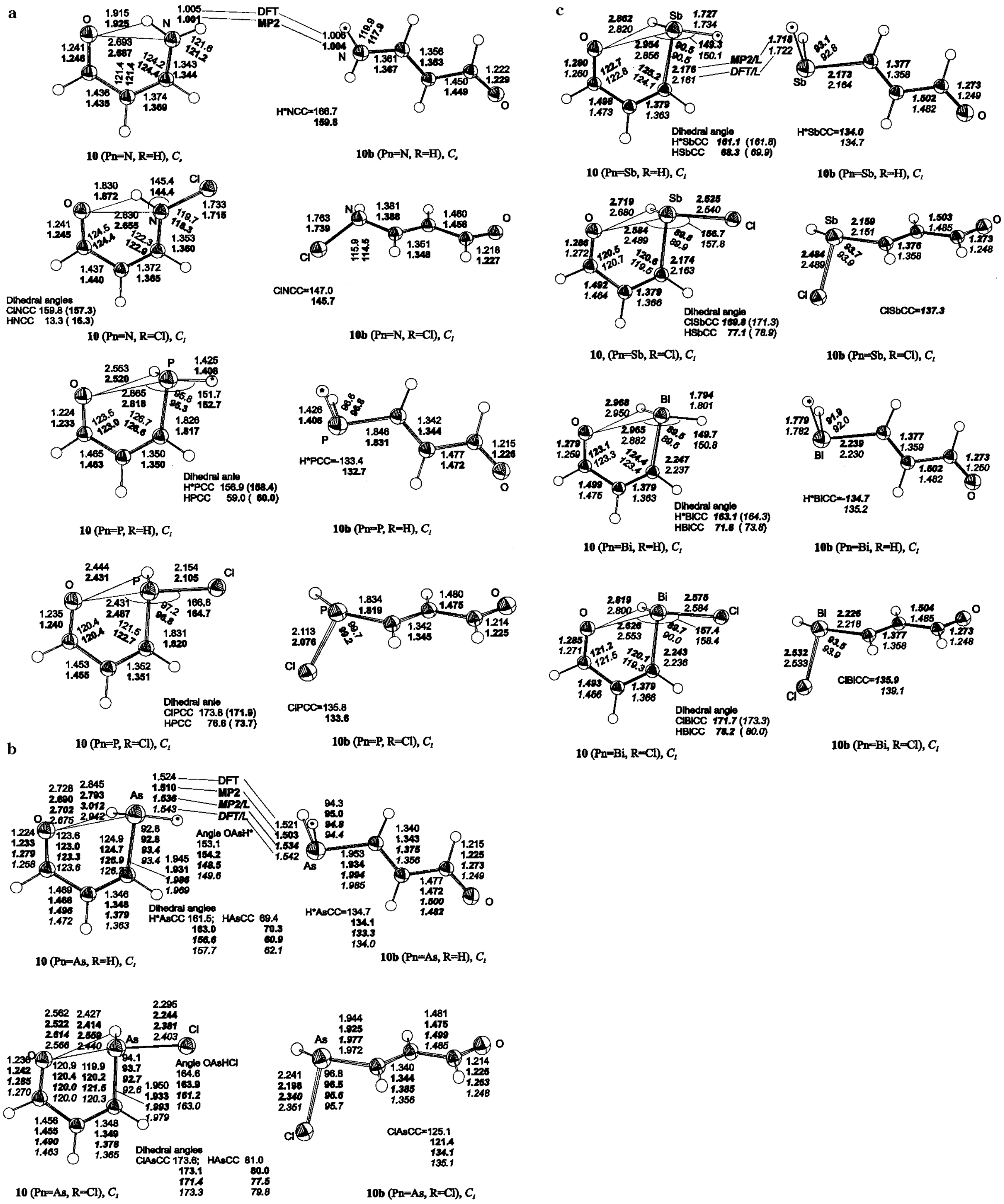


Figure 5. MP2(full)/6-31G** (MP2), B3LYP/6-31G** (DFT), MP2/LanL2DZ (MP2/L), and B3LYP/LanL2DZ (DFT/L) optimized geometries (distances in angstroms and angles in degrees) for β-pnictovinylaldehydes and their Pn−chloro derivatives: (a) **10** (Pn = N, P), (b) **10** (Pn = As), (c) **10** (Pn = Sb, Bi).[57]

of the conjugated ring closed by the intramolecular N−H···O bond. This results in rather high values of the homodesmotic stabilization energies and significant equalization of the CC bond lengths in the conformation **10** (Pn = N) as compared with **10b** of these compounds. An important role of the resonance stabilization of the conjugated systems facilitated by intramolecular hydrogen bonding has been repeatedly noted.[58]

A clear tendency to strengthening the Pn···O bond in the order Pn = P, As, Sb, Bi and with increase in the electronegativity of the substituent R can be

Table 3. Alternation of the CC Bonds $\Delta l = l_{C-C} - l_{C=C}$ (in Å) in Ring-Closed and Ring-Opened Conformations of β-Chalcovinylaldehydes, 7 and 7b, and β-Pnictovinylaldehydes, 10 and 10b, as Calculated by MP2/LanL Method

β-chalcovinylaldehydes[29,30]				β-pnictovinylaldehydes[57]			
X	R	**7** Δl	**7b** Δl	PnH	R	**10** Δl	**10b** Δl
S[a]	H	0.098	0.110	PH[b]	H	0.113	0.128
	Cl	0.062	0.113		Cl	0.104	0.130
Se	H	0.106	0.118	AsH	H	0.117	0.125
	Cl	0.067	0.125		Cl	0.112	0.114
Te	H	0.098	0.137	SbH	H	0.120	0.125
	Cl	0.048	0.124		Cl	0.113	0.127
		0.056[c]		BiH	H	0.120	0.125
					Cl	0.114	0.127

[a] MP2/6-31+G** calculation.[29] [b] MP2/6-31G** calculation. [c] X-ray structural data[36] for 3-(*p*-methoxyphenyl)-5-phenyl-1,2-oxatellurolyl-1-ium chloride.

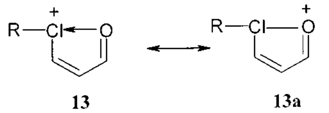
Table 4. Relative Energies (ΔE) of the Ring-Opened Conformations 13b (in kcal mol^{-1}) and Cl···O Distances (in Å) in 13 Calculated[61] by ab Initio Methods

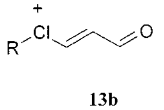
R	method	ΔE	$d_{O\cdots Cl}$	χ(O···Cl)
H	MP2(full)/6-31G**	7.1	2.557	0.43
	B3LYP/6-31+G**	5.6	2.564	0.43
F	MP2(full)/6-31G**	20.3	2.036	0.76
	B3LYP/6-31+G**	19.3	2.072	0.73

traced in **10** and the bimolecular complexes **12** according to the values of ΔE, E_{stab}, and the computed Pn···O distances. It is worth noting that adducts **12** formed by amines (Pn = N) and methylphosphine (Pn = P, R = H) are stabilized ($E_{stab} > 0$) due to only electrostatic attraction of the components. The computed Pn···O distances in these complexes are longer than the respective vdW contacts.

II.4. (*Z*)-1-(3-oxapropenyl)chloronium Cations

(*Z*)-1-(3-oxapropenyl)chloronium cations **13** are main-group 17 element analogues of β-chalco- and β-pnictovinylaldehydes. Although their salts have not yet been described, those of alkenyl iodonium cations of similar type are well characterized and amply reviewed group of compounds.[59,60] In **13**, the chlorine center bears two lone pairs, one of which is engaged into the π-system of the cation. The electronic structure of these cations is, therefore, similar to that of β-chalcovinylaldehydes **7**. As a consequence, one may expect that *trans-cis-cis* conformation **13** would be stabilized relative to **13b** by both intramolecular coordination of the hypervalent type and partial aromatic character. The values of ΔE characterizing the energy preference of structure **13** are in accord with this expectation (Table 4).


13 **13a**


13b

As seen from the data of Table 4 and Figure 6, the ring-closed structures **13** are strongly stabilized by the intramolecular coordination Cl←O interaction, whose energy depends substantially on the origin of the substituent at the chlorine atom. The attraction between these centers is additionally strengthened owing to significant polarization of this bond in the cation. The Cl···O distance in **13** (R = H) is about 0.5 Å longer than in the more delocalized structure of **13** (R = F).[61]

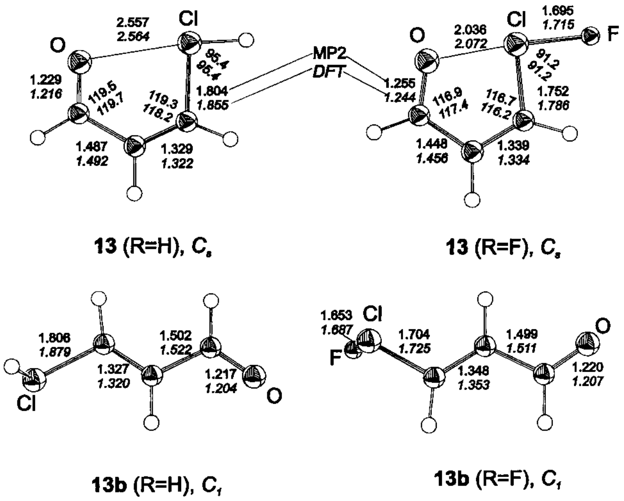
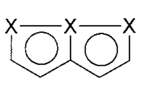


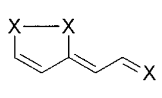
Figure 6. MP2(full)/6-31G** (MP2) and B3LYP/6-31G** (DFT) optimized geometries (distances in angstroms and angles in degrees) of *cis-s-cis* and *trans-s-trans* isomers of the chloronium cation **13**.[61]

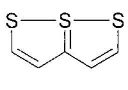
III. Heterapentalenes

III.1. 1,6,6aλ^4-Trichalcapentalenes

1,6,6aλ^4-Trithiapentalene, the archetype compound of type **1**, has been studied extensively[11,12,14,62−64] because of the early obtained experimental evidence[65] for its unique C_{2v}-symmetric structure governed by a three-center, four-electron bond at the tricoordinate central sulfur atom. As indicated in the Introduction, the VB description of the electronic structure of trithiapentalene and its analogues can be done in terms of resonance of two hypervalent structures **1b** ↔ **1b′** whereas the still often met (see, e.g., ref 62b) classical representation, **15**, of the C_{2v} structure is inaccurate even on the strength of purely geometrical data: the length of the $C_{3a}-S_{6a}$ bond in **14** (X = S) is 1.748−1.758 Å.


14, X=S, Se, Te


14a


15

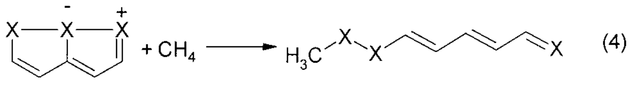
The ab initio calculations performed at the HF level, even those employed extended basis sets of of orbitals, predict that the classical C_s structure of trithiapentalene **1a** is energy preferred to the C_{2v} form. When the correlation energy was considered (at both MP2 and DFT levels), C_{2v} structures were obtained with all basis sets starting from 3-21G.[14,64] It is worth noting that the C_{2v} structures were obtained for triselena- and tritellurapentalenes **14** (X = Se, Te), even at the HF level of approximation.[57] Whereas consideration of the electron correlation is crucial for the correct estimation of relative energies

Table 5. Relative Energies (ΔE) of the Monocyclic *trans-trans* Conformations 14a (in kcal mol^{-1}) and X–X Distances (in Å) in Trichalcapentalenes 14 Calculated[29,57] by ab Initio Methods

X	method	d_{X-X}	d_{X-X} (X-ray)	ΔE	HSE
S	MP2(full)/6-31+G**	2.367[a]	2.363[65]	12.1	16.9
	B3LYP/6-31G**	2.423[b]		13.0	
	MP2/LanL2DZ	2.590		10.7	13.8
Se	MP2(full)/6-31G**	2.527	2.58[67]	25.1	
	MP2/LanL2DZ	2.757		19.8	18.8
Te	MP2/LanL2DZ	3.058		16.3	20.5

[a] The S–S bond length in trithiapentalene calculated at the highest currently reported level of approximation is 2.372 (MP2/6-311G**)[63b] and 2.429 Å[64] (B3LYP/6-311G**).

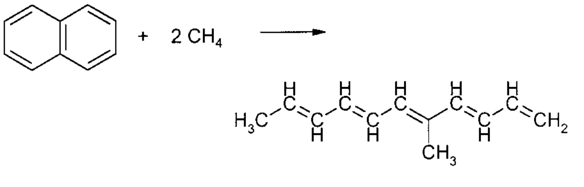
of the C_{2v} structures of trichalcapentalenes, the theoretical bond lengths in that are most sensitive to the basis set. They were found to be in sufficiently good agreement with the experimental data[65] even at the RHF level on condition that the basis set contains d functions. With the use of the pseudopotential LanL2DZ basis, the X_1–X_{6a} bond lengths are approximately 0.2 Å elongated compared with the experimental values (Table 5). The aromatic stabilization of trichalcapentalenes **14** can be assessed as the heat of the homodesmotic reaction 4.



(4)

14 **16**

The HSE values of **14** thus obtained (Table 5) constitute about 30–50% of the HSE value calculated,[57] based on the similar type reaction 5, for the most aromatic 10π electron bicyclic structure of naphthalene: 62.2 (MP2(full)/6-31G**) and 53.7 (B3LYP/6-31G**) kcal mol^{-1}. As shown in Figure 7, compounds **14** and their isoelectronic analogues possess the closed-shell π-electron system similar to that of the aromatic[3,4] pentalene dianion. Table 5 contains also the values of ΔE characterizing the enhanced stability of the bicyclic C_{2v} structures **14** relative to their unstrained monocyclic isomers **14a**.

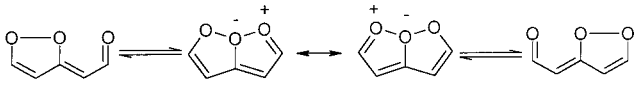


(5)

Due to the relatively low ability of the first-row elements to form three-center, four-electron bonds, the bicyclic C_{2v} structure **17** of 1,6,6a-trioxapentalene, the oxygen analogue of trichalcapentalenes, conforms not to a minimum but to a saddle point on the PES. Thus, it represents the transition state for the O–O bond switching rearrangement of the **2a** $\rightleftharpoons$ **1** $\rightleftharpoons$ **2b** type. This rearrangement may be thought of as the intramolecular S_N2 reaction at the sp^3 oxygen center. The ab initio calculations[51] predict that it occurs with a very low energy barrier (9.1 (MP2(full)/6-31G**) and 7.8 (B3LYP/6-31G**) kcal mol^{-1}), which is near the lowest limit of the characteristic NMR time scale.

Table 6. Stabilization of the Bicyclic Structures 18 of 1,6-Dioxa-6aA-chalcapentalenes (ΔE, in kcal mol^{-1}) Relative to Their Ring-Opened Isomers 19 and HSE Values (in kcal mol^{-1}) for 18 Calculated[29,57] as Heats of the Reaction 6

X	method	ΔE	HSE
S	RHF/LanL2DZ	6.1	10.5
	MP2/LanL2DZ	12.1	16.6
	B3LYP/6-31G**		23.4
	MP2(fc)/6-31+G**	20.7	24.9
Se	RHF/LanL2DZ	13.0	18.5
	MP2/LanL2DZ	19.8	26.0
	MP2(fu)/6-31G**		39.0
Te	RHF/LanL2DZ	25.0	21.9
	MP2/LanL2DZ	27.7	29.9

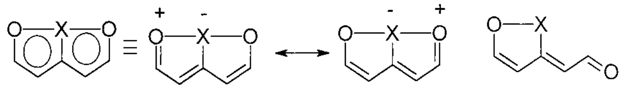


17a **17** **17b**

$d_{O...O}$ 2.696 Å d_{O-O} = 1.950 Å

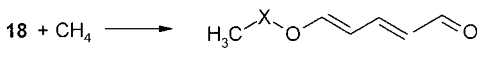
III.2. 1,6-Dioxa-6aλ^4-chalcapentalenes

1,6-Dioxa-6aλ^4-thia- and selenapentalenes became known in the beginning of 1970s'[67] and in 1983, Detty and Luss[68] completed this series of compounds by the synthesis of the first tellurium analogue, 2,5-diphenyl-1,6-dioxa-6aλ^4-tellurapentalene. All the X-ray structural determinations available for these compounds[12,33,62] are in agreement with the assumption of C_{2v} molecular symmetry corresponding to **18**. The bicyclic structure **18** is correctly reproduced by ab initio MO theory at the levels of approximation higher than RHF.[14,29] As seen from the data of Table 5, the symmetric structures **18** of 1,6-dioxa-6aλ^4-chalcapentalenes are predicted to be more stable than their monocyclic isomers **19**. The trend to stabilization of the naphthalene-like 10π electron structure **18** when going from sulfur to tellurium is clearly expressed by the values of ΔE (energy difference between **18** and **19**) and HSE. As seen from the data of Table 6, accounting for the correlation energy results in additional stabilization of the delocalized structure with the hypervalent chalcogen centers. The aromatic character of the bicyclic structure **18** is the main factor contributing to this stabilization. This conclusion is corroborated by the HSE values of **18** calculated on the basis of the homodesmotic reaction 6 similar to eq 4.



18 **18a** **18b** **19**

X=S, Se, Te



(6)

X=S, Se, Te

The calculations[29] displayed the pronounced equalization of the CC bond lengths in **18** as compared

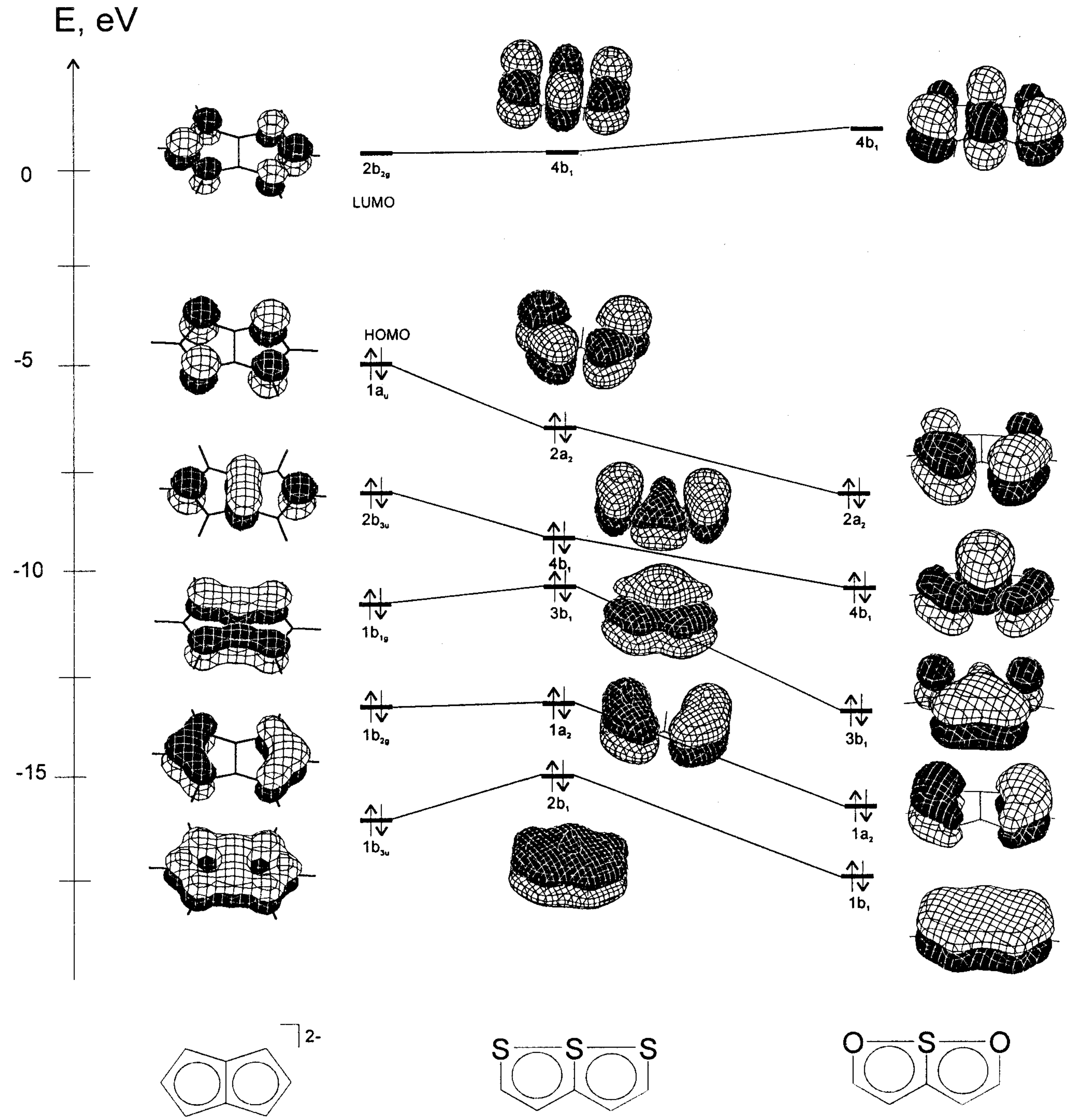
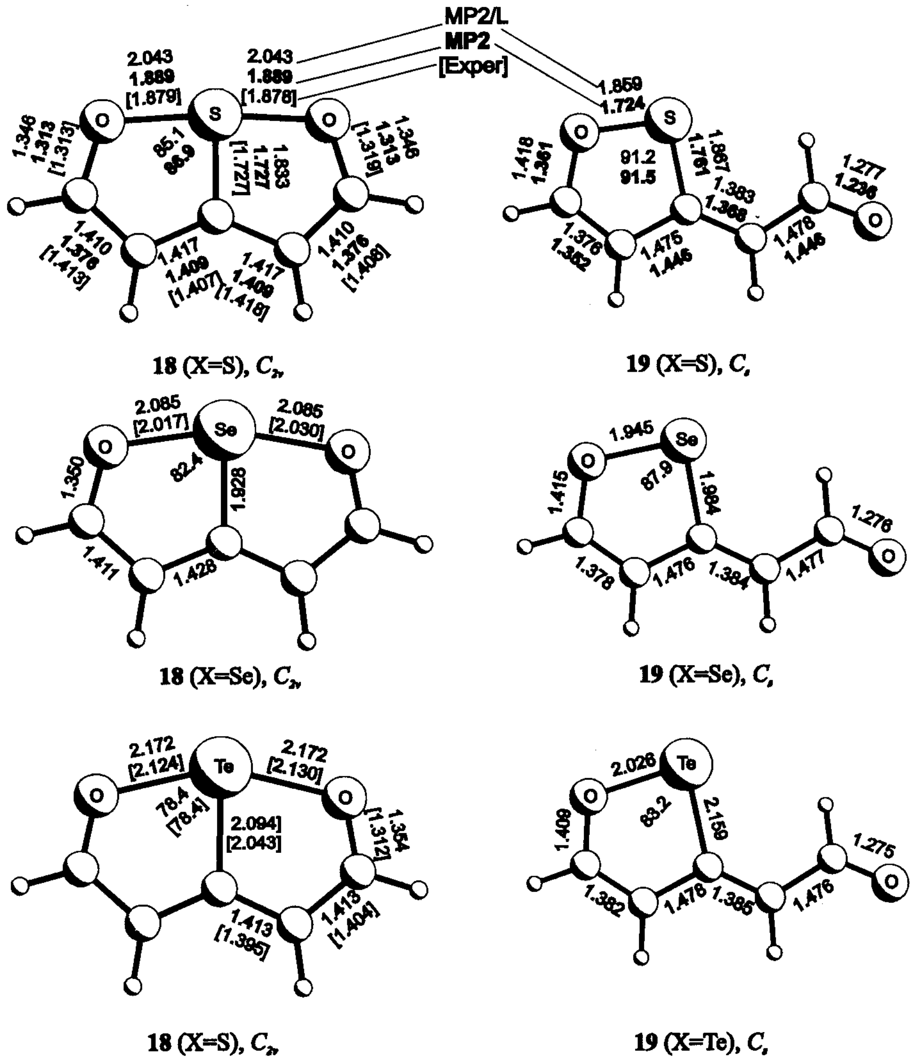


Figure 7. Canonical π-MOs of pentalene dianion, 1,6,6aλ^4-trithipentalene, and 1,6-dioxa-6aλ^4-thiapentalene as calculated with the 6-31G** basis set.[29,57]

with **19**. As Figures 2 and 8 show, further significant shortening of Chalc—O bonds is observed in **18**, even compared to that occurring in β-chalcovinylaldehydes **7** (X = Chalc) with the electronegative substituents, R = Cl. For the dioxatellurapentalene **18** (X = Te), the length of the Te—O bond is almost the same as that of standard covalent bonds of this type.[33] As for compounds **7** and **14**, the use of the pseudopotential basis set (LanL2DZ) leads to underestimation of the aromaticity and hypervalent bonding effects. This is seen in a comparison of the MP2/LanL2DZ and MP2/6-31G** or MP2/6-31+G** calculations (Figure 7, Tables 2, 4, and 5). The MP2/LanL2DZ method predicts that the bonds formed by the hypervalent chalcogen center are longer than those obtained with the employment of more sophisticated methods, whose predictions concerning bond lengths and valence angles are in excellent agreement with the experimental data available on trichalcapentalenes **14** and derivatives of dioxachalcapentalenes **19** (Tables 5 and 6).

III.3. 1,6-Dioxa-3a-aza-6aλ^4-pnictapentalenes (10-Pn-3 5-aza-2,8-dioxa-1- pnictabicyclo[3.3.0]-octa-2,4,6-trienes)

This family of compounds **20** with the hypervalent bonding arrangement across the pnictogen centers has been designed and studied in detail by Arduengo and his group.[13,18–20,69] As confirmed by the X-ray



18 (X=S), C_{2v} **19** (X=S), C_s

18 (X=Se), C_{2v} **19** (X=Se), C_s

18 (X=S), C_{2v} **19** (X=Te), C_s

Figure 8. Structural parameters for 1,6-dioxa-6a-chalcapentalenes **18** and their monocyclic isomers **19** as calculated[29] by the MP2/LanL2DZ (MP2/L) and MP2(fc)/6-31+G** (MP2) ab initio methods. Numbers in brackets are X-ray crystallography data for the derivatives of **18**: di[2,3;4,5-(4′-methoxybenzo)]-1,6-dioxa-6a-thiapentalene,[12,62] 3,4-(2,2-didimethylpropano)-2,5-diaza-1,6-dioxa-6a-selenapentalene,[62] and 2,5-diphenyl-1,6-dioxa-6a-tellurapentalene.[68] Bond lengths and angles are given in angstroms and degrees, respectively.

crystallography determination, a powerful bicyclic five-membered ring effect provides for stabilization of the central pnictogen atom in **20** in the T-shaped configuration, like that of the tricoordinated chalcogen atoms in 1,6-dioxa-6a-chalcapentalenes **18**. This similarity manifests itself also in the likeness of the electronic structure of these compounds. As shown in Figure 9, compounds **20** (for which the acronym ADPO has been coined)[19] have closed 10π electron shells and the shape of the π-orbitals in **20** closely resembles that of **14** (Figure 7). Much like as in **14**, one of the two lone pairs on the Pn^{2-} center in **20** occupies the nonbonding a_1 orbital whereas another one (b_1) is involved in the common π-system of the molecule.

Scheme 2 features important rearrangements of ADPO. Of special interest is the isomerization of **20** into the classical form **21** with both pnictogen centers possessing their usual pyramidal configuration. The relative energy of **21** may serve as a measure of the aromaticity of the planar structure **20** with the hypervalent pnictogen (Pn) center. The calculations[20] carried out for the phosphorus compounds (Pn = P) at the SCF level showed that the folded classical structure **21** is lower in energy than **20** by 9.9 kcal mol^{-1}. Inclusion of the electron correlation correction (MP2) inverts the order of stability of these isomers; the planar structure **20** becomes energy favorable by 13.9 kcal mol^{-1}.

Subsequent calculations[70] lent support to the conclusion on the higher stability of the aromatic structure **20** (Pn = P) of 10-P-3 ADPO and addressed the question on the kinetic stability of the "electromorphs" **21** (Pn = P, As). Some of the results are given in Table 7. The energy difference (ΔE) between the bicyclic, **20**, and the ring-opened, **23**, forms of ADPO (Pn = P, As) is of the same order of magnitude as that computed for 1,6-dioxa-6a-chalcapentalenes **18** (Table 6), which points to the comparable effects of the aromatic stabilization in both groups of compounds. The structural parameters computed for the parent 10-P-3 ADPO, **20** (Pn = P)[20,70] are in excellent agreement with those determined by X-ray crystallography for its 3,7-di-*tert*-butyl derivative. The MP2-(full)/6-31G** calculated Pn−O distances in **20** (Pn = P, As) are found to be only ~0.1 Å longer than the

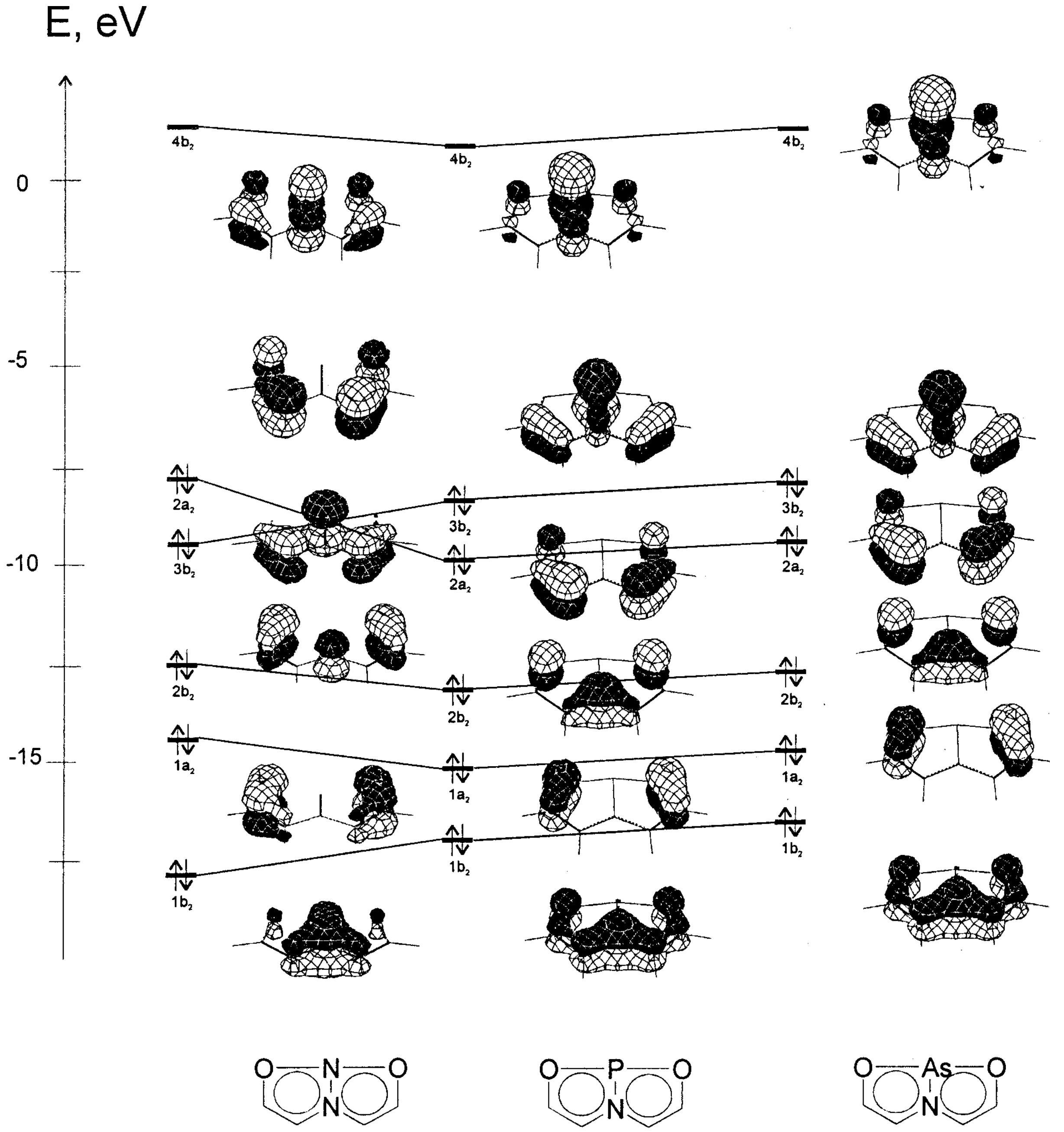


Figure 9. Canonical π-MOs of 1,6-dioxa-3a-aza-6aλ^4-pnictapentalenes **20** (Pn = N, P, As) as calculated with the 6-31G** basis set.[70]

respective covalent bond lengths. Figure 10 shows the MP2(full)/6-31G** calculated geometries for the isomers of 1,6-dioxa-3a-aza-6a-pnictapentalenes.

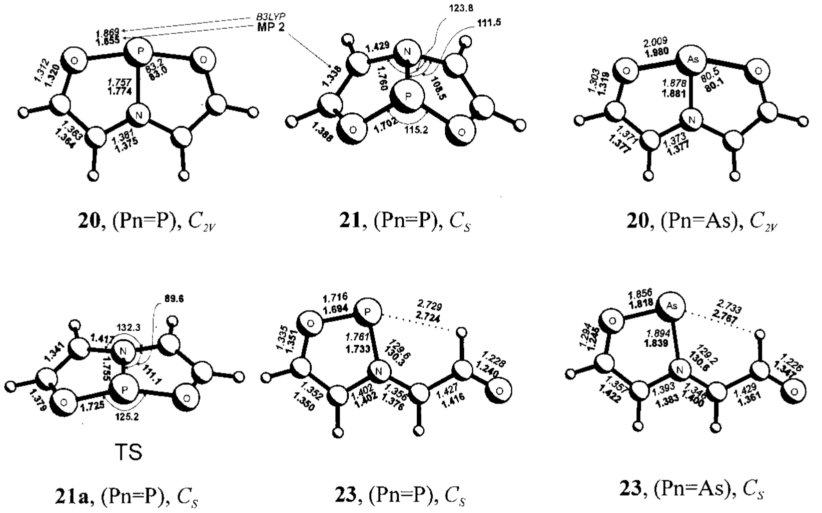
The structure **21a** in this figure portrays the transition state for the interconversion between the aromatic hypervalent, **20**, and classical, **21**, isomers of ADPO (Pn = P). The energy barrier to this rearrangement is calculated to be 16.9 kcal mol^{-1} from the side of the more stable form **20**, but it is only 0.3 kcal mol^{-1} from the side of the minor isomer **21**. This finding points to the extreme flatness of the PES in the region of **21** (Pn = P). Therefore, a possibility to experimentally observe this rearrangement seems to be quite ambiguous.

By contrast with the ADPO compounds formed by the second- and third-row pnictogen atoms readily acquiring the T-shaped hypervalent arrangements in

Table 7. Relative (with respect to 20) Energies of the Isomers of 5-Aza-2,8-dioxapnictabicyclo[3.3.0]octa-2,4,6-trienes (Pn = P, As)[70]

Pn	isomeric structure	method	ΔE, kcal mol^{-1}
P	**21**	RHF/6-31G**	−9.5
		MP2(full)/6-31G**	16.6
		B3LYP/6-31G**	*a*
	23	RHF/6-31G**	23.2
		MP2(full)/6-31G**	34.8
		B3LYP/6-31G**	27.4
As	**21**	RHF/6-31G**	−0.6
		MP2(full)/6-31G**	*a*
		B3LYP/6-31G**	*a*
	23	RHF/6-31G**	23.1
		MP2(full)/6-31G**	27.6
		B3LYP/6-31G**	30.4

[a] No local minimum corresponding to this structure has been found on the PES.

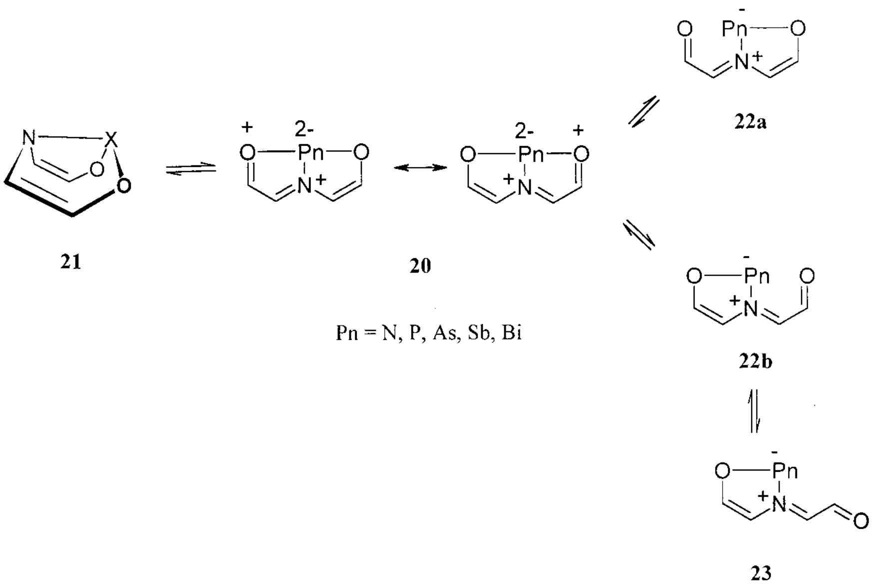


20, (Pn=P), C_{2v} **21**, (Pn=P), C_S **20**, (Pn=As), C_{2v}

21a, (Pn=P), C_S **23**, (Pn=P), C_S **23**, (Pn=As), C_S

Figure 10. MP2(full)/6-31G** (MP2) and B3LYP/6-31G** (DFT) optimized geometries (distances in angstroms and angles in degrees) of isomers of 1,6-dioxa-3a-aza-6a-pnictapentalenes **20** (Pn = P, As).[70]

Scheme 2

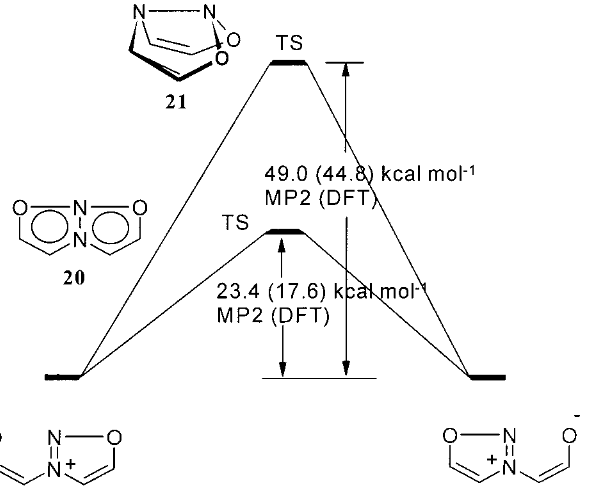


21 **20** **22a** **22b** **23**

Pn = N, P, As, Sb, Bi

20 (Pn = P, As), their first-row analogue **20** (Pn = N) is stable in the monocyclic form **22** (Pn = N). This situation is completely similar to that described in section III.1 for 1,6,6a-trioxapenalenes **17**. According to the data of ab initio (MP2(full)/6-31G** and B3LYP/6-31G**) calculations,[70] the C_{2v} structure **20** (Pn = N) represents the transition state for the in-plane N–O bond switch reaction. The **22a** $\rightleftharpoons$ **22b** interconversion proceeds as a concerted one-step reaction via a tricyclic transition-state structure and may be regarded as an example of the Boulton–Katritzky rearrangement. As shown by recent ab initio calculations, the same type of reaction mechanism is also realized for degenerate Boulton–Katritzky rearrangements of the anions of the 3-formylamino-1,2,4-oxadiazole, 3-formylmethylisoxazole, and 3-hydroxyiminomethyl-1,2,5-oxadiazole[71] and 4-nitro-benzofuroxan.[72] Interestingly, the **22a** $\rightleftharpoons$ **22b** rearrangement can occur also through another, higher energy transition state with the folded C_s structure **21** (Pn = N).[70] The rearrangements considered above are depicted by Scheme 3.

Scheme 3



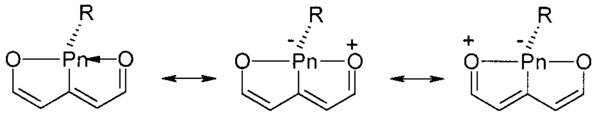
21 **20** **22a** **22b**

Table 8. Stabilization of the Bicyclic Structures 24 of 1,6-Dioxa-6aλ^5-pnictapentalenes (ΔE) Relative to Their Ring-Opened Isomers 25, HSE Values for 24,[57] and Hybridization of the Lone Electron Pair (LP) at the Pnictogen Center of 24

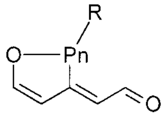
PnR	method	ΔE, kcal mol^{-1}	HSE, kcal mol^{-1}	LP
NH	MP2(full)/6-31G**	−19.6	-	sp$^{1.8}$
	B3LYP/6-31G**	−13.8	-	
PH	MP2(full)/6-31G**	15.0	15.4	sp$^{0.9}$
	B3LYP/6-31G**	14.8	12.8	
PF	MP2(full)/6-31G**	4.1	1.8	sp$^{0.6}$
	B3LYP/6-31G**	6.0	0.7	
AsF	MP2(full)/6-31G**	9.2	7.2	sp$^{0.4}$
	B3LYP/6-31G**	10.4	6.6	

III.4. 1,6-Dioxa-6aλ^5-pnictapentalenes

1,6-Dioxa-6aλ^5-pnictapentalenes **24** are the heterapentalenes which have not yet been synthesized. In a formal way, they can be derived by annelation of a five-membered furan ring to a molecule of *cis*-β-pnictovinylaldehyde **10**, just as 1,6-dioxa-6aλ^4-chalcapentalenes **18** are derived from *cis*-β-chalcovinylaldehydes **7**.



24 **24a** **24b**

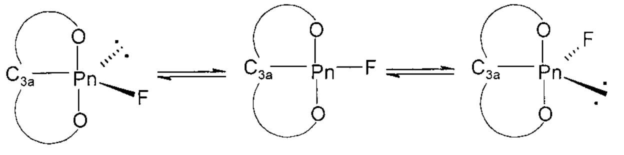


25

As in the case of β-pnictovinylaldehydes **10**, 1,6-dioxa-6aλ^5-pnictapentalenes **24** (Pn = P, As) are prone to formation of rather strong intramolecular coordination Pn←O bonds, which support a *cis*-configuration around the CC double bonds and provide for the stable heterapentalene-like structure of their molecules. This conclusion is validated by results of the calculations[57] (Table 8), which witness energy preference of the bicyclic hypervalent structures **24** (Pn = P, As) over the isomeric unstrained monocyclic forms **25**. The energy difference between **24** and **25** increases in the sequence Pn = N, P, As. The HSE values calculated for compounds **24** according to eq 6, where X = PnR (Table 8), are lower than those of the chalcogen analogues **18** listed in Table 6. This indicates that the aromatic character of heterapentalenes **24** is significantly weaker than that of 1,6-dioxa-6aλ^4-chalcapentalenes **18** (X = S, Se, Te). Whereas the aromaticity of **18** and ADPO **20** is a direct consequence of the full analogy in their electronic structure with that of pentalene dianion,[9,12,70] the aromatic character of 1,6-dioxa-6aλ^5-pnictapentalenes **24** must depend on the degree of involvement of a single lone electron pair (LP) at the pnictogen atom into the cyclic π-conjugation. According to the NBO analysis, the axis of the LP orbital is declined from the molecular plane at angles 121−136° and the p character of the orbital decreases in the sequences Y = N, P, As and R = H, F. The higher p character of the LP orbital centered at the pnictogen atom of **24**, the larger is the HSE.

Optimized geometries of selected 1,6-dioxa-6aλ^5-pnictapentalenes **24** (Pn = N, P, As), their monocyclic isomers **25**, and transition-state structures for the low-energy barrier transformations of **24** are shown in Figure 11. As for the oxygen analogue **17**, the symmetric structure of 1,6-dioxa-6aλ^5-azapentalene **24** (Pn = N, R = H) conforms not to a minimum but to a saddle point on the PES, which corresponds to the transition state for the N−O bond switch rearrangement involving **26** and its mirror-image isomer. This rearrangement proceeds apparently as the intramolecular S_N2 substitution at the tricoordinated nitrogen atom placed within a molecular framework suitable for the stereoelectronic demands of this mechanism. The ΔE values given in Table 8 represent the energy barriers for this rearrangement. They are close to that (27.7 kcal mol^{-1} at the MP2(full)/6-31G** level) for the energy barrier against the intramolecular nucleophilic substitution at the tetrahedral carbon atom in a structurally similar system of 2,3-dihydro-3-formylmethylenefuran.[73]

For all the compounds shown in Figure 11, the bicyclic structures **24** are slightly folded along the Pn−C_{3a} bond. The C_{2v} structures **27** were also found on the PESs of **24** (Pn = P, As, R = F) and identified as the transition states for a peculiar polytopal rearrangement of these compounds sketched below.

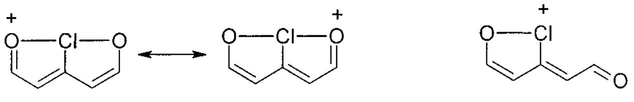


24, C_s **27**, C_{2v} **24a**, C_s

The trigonal bipyramidal-like (bisphenoidal) structures **24** (Pn = P, As) interconvert by passing through the planar C_{2v} transition-state structure **27**, whereas in the unstrained bisphenoids the topomerization occurs, as usual, through square pyramidal transition-state structures, see e.g., ref 74. The energy barriers to the **24** ⇌ **27** ⇌ **24a** rearrangement were calculated[57] to be 25.1 (B3LYP/6-31G**) and 15.6 (MP2(full)/6-31G**) kcal mol^{-1} for the phospha-1,6-dioxa-6aλ^5-pnictapentalenes (Pn = P) and 46.7 (B3LYP/6-31G**) and 32.7 (MP2(full)/6-31G**) kcal mol^{-1} for the arsa-1,6-dioxa-6aλ^5-pnictapentalenes (Pn = As).

III.5. 1,6-Dioxa-6aλ^4-cloroniapentalene

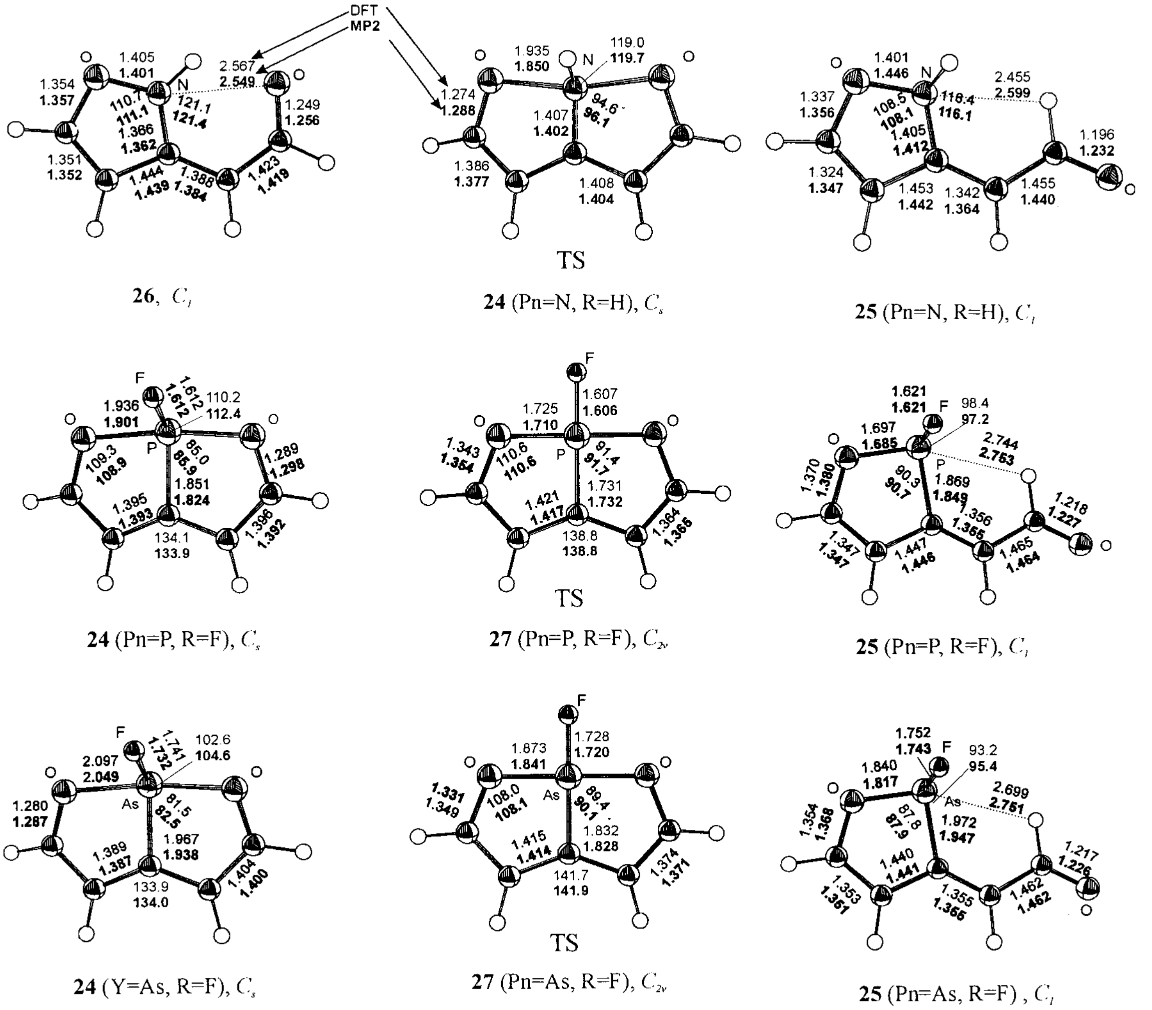
This hypothetical perchloronium cation **28** is an isoelectronic analogue of 1,6-dioxa-6aλ^4-chalcapen-



28a **28b** **29**

E_{rel} (kcal mol^{-1}): 0 MP2(full)/6-31G** 34.1

0 B3LYP/6-31G** 46.1



26, C_s

24 (Pn=N, R=H), C_s

25 (Pn=N, R=H), C_1

24 (Pn=P, R=F), C_s

27 (Pn=P, R=F), C_{2v}

25 (Pn=P, R=F), C_1

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

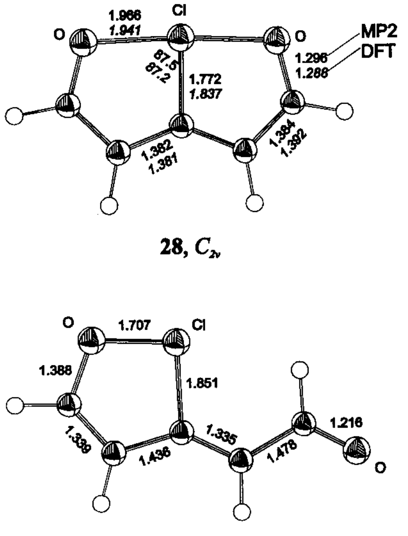
27 (Pn=As, R=F), C_{2v}

25 (Pn=As, R=F) , C_1

Figure 11. MP2(full)/6-31G** (MP2) and B3LYP/6-31G** (DFT) optimized geometries[57] (distances in angstroms and angles in degrees) of the bicyclic and monocyclic isomers of 1,6-dioxa-6aλ^5-pnictapentalenes and the transition-state structures for their interconversion: (a) Pn = N; (b) Pn = P; (c) Pn = As.

talenes. Its planar C_{2v} structure with the hypervalent arrangement across the chlorine center corresponds to a deep local minimum on the PES, and it is strongly stabilized with respect to the monocyclic isomer **29**.[61]

Although for **28** the HSE value could not be calculated by using eq 6 because the reference ring-opened structure (X = Cl^+) under optimization of its geometry appeared to eliminate a molecule of methyl chloride, high values of E_{rel} (ΔE) indicate a significant degree of the aromatic stabilization. The calculated geometry of cation **28** is shown in Figure 12. Very strong hypervalent bonding in the $(O-Cl-O)^+$ triad of **28** is stressed by the pronounced (~1.3 Å) shortening of the Cl−O contact as compared with the respective vdW contact.



28, C_{2v}

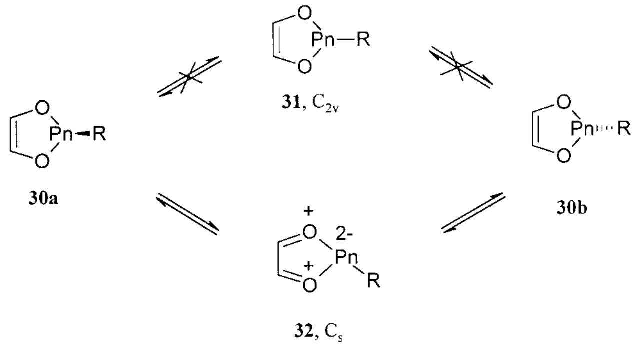
29, C_s

Figure 12. MP2(full)/6-31G** (MP2) and B3LYP/6-31G** (DFT) optimized geometries (distances in angstroms and angles in degrees) of 1,6-dioxa-6aλ^4-cloroniapentalene **28** and its monocyclic isomer **29**.[61]

IV. Aromatic Stabilization of the Transition-State Structures with Hypervalent Centers

Configurational inversion in the cyclic tricoordinate pnictogen compounds serves as an illustrative example of the impact which aromatic stabilization of a transition-state structure with the hypervalent center may have on the reaction mechanism.[75] Scheme 4 features two alternative nondissociative reaction pathways for the inversion of pyramidal configura-

Scheme 4



tion at the tricoordinate pnictogen atom in derivatives of 2*H*-1,3,2-dioxaphosphole and 2*H*-1,3,2-dioxaarsole **30** (Pn = P, As).

The generally accepted vertex inversion mechanism involves passage via the transition-state structure **31** with a trigonal pnictogen center, at which the lone electron pair possess pure p character and the π-system of the molecule containing as a whole eight electrons is antiaromatic. On the other hand, if the topomerization proceeds according to the edge inversion pathway,[69,76] the transition-state or intermediate structure **32** with a T-shaped arrangement at the hypervalent pnictogen center acquires an aromatic 6π electron configuration due to withdrawal of a pair of π-electrons to the nonbonding orbital at the pnictogen atom. It may, therefore, be expected that the edge inversion route **30a** $\rightleftharpoons$ **32** $\rightleftharpoons$ **30b** is energy favored for compounds **30** capable of formation of sufficiently strong hypervalent bonds across the pnictogen center, i.e., those with pnictogen atoms of the second to lower row in the periodic table and with electronegative substituents R attached to these atoms. The ab initio calculations[75] performed at the MP2(full)/6-31G** level have found, indeed, that the configurational inversions of 2-fluoro-2*H*-1,3,2-dioxaphosphole **30** (Pn = P, R = F) and arsole **30** (Pn = As, R = F) described by Scheme 4 take place through the edge inversion mechanism, i.e., by passage via the aromatic transition-state structures **32**. Figure 13 shows the shapes of three occupied π orbitals of the aromatic transition-state structure **32** with the tricoordinate hypervalent phosphorus atom.

The energy barriers calculated for these topomerizations are 31.0 (Pn = P) and ~ 23 (Pn = As) kcal mol^{-1}. [The MP2(full)/6-31G** structure **32** conforms to a very shallow minimum (the minimal vibrational frequency is 46 cm^{-1}) on the PES. On the B3LYP/6-31G** PES, this structure is a true saddle point.[75]] According to the calculations, none of compounds **30** (Pn = N, P, As; R = H and Pn = N, R = F) is susceptible of realization of the vertex inversion mechanism **30a** $\rightleftharpoons$ **31** $\rightleftharpoons$ **30b** with passage the antiaromatic transition state. When molecules of **30** were computationally forced to accept the C_{2v} structure **31**, a Pn−O bond in **30** broken to form rather stable zwitterionic compounds R−Pn^{-}−O^{+}=CH−CH=O. Structural parameters calculated for 2*H*-1,3,2-dioxaphosphole and arsole and the transition-state structures for their configurational inversion are shown in Figure 14.

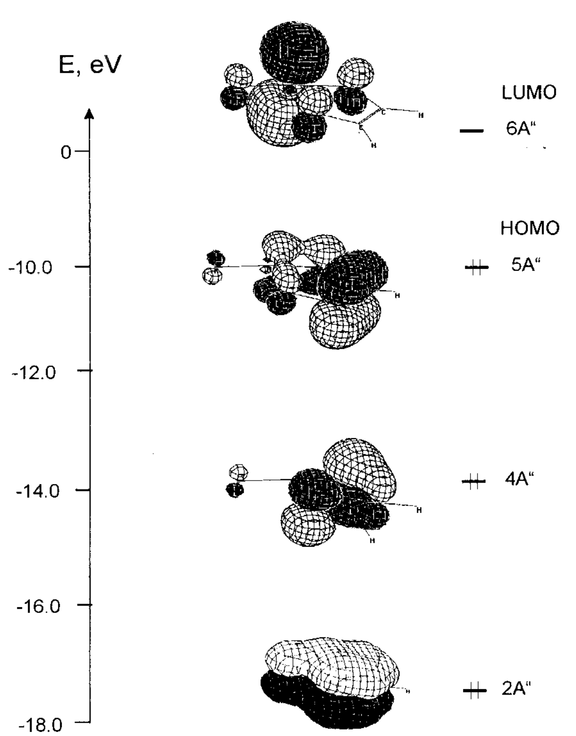
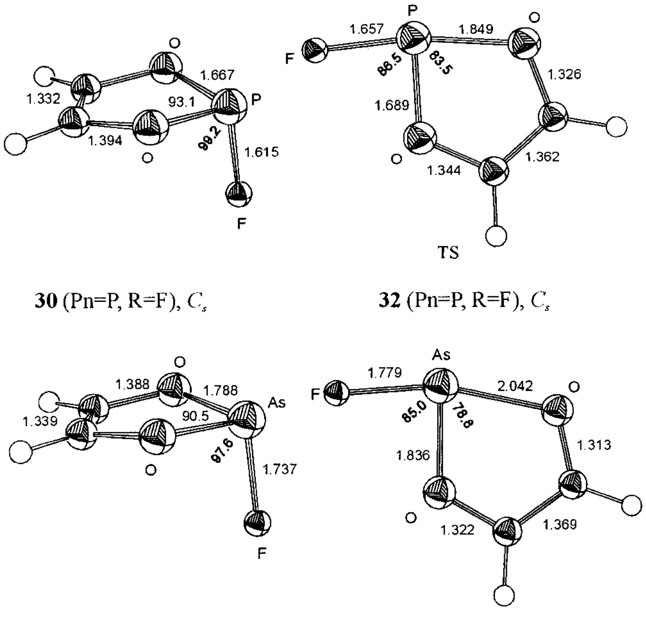


Figure 13. π-MOs of the aromatic transition-state structure **32** for the inversion of pyramidal configuration at the phosphorus atom of 2*H*-1,3,2-dioxaphosphole calculated with the 6-31G** basis set.[75]



30 (Pn=P, R=F), C_s **32** (Pn=P, R=F), C_s

30 (Pn=As, R=F), C_s **32** (Pn=As, R=F), C_s

Figure 14. MP2(full)/6-31G** optimized geometries (distances in angstroms and angles in degrees) of 2*H*-1,3,2-dioxaphosphole and arsole **30** and the transition-state structures **32** for their configurational inversion.[75]

V. Summary

Strong attractive intramolecular X←Y(S, NR′) interactions of 1,5-type occurring between terminal electron-rich main-group 15−17 centers (X = pnictogen, chalcogen, or halogen) and carbonyl, thione, or imine groups (Y = O, S, NR′) incorporated into the conjugated −X−CH=CH−CH=Y fragments result in significant stabilization of *cis-s-cis* structure of these molecules, which may be viewed as the five-membered pseudo-heterocycles with the hypervalent arrangements across the pnictogen, chalcogen, or halogen centers. In derivatives of β-chalcovinylaldehydes and isoelectronic chloronium cations, one of two lone electron pairs at $X = S$, Se, Te, Cl^+ possesses pure p character and is involved in conjugation with the π-system of the rest of the molecule, which leads to an appreciable contribution of the aromatic stabilization of the 6π-electron ring closed by the $X \leftarrow Y$ bond. The aromaticity of these structures evaluated through calculation of the homodesmotic stabilization energies (HSE) increases in parallel with an increase in the strength of the intramolecular coordination bonds, i.e., in the order $X = S$, Se, Te and with an increase in electronegativity of a substituent attached to the chalcogen atom. Clear manifestation of the aromatic character of the *cis-s-cis* isomers of β-chalcovinylaldehydes, their imines, as well as congeneric thiones and chloronium cations comes from the theoretical and experimental evidence for the pronounced equalization (as compared with the open *trans-s-trans* isomers) of the CC bond lengths.

The cooperative effects of the hypervalent bonding and aromaticity are most distinct in the bicyclic structures of 1,6,6aλ^4-trichalcapentalenes, their 1,6-dioxa(aza) analogues, and 1,6-dioxa-3a-aza-6aλ^4-pnictapentalenes, in which two conjugated $-X-CH{=}CH-CH{=}Y$ fragments are fused together via the symmetric $-Y-X-Y-$ triad. The assessments based on the HSE values indicate that the aromaticity of these 10π-electron compounds is estimated as about 30−50% of the aromatic character of the most aromatic bicyclic structure of naphthalene.

As shown by extensive ab initio calculations, substantial hypervalent bonding effects also operate in the case of β-pnictovinylaldehydes formed by second and lower row pnictogen atoms ($X = P$, As, Sb, Bi), providing for the enhanced stability of their *cis-s-cis* configuration with respect to the free-of-strain *trans-s-trans* structures. The bicyclic 1,6,6aλ^5-dioxapnictapentalene structure is also the most energy favorable form of these compounds. However, by contrast with the chalcogen and halonium analogues, the pseudo-cyclic structure of β-pnictovinylaldehydes and the bicyclic structure of 1,6,6aλ^5-dioxapnictapentalenes are maintained through primarily the occurrence of the hypervalent bonding across the pnictogen centers, whereas π-delocalization is not (or weakly) operative in these compounds. A possible explanation for this finding is the low p character of the single lone electron pair at the pnictogen and orientation of the axis of its orbital, which is unfavorable for the optimal overlap with the π-system of the rest of a molecule.

As first proposed by Arduengo and Dixon,[18−20] configurational isomerizations at the second and lower row tricoordinate pnictogen centers may proceed through the T-shaped hypervalent structures. Such a structure is strongly stabilized in the aromatic 1,6-dioxa-3a-aza-6aλ^4-pnictapentalenes. It was found by calculations that the aromatic stabilization of the T-shaped hypervalent arrangement at the tricoordinate pnictogen center in 2*H*-1,3,2-dioxaphosphole and arsole arising due to withdrawal of two electrons from the π-system of the ring onto the hypervalent electron-excessive center facilitates the rearrangement and directs it along the reaction path with the aromatic transition-state structure. Investigation of the influence of cooperative effects of hypervalent bonding and aromaticity on stability and mechanisms of reactions of main-group 14−17 compounds not considered in this review is the subject of our continuing research.

VI. Acknowledgments

This work has been supported by the Russian Fund for Basic Research (Grant Nos. 00-15-97320 and 98-03-33169a). V.I.M. gratefully acknowledges support by the Alexander von Humboldt Foundation (1999 A.v.H. Research Award).

VII. References

(1) Dewar, M. J. S. *The Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1969; pp 176−184.
(2) (a) *Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity*; Bergmann, E. D., Pullman, B., Eds.; Israel Academy of Sciences and Humanities: Jerusalem, 1971; *Jerusalem Symposium on Quantum Chemistry and Biochemistry*, Vol. III. (b) Agranat, I. In *Theoretical Aromatic Chemistry*; Zollinger, H., Ed.; MTP International Review of Science; Butterworth: London, 1973; Vol. 3 (Aromatic Compounds); pp 140−173.
(3) Garrat, P. J. *Aromaticity*; Wiley: New York, 1986.
(4) Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Ya. *Aromaticity and Antiaromaticity*: *Electronic and Structural Aspects*; Wiley: New York, 1994.
(5) (a) Schleyer, P. v. R.; Freeman, P. K.; Jiao, H.; Goldfluss, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 337. (b) Schleyer, P. v. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *68*, 209. (c) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.
(6) Krygowski, T. M.; Cyrañski, M. K.; Czarnocki, Z.; Häfelinger, G.; Katritzky, A. R. *Tetrahedron* **2000**, *56*, 1783.
(7) Cook, M. J.; Linda, P.; Katritzky. A. R. *Adv. Heterocycl. Chem.* **1974**, *17*, 255.
(8) Katritzky, A. R.; Karelson, M.; Malhotra, N. *Heterocycles* **1991**, *32*, 127.
(9) Simkin, B. Ya.; Minkin, V. I.; Glukhovtsev, M. N. *Adv. Heterocycl. Chem.* **1993**, *56*, 303.
(10) (a) Balaban, A. T. *Pure Appl. Chem.* **1980**, *52*, 1409. (b) Balaban, A. T. *J. Chem. Inf. Comput. Sci.* **1985**, *25*, 34.
(11) Reid, D. H. *Organic Compounds of Sulfur, Selenium and Tellurium*; The Chemical Society: London, 1970; Vol. 1, p 321.
(12) Gleiter, R.; Gygax, R. *Topics Curr. Chem.* **1976**, *63*, 49.
(13) Dixon, D. A.; Arduengo, A. J., III *Phosphorus, Sulfur Silicon* **1991**, *55*, 35.
(14) Cimiraglia, R.; Hoffmann, H.-J. *J. Am. Chem. Soc.* **1991**, *113*, 6449.
(15) (a) Musher, J. I. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54. (b) Rundle, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 112.
(16) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; pp 258−276.
(17) Landrum, G. M.; Goldberg, N.; Hoffmann, R.; Minyaev, R. M. *New J. Chem.* **1998**, 883.
(18) Arduengo, A. J., III *Pure Appl. Chem.* **1987**, *59*, 1053.
(19) Arduengo, A. J., III; Stewart, C. A.; Davidson, F.; Dixon, D. A.; Becker, J. Y.; Culley, S. A.; Mizen, M. *J. Am. Chem. Soc.* **1987**, *109*, 627.
(20) Arduengo, A. J., III; Stewart, C. A. *Chem. Rev.* **1994**, *94*, 1215.
(21) Zefirov, Yu. V.; Zorky, P. M. *Usp. Khim. (Russ. Chem. Rev.)*. **1995**, *64*, 446.
(22) Kuz′mina, L. G. *Koord. Khim.* **1999**, *25*, 643.
(23) Bürgi, H.-B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153.
(24) Ángyán, J. G.; Poirier, R. A.; Kucsman, A.; Csizmadia, I. G. *J. Am. Chem. Soc.* **1987**, *109*, 2237.
(25) Barton, D. H. R.; Hall, M. B.; Lin, Z.; Parekh, S. I.; Reibeuspies, J. *J. Am. Chem. Soc.* **1993**, *115*, 5056.
(26) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597.
(27) McWhinnie, W. R.; Sadekov, I. D.; Minkin, V. I. *Sulfur Repts.* **1996**, *18*, 295.
(28) Nagao, Y.; Hirata, T.; Goto, S.; Sano, S.; Kakehi, A.; Iizuka, K.; Shiro, M. *J. Am. Chem. Soc.* **1998**, *120*, 3104.
(29) Minyaev, R. M.; Minkin, V. I. *Can. J. Chem.* **1998**, *76*, 766.
(30) Minkin, V. I. *Russ. Chem. J.* **1999**, *43*, 10.

(31) Kucsman, A.; Kapovits, I. In *Organic Sulfur Chemistry: Theoretical and Experimental Advances*; Csizmadia, I. G., Mangini, A., Bernardi, F., Eds.; Elsevier: Amsterdam, 1985; pp 191−245.

(32) Kucsman, A.; Kapovits, I.; Czugler, M. *J. Mol. Struct.* **1989**, *198*, 339.

(33) Hargittai, I.; Rozondai, R. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1985; Vol. 1, p 65.

(34) Minkin, V. I.; Sadekov, I. D.; Rivkin, B. B.; Zakharov, A. V.; Nivorozhkin, V. L.; Kompan, O. E.; Struchkov, Yu. T. *J. Organomet. Chem.* **1997**, *536−537*, 233.

(35) Sadekov, I. D.; Ladatko, A. A.; Nivorozhkin, V. L.; Kompan, O. E.; Struchkov, Yu. T.; Minkin, V. I. *Zh. Obsch. Khim.* **1990**, *60*, 2764.

(36) Detty, M. R.; Murray, B. J.; Smith, D. L.; Zumbulyadis, J. *J. Am. Chem. Soc.* **1983**, *105*, 875.

(37) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(38) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(39) Detty, M. R.; Murray, B. J. *J. Am. Chem. Soc.* **1983**, *105*, 883.

(40) Detty, M. R.; Lenhart, W. C.; Gassman, P. G.; Callstrom, M. R. *Organometallics* **1989**, *8*, 866.

(41) Sadekov, I. D.; Maksimenko, A. A.; Maslakov, A. G.; Minkin, V. I. *J. Organomet. Chem.* **1990**, *391*, 179.

(42) Sadekov, I. D.; Nivorozhkin, V. L.; Zakharov, A. V.; McWhinnie, W. R.; Minkin, V. I. *Doklady Akad. Nauk Ser. Khim. (Proc. Russ. Acad. Sci.).* **1997**, *357*, 504.

(43) Gough, K. M.; Millington, J. *Can. J. Chem.* **1995**, *73*, 1287.

(44) Bader, R. F. W. *Atoms in Molecules−a Quantum Theory*; Oxford University Press: Oxford, 1990.

(45) Friedman, P.; Ferris, K. F. *J. Mol. Struct. (THEOCHEM).* **1997**, *418*, 119.

(46) Xie, Y.; Schaefer, H. F., III *J. Mol. Struct. (THEOCHEM).* **1991**, *234*, 247.

(47) Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434.

(48) Suidan, L.; Badenhoop, J. K.; Glendening, E. D.; Weinhold, F. *J. Chem. Educ.* **1995**, *72*, 583.

(49) Dobado, J. A.; Martínez-García, H.; Molina, J. M.; Sundberg, M. R. *J. Am. Chem. Soc.* **1998**, *120*, 8461; **1999**, *121*, 3156.

(50) Minkin, V. I.; Minyaev, R. M. *Mendeleev Commun.* **2000**, 171.

(51) Nesterova, E. G.; Minyaev, R. M.; Minkin, V. I. *Zh. Org. Khim.* **2001**, accepted for publication.

(52) (a) Gimarc, B. M.; Zhao, M. *Coord. Chem. Rev.* **1997**, *158*, 385. (b) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. *Theor. Chim. Acta* **1975**, *38*, 121.

(53) Cremer, D. *Tetrahedron* **1988**, *44*, 7427.

(54) Nakanishi, W.; Hayashi, S.; Sakaue, A.; Ono, G.; Kawada, Y. *J. Am. Chem. Soc.* **1998**, *120*, 3635.

(55) Murafuji, T.; Mutoh, T.; Satoh, K.; Tsunenari, T.; Azuma, N.; Suzuki, H. *Organometallics* **1995**, *14*, 3848.

(56) Emsley, J. *The Elements*; Clarendon Press: Oxford, 1991.

(57) Minkin, V. I.; Minyaev, R. M.; Milov, A. A.; Gribanova, T. N. *Bull. Russ. Acad. Sci.* **2001**, No. 11.

(58) Dannenberg, J. J.; Rios, R. *J. Phys. Chem.* **1994**, *98*, 6714.

(59) Stang, P. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 274.

(60) Pirkuliev, N. S.; Brel, V. K.; Zefirov, N. S. *Usp. Khim. (Russ. Chem. Rev.)* **2000**, *69*, 118.

(61) Minyaev, R. M.; Minkin, V. I. *Mendeleev Commun.* **2000**, 173.

(62) (a) Pedersen, C. Th. *Sulfur Repts.* 1980, *1*, 1. (b) Lozaćh, N. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon Press: Oxford, 1984; Vol. 6, p 1049. (c) Pedersen, C. Th. *Phosphorus Sulfur Silicon* **1991**, *58*, 17.

(63) (a) Spanget-Larsen, J.; Erting, C.; Shim, I. *J. Am. Chem. Soc.* **1994**, *116*, 11433. (b) Andersen, K. B.; Abildgaard, J.; Radziszewski, J. G.; Spanget-Larsen, J. *J. Phys. Chem.* **1997**, *A 101*, 4475.

(64) Takane, S.; Sakai, S. *J. Mol. Struct. (THEOCHEM).* **1999**, *488*, 1.

(65) Hansen, L. K.; Hordvik, A. *Acta Chem. Scand.* **1973**, *27*, 411.

(66) Hordvik, A.; Julshamn, K. *Acta Chem. Scand.* **1971**, *257*, 2507.

(67) Reid, D. H.; Webster, R. G. *J. Chem. Soc., Perkin Trans. 1* **1975**, 775.

(68) Detty, M. R.; Luss, H. R. *J. Org. Chem.* **1983**, *48*, 5149.

(69) (a) Dixon, D. A.; Arduengo, A. J., III; Fukunaga, T. *J. Am. Chem. Soc.* **1986**, *108*, 2461. (b) Arduengo, A. J., III; Dixon, D. A.; Roe, D. C. *J. Am. Chem. Soc.* **1986**, *108*, 6821. (c) Arduengo, A. J., III; Dixon, D. A.; Stewart, C. A. *Phosphorus Sulfur* **1987**, *30*, 341. (d) Dixon, D. A.; Arduengo, A. J., III *Int. J. Quant Chem: Quantum Chem. Symp.* **1988**, *22*, 85. (e) Arduengo, A. J., III; Dixon, D. A.. In *Heteroatom Chemistry ICHA C-2*; Block, E., Ed.; VCH: New York. 1990; p. 47.

(70) Nesterova, E. G.; Gribanova, T. N.; Minyaev, R. M.; Minkin, V. I. *Bull. Russ. Acad. Sci.* **2001**, No. 2.

(71) La Manna, G.; Buscemi, S.; Vivona, N. *J. Mol. Struct. (THEOCHEM).* **1998**, *452*, 67.

(72) (a) Eckert, F.; Rauhut, D. *J. Am. Chem. Soc.* **1998**, *120*, 13478. (b) Eckert, F.; Rauhut, G.; Katritzky, A. R.; Steel, P. J. *J. Am. Chem. Soc.* **1999**, *121*, 6700.

(73) Minyaev, R. M.; Minkin, V. I. *Russ. Chem. Bull.* **1999**, 1246; *Engl. Transl.* **1999**, 1234.

(74) Fowler, J. G.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1994**, *116*, 9596.

(75) Minyaev, R. M.; Minkin, V. I. *Dokl. Akad. Nauk Ser. Khim. (Proc. Russ. Acad. Sci.)* **2000**, *375*, No. 5.

(76) (a) Stecler, R.; Truhlar, D. J. *J. Chem. Phys.* **1990**, *93*, 6570; (b) Moc, J.; Morokuma, K. *Inorg. Chem.*, **1994**, *33*, 551. (c) Schwerdtfeger, P.; Boyd, P. D. W.; Fischer, Th.; Hunt, P.; Liddell, M. *J. Am. Chem. Soc.* **1994**, *116*, 9620.

CR990358H