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Intramolecular Hypervalent $X \leftarrow X$ Interaction in Mono- and Bicyclic Heteroelement Compounds Containing Se and Te Atoms*

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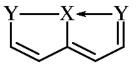
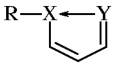
Abstract—Chalcogen-containing heterapentalene and quasimonocyclic compounds having Se–Se–Se and Te–Te–Te triads or Se–Se and Te–Te diads were studied by the *ab initio* [MP2(full)/6-31G**, MP2(fc)/6-31+G**, and MP2(fc)/LANL2DZ] and DFT methods (B3LYP/6-31G**, B3LYP/6-31+G**, and B3LYP/LANL2DZ). Heterapentalene compounds were found to be stable as planar bicyclic structures having a C_{2v} symmetry. The stability of quasimonocycic β-chalcogenovinyl aldehydes increases with increase in the electron-acceptor power of the substituent at the X atom.

Intramolecular hypervalent interaction between electron-rich centers in compounds **Ia**–**Ie** and **IIa**–**IIf** have been studied by experimental [1–3] and theoretical methods [1, 2, 4].



Ia–Ie



IIa–IIf

I, X = S, Y = O (**a**), NR (**b**); X = Se: Y = O (**c**), S (**d**); X = Te, Y = O (**e**); **II**, X = S, Y = O: R = H (**a**), Cl (**b**); X = Se, Y = O: R = H (**c**), Cl (**d**); X = Te, Y = O: R = H (**e**), Cl (**f**).

Hypervalent $X \leftarrow Y$ interaction in molecules **I** and **II** leads to considerable shortening of the $X \cdots Y$ distance relative to the sum of the van der Waals radii of X and Y atoms (3.30 Å for $O \cdots S$, 3.40 Å for $O \cdots Se$, and 3.60 Å for $O \cdots Te$ [5]), and the energy of this interaction increases in the series S < Se < Te. According to the calculation data [4], the $X \cdots O$ distance in molecules of 1,6-dioxa-6a-heterapentalenes **I** is 2.043, 2.085, and 2.172 Å for compounds **Ia**, **Ic**, and **Ie**, respectively. These distances are shorter by more than 1 Å than the sum of the van der Waals radii of X and O atoms. The results of experimental and theoretical studies [1–4] showed that chalcogen-containing 10π-electron pentalene systems **I** have planar structures having a C_{2v} symmetry with *T*-configuration of the X center, i.e., both X–O bonds are equivalent. The energy of $X \cdots Y$ interaction in **I** increases from 12.1 kcal/mol for the O–S bond to 19.8 and 27.7 kcal/mol for the O–Se and O–Te bonds, respectively [4].

However, the $O{-}O \leftarrow O \longleftrightarrow O \rightarrow O{-}O$ interaction in trioxapentalene system **IIIa** having an O–O–O triad is repulsive (according to the theoretical data in [6]), which leads to stabilization of planar monocyclic structure with one covalent O–O bond and nonvalence van der Waals $O \cdots O$ contact. On the other hand, compounds **IIIb** having an S–S–S triad were shown by experimental [2] and theoretical methods [3, 6] to be characterized by strong attractive hypervalent interaction which stabilizes planar bicyclic structure with a C_{2v} symmetry and shortened S–S distances.

The strength of the $X \cdots O$ interaction in quasimonocyclic structure **II** depends to a considerable extent on the substituent R attached to X. Some shortening of the $X \cdots O$ distance relative to the sum of the van der Waals radii of X and O atoms was observed even when the substituent R was electon-donating (R = H). This distance becomes appreciably shorter when the electronegativity of R increases:

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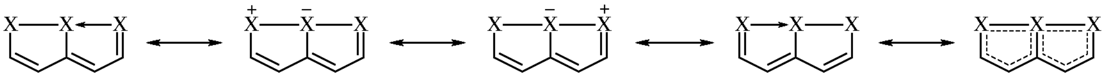
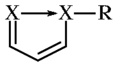


III

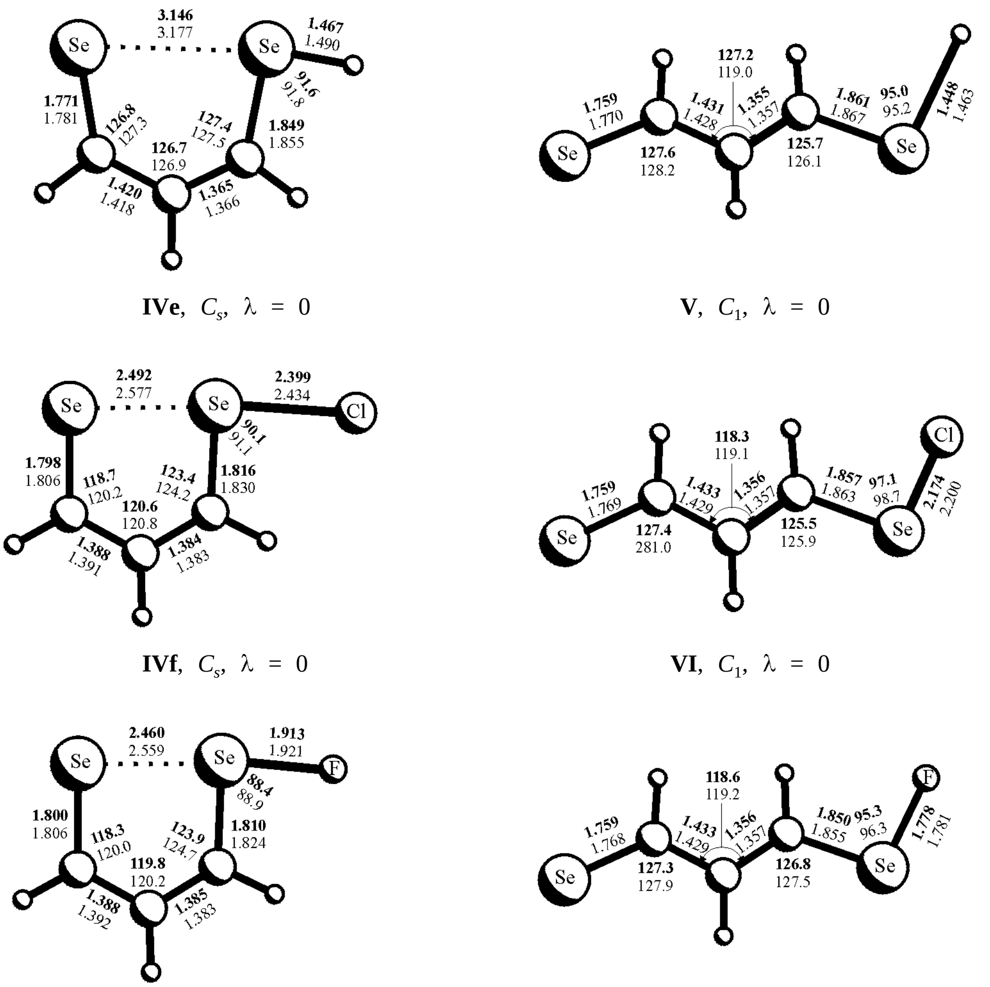


IV

III, X = O (**a**), S (**b**), Se (**c**), Te (**d**); **IV**, X = O: R = H (**a**), F (**b**); X = S: R = H (**c**), F (**d**); X = Se: R = H (**e**), Cl (**f**), F (**g**); X = Te: R = H (**h**), Cl (**i**), F (**j**).

for R = Cl, the X···O distance is 2.395, 2.307, and 2.294 Å in molecules **IIb**, **IId**, and **IIf**, respectively [4]. As in heterapentalene systems, the above distance is shorter than the sum of the van der Waals radii of X and O atoms by more than 1 Å. Apart from considerable shortening of the X···O distance, increase of the electron-acceptor power of the substituent R is accompanied by rise in the X···O interaction energy. The X···O interaction energies in structures **IIc** and **IIe** are low and are 0.89 and 3.81 kcal/mol, respectively, while they increase to 10.54 kcal/mol for compound **IId** and 16.47 kcal/mol for **IIf** [4].

Until present, the energies of X–X interaction in compounds **IIIc** and **IIId** having Se–Se–Se and Te–Te–Te triads and in compounds **IVe**–**IVj** having Se–Se and Te–Te diads, as well as concomitant variations of aromaticity of these compounds, have not been estimated.



IVe, C_s, λ = 0

V, C_1, λ = 0

IVf, C_s, λ = 0

VI, C_1, λ = 0

IVg, C_s, λ = 0

VII, C_1, λ = 0

Fig. 1. Geometric parameters of structures **IVe**–**IVg** and **V**–**VII**, calculated by the MP2(fc)/6-31+G** (boldface numbers) and DFT methods (B3LYP/6-31+G**). The bond lengths are given in angstroems, and bond angles, in degrees.

Table 1. Parameters of structures **IVe**–**IVg** and **V**–**VII**, calculated *ab initio* [(MP2(fc)/6-31+G**) and DFT (B3LYP/6-31G**)] and of **IVh**–**IVj** and **VIII**–**X**, calculated by the MP2(fc)/LANL2DZ and DFT (B3LYP/LANL2DZ) methods[a]

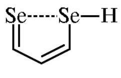
Comp. no.	Method	λ	E_{tot}, a.u.	ΔE, kcal/mol	ZPE, a.u.	ΔE_{ZPE}, kcal/mol	ΔH, kcal/mol	ω, cm^{-1}
IVe	MP2	0	–4911.888771	0	0.059761	0	0	114.7
	B3LYP	0	–4915.507384	0	0.058659	0	0	108.8
V	MP2	0	–4911.888001	0.5	0.059027	0.1	0.4	119.3
	B3LYP	0	–4915.507816	–0.3	0.058087	–0.6	–0.3	118.5
IVf	MP2	0	–5370.956172	0	0.052919	0	0	73.3
	B3LYP	0	–5375.140701	0	0.051973	0	0	87.6
VI	MP2	0	–5370.921790	21.6	0.052056	21.0	21.4	73.6
	B3LYP	0	–5375.107375	20.9	0.051237	20.5	20.8	30.9
IVg	MP2	0	–5010.949607	0	0.053628	0	0	96.2
	B3LYP	0	–5014.776721	0	0.052690	0	0	122.0
VII	MP2	0	–5010.903789	28.8	0.052537	28.1	28.6	30.4
	B3LYP	0	–5014.737741	24.5	0.051774	23.9	24.4	40.4
IVh	MP2	0	–131.856449	0	0.055174	0	0	79.3
	B3LYP	0	–132.747020	0	0.055905	0	0	85.6
VIII	MP2	0	–131.852596	2.4	0.054000	1.7	2.2	73.0
	B3LYP	0	–132.741086	3.7	0.055093	3.2	3.7	84.4
IVi	MP2	0	–146.052560	0	0.049532	0	0	51.8
	B3LYP	0	–147.141709	0	0.050270	0	0	55.3
IX	MP2	0	–146.027495	15.7	0.048642	15.2	9.8	41.9
	B3LYP	0	–147.104531	23.3	0.049466	22.8	23.2	26.6
IVj	MP2	0	–230.870744	0	0.050254	0	0	77.6
X	MP2	0	–230.845017	16.1	0.049297	15.5	16.0	37.2

[a] λ is the number of negative Hessian eigenvalues for a given stationary point; E_{tot} and ΔE are the total and relative energies (1 a.u. = 627.5095 kcal/mol); ZPE is the zero-point energy; ΔE_{ZPE} is the relative energy corrected for zero-point energy; ΔH is the relative enthalpy; and ω_1 is the lowest or imaginary harmonic frequency.

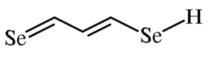
The goal of the present work was to study the nature and energy of intramolecular hypervalent X···X interaction in chalcogen-containing heterapentalene (**IIIc**–**IIId**) and quasicyclic (**IVe**–**IVj**) systems and to estimate structural parameters of these compounds by *ab initio* [MP2(full)/6-31G**, MP2(fc)/6-31+G**, and MP2(fc)/LANL2DZ] and density functional theory calculations (B3LYP/6-31G**, B3LYP/6-31+G**, and B3LYP/LANL2DZ).

Calculation procedure. The calculations were performed in terms of the nonempirical Hartree–Fock method (RHF) with account taken of electron correlation (full for valence-split basis sets 6-31G** and 6-31+G** and fc for pseudopotential LANL2DZ basis set), using the Moeller–Plesset second-order perturbation theory (MP2), and in terms of the density functional theory (DFT, Becke3LYP). Gaussian-94 [7] and GAMESS [8] software packages were used. Full geometry optimization of molecular structures corresponding to stationary points (λ = 0 for a minimum, where λ is the number of negative Hessian eigenvalues in the given stationary point [9]) on the potential energy surface (PES) was performed up to a gradient of 10^{-5} a.u./bohr, using GAMESS program ("tight" mode, Gaussian-94 software). Graphical images were obtained using PD program (PLUTO mode; PCMODEL software [10]).

Results and discussion. 3-Hydroselenopropeneselenal. According to the MP2 and DFT calculations, *cis-s-cis* structure **IVe** of 3-hydroselenopropeneselenal with a shortened Se···Se distance is a stable



IVe



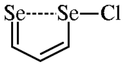
V

form corresponding to an energy minimum ($\lambda = 0$) on the PES. The Se···Se distance is considerably shorter (MP2: 3.146 Å, B3LYP: 3.177 Å) than the corresponding sum of van der Waals radii (4.0 Å) [5], indicating attractive character of the Se···Se interaction in molecule **IVe**.

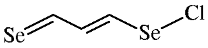
According to the MP2 calculations, the corresponding *trans-s-trans* structure **V**, which is also characterized by an energy minimum on the PES, is less stable than **IVe** by 0.5 kcal/mol. The DFT calculations give the reverse results: *trans-s-trans* structure **V** is by 0.3 kcal/mol more favorable than **IVe**. These data indicate that the Se···Se interaction in structure **IVe** is quite weak. As shown in [11], the DFT procedure describes weak interactions with insufficient reliability. The calculated geometric and energy parameters of structures **IVe** and **V** are given in Fig. 1 and Table 1.

In going from *cis-s-cis* structure **IVe** to *trans-s-trans* structure **V** the alternation of C–C bonds becomes more appreciable: the differences between formally single and double C–C bonds are as follows: Δl(R = H) = 0.055 (MP2), 0.052 Å (B3LYP) (**IVe**); Δl(R = H) = 0.071 (MP2), 0.076 Å (B3LYP) (**V**). This indirectly suggests higher aromaticity of *cis-s-cis* form **IVe**, as compared to *trans-s-trans*-**V**.

3-Chloroselenopropeneselenal. *cis-s-cis* Structure **IVf** with a strongly shortened Se···Se contact is a stable form corresponding to a minimum ($\lambda = 0$) on the PES of 3-chloroselenopropeneselenal. The calculated Se···Se distance is 2.492 (MP2) or 2.577 Å (B3LYP); these values are by almost 1.5 Å lower than the sum of standard van der Waals radii of selenium atoms (4.0 Å) [5] and by only 0.15 (MP2) or 0.23 Å (B3LYP) greater than the sum of the covalent Se radii (2.34 Å) [5].



IVf

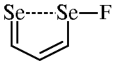


VI

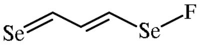
trans-s-trans Structure **VI** having no symmetry elements (S_1) also occupies a minimum point on the potential energy surface and is by 21.6 (MP2) or 20.9 kcal/mol (B3LYP) less stable than structure **IVf**. These values may be regarded as a semiquantitative estimate of the energy of attractive Se···Se interaction in **IVf**. An analogous sharp shortening of the X···X distance and increase in the energy of X···X interaction on replacement of R = H by R = Cl was observed for sulfur-containing analogs of **IV** [6] and for compound **IIb** [1, 3]. The calculated geometric and energy parameters of structures **IVf** and **VI** are given in Fig. 1 and Table 1.

The small differences between the lengths of single and double C–C bonds in *cis-s-cis*-structure **IVf** [Δl 0.004 (MP2), 0.008 Å (B3LYP)] indicate almost complete absence of bond alternation and suggest a considerable aromatic character of that structure. The above differences strongly increase in going to nonaromatic polyene *trans-s-trans*-structure **VI**: Δl 0.077 (MP2), 0.072 Å (B3LYP).

3-Fluoroselenopropeneselenal. Like 3-chloroselenopropeneselenal, the molecule of 3-fluoroselenopropeneselenal is the most stable in *cis-s-cis*-form **IVg** with a strongly shortened Se···Se contact. It is by 28.8 (MP2) or 24.5 kcal/mol (B3LYP) more stable than *trans-s-trans* structure **VII**, indicating a strong attractive Se···Se interaction in **IVg**. The Se···Se distance in **IVg** is shorter than the sum of the van der Waals radii of selenium atoms (4.0 Å) [5] by 1.54 (MP2) or 1.441 Å (B3LYP), i.e., its length approaches that of covalent Se–Se bond [5].



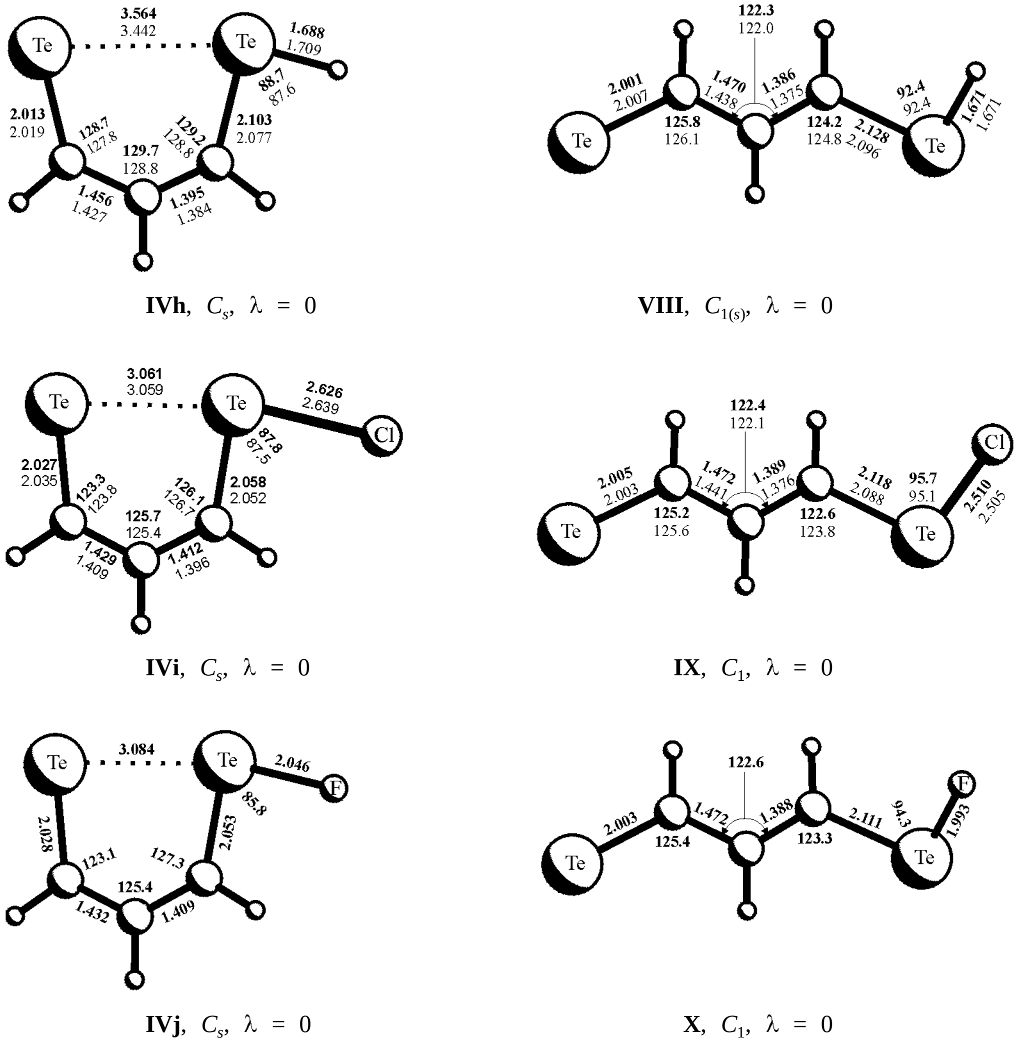
IVg



VII

The calculated geometric and energy parameters of structures **IVg** and **VII** are presented in Fig. 1 and Table 1. Like structure **IVf**, molecule **IVg** (*cis-s-cis*) is characterized by a weak C–C bond alternation: Δl 0.003 (MP2) and 0.009 Å (B3LYP); this suggests essentially aromatic character of structure **IVg**. As expected, strong C–C bond alternation is observed in polyene *trans-s-trans* isomer **VII**: Δl 0.077 (MP2) and 0.072 Å (B3LYP).

Replacement of the chlorine atom in molecule **IVf** by fluorine almost does not affect the character and energy of the Se···Se interaction, despite the large difference in the electronegativities of these halogen atoms. This fact is readily explained in terms of the natural bond orbital (NBO) concept [12]. The greatest contribution to stabilization of *cis-s-cis*-structure **IVf** is that produced by interaction between the n_{Cl} and $\sigma^*_{\mathrm{Se-Se}}$ orbitals oriented along the Se–Se bond. The energy of this interaction is 145.5 kcal/mol. Electron density transfer from n_{Cl} to $\sigma^*_{\mathrm{Se-Se}}$ is estimated at ~0.34 *e*. The energy of analogous orbital interaction in molecule **IVg** ($n_{\mathrm{F}} \to \sigma^*_{\mathrm{Se-Se}}$) is 124.9 kcal/mol, which is comparable with the $n_{\mathrm{Cl}} \to \sigma^*_{\mathrm{Se-Se}}$ interaction energy. The electron density transfer from n_{F} to $\sigma^*_{\mathrm{Se-Se}}$ in **IVg** is about 0.21 *e*. On the other hand, the energy of interaction between n_{Se} and $\sigma^*_{\mathrm{Se-H}}$ in **IVe** (though it remains attractive) is as low as 11.9 kcal/mol (NBO calculations), and the electron density transfer from n_{Se} to $\sigma^*_{\mathrm{Se-H}}$ is 0.04 *e*.



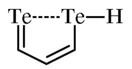
IVh, C_s, $\lambda = 0$ **VIII**, $C_{1(s)}$, $\lambda = 0$

IVi, C_s, $\lambda = 0$ **IX**, C_1, $\lambda = 0$

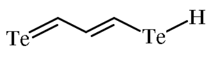
IVj, C_s, $\lambda = 0$ **X**, C_1, $\lambda = 0$

Fig. 2. Geometric parameters of structures **IVh–IVj** and **VIII–X**, calculated by the MP2(fc)/LANL2DZ (boldface numbers) and DFT methods (LANL2DZ). The bond lengths are given in angstroems, and bond angles, in degrees.

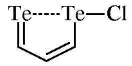
3-Hydrotelluropropenetellural, 3-chlorotelluropropenetellural, and 3-fluorotelluropropenetellural. According to the calculations, the *cis-s-cis* configurations of compounds **IVh**–**IVj** correspond to energy minima on the PES and are thermodynamically more stable than *trans-s-trans* structures **VIII**–**X**. The energy difference between the *cis-s-cis* and *trans-s-trans* structures can be regarded as semiquantitative estimate of the Te···Te interaction. Following this scheme, the Te···Te interaction energies are 2.4 (MP2) and 3.7 kcal/mol (B3LYP) for compound **IVh**, 15.7 (MR2) and 23.3 kcal/mol (B3LYP) for **IVi**, and 16.1 kcal/mol (MP2) for **IVj**. It is seen that the Te···Te interaction energy increases with increase in the electronegativity of the atom attached to tellurium. Simultaneously, the Te···Te distance strongly shortens: from 3.564 (MP2) or 3.442 Å (B3LYP) in **IVh** to 3.061 (MP2) or 3.059 Å (B3LYP) in **IVi** and to 3.084 Å (MP2) in **IVj**. The Te–Te distances in structures **IVi** and **IVj** are shorter than the double van der Waals radius of tellurium atom (4.4 Å [5]) by



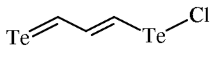
IVh



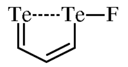
VIII



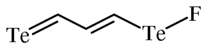
IVi



IX



IVj



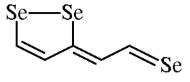
X

more than 1.3 Å, so that they approach the length of standard covalent Te–Te bond (2.86 Å [5]).

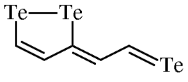
It should be noted that, according to the B3LYP/LANL2DZ calculations, *cis-s-cis*-structure **IVj** is not stable. Geometry optimization leads only to *trans-s-trans* structure **X**. The calculated geometric and energy parameters of structures **IVh**–**IVj** and **VIII**–**X** are given in Fig. 2 and Table 1. No considerable C–C bond alternation is observed in *cis-s-cis* structures **IVh**–**IVj**. The differences Δl between the lengths of formally single and formally double bonds are as follows: **IVh**: 0.061 (MP2), 0.043 Å (B3LYP); **IVi**: 0.017 (MP2), 0.013 Å (B3LYP); **IVj**: 0.023 Å (MP2). The Δl values remain almost unchanged in going from **IVh** to *trans-s-trans* structure **VIII**: Δl 0.044 (MP2) and 0.063 Å (B3LYP); however, these values strongly increase for structures **IX** and **X**: Δl 0.083 (MP2), 0.065 Å (B3LYP) (**IX**); 0.084 Å (MP2) (**X**). A similar tendency to stabilization of quasimonocyclic structure and increase in the energy of X–Y interaction with increasing electronegativity of the substituent R was observed previously for compounds **IIe** and **IIf**.

According to the NBO calculations, the energy of the $n_{\mathrm{Te}} \rightarrow \sigma^*_{\mathrm{Te-H}}$ orbital interaction in molecule **IVi** is fairly small (12.1 kcal/mol), and this is responsible for a weak attractive character of the Te···Te interaction. On replacement of hydrogen by chlorine, the $n_{\mathrm{Te}} \rightarrow \sigma^*_{\mathrm{Te-Cl}}$ energy of **IVi** increases to 116.2 kcal/mol, leading to sharp enhancement of the Te···Te interaction.

2-(1,2-Diselenol-3-ylidene)ethaneselenal (XI) and 2-(1,2-ditellurol-3-ylidene)ethanetellural (XII). Pentalene structures **IIIc** and **IIId** were found to be stable in the planar form having a C_{2v} symmetry with equivalent X–X bonds. The X···X distances in these structures are much shorter than the sum of the corresponding van der Waals radii (4.0 Å for selenium and 4.4 Å for tellurium [5]) and are 2.527 (MP2) or 2.589 Å (B3LYP) for **IIIc** and 3.096 Å (MP2) for **IIId**. The calculated geometric and energy parameters of structures **IIIc**, **IIId**, **XI**, and **XII** are presented in Fig. 3 and Table 2.

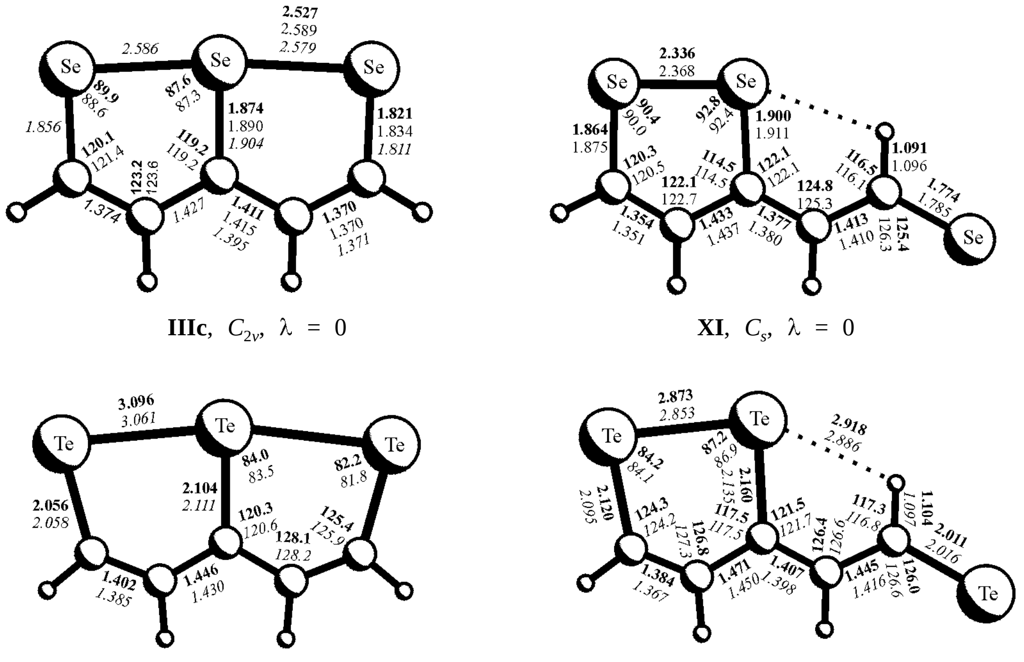


XI



XII

According to the calculations, *trans-s-trans* structures **XI** and **XII** are less stable than the corresponding *cis-s-cis* isomers by 26.4 (MP2) or 24.1 kcal/mol (B3LYP) (**XI**) and 16.3 (MP2) or 21.2 kcal/mol



IIIc, C_{2v}, $\lambda = 0$

XI, C_s, $\lambda = 0$

IIId, C_{2v}, $\lambda = 0$

XII, C_s, $\lambda = 0$

Fig. 3. Geometric parameters of structures **IIIc**, **IIId**, **XI**, and **XII**, calculated by the MP2(full)/6-31G** (**IIIc**, **XI**) (boldface numbers), MP2(fc)/LANL2DZ (**IIId**, **XII**) (boldface numbers), and DFT methods (B3LYP/6-31G**, **IIIc**, **XI**; B3LYP/LANL2DZ, **IIId**, **XII**). Italicized numbers refer to the experimental data. The bond lengths are given in angstroems, and bond angles, in degrees.

Table 2. Results of *ab initio* and DFT calculations of structures **IIIc** and **XI** [MP2(fc)/6-31+G** and B3LYP/6-31G**] and **IIId** and **XII** [MP2(fc)/LANL2DZ and B3LYP/LANL2DZ]^{a}

Comp. no.	Method	λ	E_{tot}, a.u.	ΔE, kcal/mol	ZPE, a.u.	ΔE_{ZPE}, kcal/mol	ΔH, kcal/mol	ω, cm^{-1}
IIIc	MP2	0	–7385.637455	0	0.075697	0	0	76.1
	B3LYP	0	–7391.092892	0	0.074218	0	0	89.5
XI	MP2	0	–7385.595390	26.4	0.074200	25.5	25.8	35.0
	B3LYP	1	–7391.054467	24.1	0.073206	23.5	23.8	42.4
IIId	MP2	0	–215.654339	0	0.071126	0	0	48.9
	B3LYP	0	–217.038363	0	0.072516	0	0	54.3
XII	MP2	0	–215.628370	16.3	0.069730	15.4	15.8	24.5
	B3LYP	0	–217.004585	21.2	0.071593	20.6	20.9	31.7

[a] λ is the number of negative Hessian eigenvalues for a given stationary point; E_{tot} and ΔE are the total and relative energies (1 a.u. = 627.5095 kcal/mol); *ZPE* is the zero-point energy; ΔE_{ZPE} is the relative energy corrected for zero-point energy; ΔH is the relative enthalpy; and ω_1 is the lowest or imaginary harmonic frequency.

(B3LYP) (**XII**). Therefore, a strong attractive $X\cdots X$ interaction exists in compounds **IIIc** and **IIId**.

In going from *cis-s-cis* structures **IIIc** and **IIId** to *trans-s-trans* isomers **XI** and **XII** the difference between the formally single and formally double C–C bond lengths increases by about 0.04–0.05 Å, indicating higher aromaticity of the heterapentalene structure relative to monocyclic compounds **II**. The structural parameters of molecule **IIIc**, calculated in the present work, are consistent with the experimental data obtained previously for triselenapentalene by X-ray analysis [2] (Fig. 3).

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