



Dedicated to the memory of  
Professor Candin Liteanu on his 100<sup>th</sup> anniversary

AROMATIC  $\lambda^3$ -HETEROCYCLES. 19.<sup>1</sup>  
THERMODYNAMIC STABILITY OF ALTERNANT CONJUGATED  
HETEROCYCLES  $(\lambda^3\text{-X-}\lambda^3\text{-Y})_3$  (X, Y= CH, N, P, As, Sb, Bi) CALCULATED  
BY SEMIEMPIRICAL MO, *AB INITIO* AND DFT METHODS

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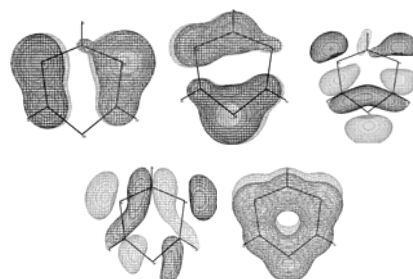
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The existence and stability of alternant conjugated heterocycles six-member rings  $(\lambda^3\text{-X-}\lambda^3\text{-Y})_3$  (X,Y = CH,N,P,As,Sb,Bi) with elements of the 15th group was investigated using two semi-empirical MO methods: PM3 and PM6, as well as the *ab initio* RHF method with LACV3P\*\*++ basis set and the DFT method with hybrid functional B3LYP/LACV3P\*\*++. 21 heterocycles were studied, of which 12 were investigated for the first time in this paper. An analysis of the standard enthalpies of formation  $\Delta_f H^0$ (kcal/mol) calculated with PM3 and PM6, standard enthalpies  $\Delta_f H^0$ (kcal/mol) and standard free enthalpies  $\Delta G^0$ (kcal/mol) calculated with the *ab initio* RHF method with the LACV3P\*\*++ basis set and the DFT/B3LYP/LACV3P\*\*++ for 21 compounds was performed. The values of thermodynamic data for the studied heterocycles suggest that the 6-member rings:  $(\lambda^3\text{-P})_6$ ,  $(\lambda^3\text{-As})_6$ ,  $(\lambda^3\text{-Sb})_6$ ,  $(\lambda^3\text{-Bi})_6$ ,  $(\text{CH})_3\text{-}(\lambda^3\text{-P})_3$ ,  $(\lambda^3\text{-N-}\lambda^3\text{-P})_3$ ,  $(\lambda^3\text{-N-}\lambda^3\text{-As})_3$ ,  $(\lambda^3\text{-P-}\lambda^3\text{-Sb})_3$ ,  $(\lambda^3\text{-P-}\lambda^3\text{-Bi})_3$ ,  $(\lambda^3\text{-As-}\lambda^3\text{-Bi})_3$ ,  $(\lambda^3\text{-Sb-}\lambda^3\text{-Bi})_3$  could be thermodynamically stable. Their bond lengths increase in the group, the angle X-Y-X decreases and the angle Y-X-Y increases with the increase of the atomic radius. All the studied compounds have positive standard enthalpy ( $\Delta_f H^0 > 0$ ) and a negative free standard enthalpy ( $\Delta G^0 < 0$ ), therefore these compounds have a high tendency to undergo chemical reactions.



## INTRODUCTION

Quantum chemistry, developed to explain the nature of the chemical bond,<sup>2</sup> has also a predictive role. Six member hetero-aromatic rings  $(\lambda^3\text{-X-}\lambda^3\text{-$

$\text{Y})_3$  (X,Y=CH,N,P,As) with elements of the 15<sup>th</sup> group were studied through various quantum chemical methods and their existence was proven through chemical synthesis with various physicochemical methods or chemical traps:

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$C_3H_3N_3$ ,<sup>3</sup>  $C_3H_3P_3$ ,<sup>4</sup>  $N_3P_3$ ,<sup>5</sup>  $N_6$ ,<sup>6</sup>  $P_6$ ,<sup>7</sup>  $As_6$ .<sup>8</sup> The majority of alternant heterocycles  $(\lambda^3-X-\lambda^3-Y)_3$  ( $X, Y, = CH, N, P, As, Sb, Bi$ ) with a potential aromatic character were not studied until now. More than 15 years ago we published a comparative study of the geometries of  $C_3H_3X_3$ , ( $X = CH, N, P, As, Sb, Bi$ ) calculated with quantum chemical methods.<sup>9</sup>

In this paper we report the results of the computed thermodynamic stability of 21 compounds  $(\lambda^3-X-\lambda^3-Y)_3$  ( $X, Y, = CH, N, P, As, Sb, Bi$ ) analyzing their computed formation enthalpies  $\Delta_f H^0$  (kcal/mol) in standard conditions ( $T=298,15$ ,  $p = 1$  atm). Like other authors who have used the standard enthalpy of formation for comparing the stability of some chemical compounds,<sup>10</sup> we use here the standard enthalpy of formation  $\Delta_f H^0$  considering this is the best measure to compare the thermodynamic stability of chemical structures. In previous works we demonstrated the aromatic character.<sup>1b-1e</sup> All the semiempirical MO methods MINDO/3, MNDO, AM1, PM3 developed by M. J. S. Dewar and his collaborators,<sup>10e,11,12</sup> and PM6 method available in different software packages, developed by J. J. P. Stewart,<sup>13,14</sup> have an optimal parametrization based on experimental standard formation enthalpies  $\Delta_f H^0$ . In this paper we report the calculated standard enthalpies  $\Delta_f H^0$  (kcal/mol), which reflect the total energetic content of compounds, as well as the standard free enthalpies  $\Delta G^0$  (kcal/mol), which reflect the chemical reactivity of compounds. These data are computed with *ab initio* RHF/LACV3P\*\*++ and DFT/B3LYP/LACV3P\*\*++ methods.<sup>15-20</sup> We also report some geometric data: bond lengths ( $d_{X-Y}$ ) and valence angles ( $\angle Y-X-Y, \angle X-Y-X$ ) computed for the new hypothetical heterocycles in comparison to the similar data of known heterocycles.

## COMPUTATIONAL METHODS

Calculations of structural parameters and thermodynamic properties were carried out using two semiempirical MO methods: PM3 from the HyperChem7.52,<sup>11e-11g,12,13a,13b</sup> software and PM3 and PM6 from the MOPAC2009 9.069W software.<sup>13c,14</sup> For the semiempirical as well as for the *ab initio* methods (implemented in Jaguar program),<sup>15</sup> we used LCAO-MO-SCF restricted Hartree-Fock (RHF).<sup>16</sup> Density functional theory (DFT),<sup>17</sup> with the three-parameter hybrid functional (B3),<sup>18</sup> for the exchange part and the Lee, Yang, and Parr (LYP) correlation function,<sup>19</sup> using the

LACV3P++\*\* basis sets were also used.<sup>20</sup> The energy minima with respect to the nuclear coordinates were obtained by the simultaneous relaxation of all the geometric parameters and the optimized geometries were minimized without any constraint in potential energy surface (PES), at RHF and DFT levels. The optimized structural parameters were used in vibrational frequency calculations at RHF and DFT levels.

For the PM3 method in the HyperChem7.52 package we used an SCF convergence of  $10^{-5}$ , and the Polak-Ribiere optimization algorithm with a RMS gradient of  $10^{-2}$  kcal/molÅ. Starting geometries have been optimized with the MM+ force field implemented in the HyperChem7.52 software.<sup>12</sup> To optimize the geometries and to calculate the  $\Delta_f H^0$  using the PM3 and PM6 methods from the MOPAC2009 program we used SCFCRT = 1.D-10, PRECISE, GNORM=0.01, FORCE, THERMO, GEO-OK keywords.<sup>14</sup> The starting geometries were those optimized with PM3/HyperChem7.52. For the *ab initio* RHF/LACV3P\*\*++ and DFT/B3LYP/LACV3P\*\*++ calculations of  $\Delta H^0$  and  $\Delta G^0$ , the following criteria were used: the SCF convergence of  $10^{-8}$ , maximal number of SCF iterations 100, maximal optimization steps 100,<sup>15</sup> and the starting geometries were those optimized with the PM3/HyperChem7.52 method.

## RESULTS AND DISCUSSION

Results of the calculations using the PM3 (HyperChem7.52 and MOPAC2009) and PM6 (MOPAC2009) methods are shown in Table 1. For comparison reasons we also performed the same calculations for similar heterocycles containing C atoms  $(CH)_3-(\lambda^3-Y)_3$  ( $Y, = CH, N, P, As, Sb, Bi$ ).<sup>9</sup> By using the same semiempirical Hamiltonian and parametrization in two different softwares, one can suppose that the results should be indifferent to the programming method. However, data in Table 1 show some small, but acceptable, differences between the results obtained with the PM3/HyperChem7.52 method and those obtained with the PM3/MOPAC2009 method.

The PM3/HyperChem7.52 method gives for  $N_6$  and  $Sb_6$  plausible geometries with equal bond lengths and valence angles of  $120^\circ$ . However, these  $N_6$  and  $Sb_6$  molecules have a negative fundamental normal vibration ( $\nu_{IBIU}(N_6) = -587.08$   $cm^{-1}$ ;  $\nu_{IBIU}(Sb_6) = -24.55$   $cm^{-1}$ ), which suggests that the calculated structure is not a stationary state. Using

the PM3/HyperChem7.52 method for optimizing the  $\text{As}_3\text{Sb}_3$  geometry we observed that during the first steps, the structure was not SCF convergent. It became SCF convergent only after 10 points of optimization. Setting the SCF convergence to  $10^{-8}$  and the RMS gradient to  $10^{-4}$ , the fundamental vibration remains negative and not significantly different from those with an SCF convergence of

$10^{-5}$  and a RMS gradient of  $10^{-2}$ . The optimized  $\text{As}_3\text{Sb}_3$  geometry is plausible and corresponds to the theoretical point group,  $D_{3h}$ . Although the geometry seems plausible, the lowest three vibrations are negative ( $\nu_0(\text{As}_3\text{Bi}_3) = -761.67 \text{ cm}^{-1}$ ;  $\nu_1(\text{As}_3\text{Bi}_3) = -517.78 \text{ cm}^{-1}$ ;  $\nu_2(\text{As}_3\text{Bi}_3) = -43.95 \text{ cm}^{-1}$ ) and an assignment of the irreducible representations cannot be done.

Table 1

Standard formation enthalpies ( $\Delta_f H^0$ ) and bond lengths ( $d_{X-Y}$ ) calculated with PM3(HyperChem), PM3(MOPAC) and PM6(MOPAC) for heterocycles  $(\lambda^3 X)_3-(\lambda^3 Y)_3$  (X, Y = CH, N, P, As, Sb, Bi)

Heteroatom X	Y		CH	N	P	As	Sb	Bi
	method	kcal/mol						
CH	PM3(HyChm)	$\Delta_f H^0$	23.292	46.093	76.064	140.815	196.205	241.035
		$d_{X-Y}$	1.3911	1.3577	1.6790	1.8252	2.0348	2.1007
	PM3(MOPAC)	$\Delta_f H^0$	23.387	46.130	76.134	140.832	196.276	241.117
		$d_{X-Y}$	1.3911	1.3577	1.6790	1.8252	2.0348	2.1008
	PM6(MOPAC)	$\Delta_f H^0$	24.191	59.080	76.526	128.161	92.142	232.294
		$d_{X-Y}$	1.3986	1.3676	1.7553	1.7834	1.9799	2.1322
Symmetry			$D_{6h}$	$D_{3h}$	$D_{3h}$	$D_{3h}$	$D_{3h}$	$D_{3h}$
N	PM3(HyChm)	$\Delta_f H^0$		186.705 <sup>a</sup>	-17.702	71.080	139.626	236.789
		$d_{X-Y}$		1.3000	1.6658	1.7717	1.9437	2.0233
	PM3(MOPAC)	$\Delta_f H^0$		52.654	-17.685	71.050	139.651	236.818
		$d_{X-Y}$		b	1.6658	1.7717	1.9436	2.0233
	PM6(MOPAC)	$\Delta_f H^0$		175.959	38.775	126.536	286.996	10.097
		$d_{X-Y}$		c	1.6818	c	b	b
Symmetry			$D_{6h}$	$D_{3h}$	$D_{3h}$	$D_{3h}$	$D_{3h}$	$D_{3h}$
P	PM3(HyChm)	$\Delta_f H^0$		10.589	35.624	95.030	-25.499	
		$d_{X-Y}$		2.0012	2.1010	2.2550	2.1272	
	PM3(MOPAC)	$\Delta_f H^0$		10.625	35.619	95.079	-25.440	
		$d_{X-Y}$		2.0012	2.1010	2.2550	b	
	PM6(MOPAC)	$\Delta_f H^0$		33.697	264.347	-19.090	-369.292	
		$d_{X-Y}$		2.0937	2.4323	2.4827	2.3977	
Symmetry			$D_{6h}$	$D_{3h}$	$D_{3h}$	$D_{3h}$	$D_{3h}$	
As	PM3(HyChm)	$\Delta_f H^0$		65.634	94.122 <sup>d</sup>	-4.759		
		$d_{X-Y}$		2.2144	2.4030	2.7072		
	PM3(MOPAC)	$\Delta_f H^0$		62.190	94.127	-4.743		
		$d_{X-Y}$		2.2314	2.4030	b		
	PM6(MOPAC)	$\Delta_f H^0$		58.104	174.257	-255.453		
		$d_{X-Y}$		2.2201	2.7104	2.4858		
Symmetry			$D_{6h}$	$D_{3h}$	$D_{3h}$	$D_{3h}$		
Sb	PM3(HyChm)	$\Delta_f H^0$		105.392 <sup>a</sup>	-0.919			
		$d_{X-Y}$		2.5424	2.7072			
	PM3(MOPAC)	$\Delta_f H^0$		104.515	-0.841			
		$d_{X-Y}$		2.5571	2.7071			
	PM6(MOPAC)	$\Delta_f H^0$		78.401	-495.056			
		$d_{X-Y}$		2.7353	2.5243			
Symmetry			$D_{6h}$	$D_{3h}$	$D_{3h}$	$D_{3h}$		
Bi	PM3(HyChm)	$\Delta_f H^0$		8.856				
		$d_{X-Y}$		2.8428				
	PM3(MOPAC)	$\Delta_f H^0$		-6.404				
		$d_{X-Y}$		2.8913				
	PM6(MOPAC)	$\Delta_f H^0$		98.971				
		$d_{X-Y}$		c				
Symmetry			$D_{6h}$	$D_{6h}$				

a) non-stationary states – negative vibrations, unreliable thermodynamic data; b) deformed planar structure – no chemical meaning; c) deformed planar structure; d) not SCF convergent, not stationary states – negative vibrations, unreliable thermodynamic data.

The existence of some negative (imaginary) vibrations suggests that for the above three molecules the thermodynamic values, calculated with PM3/HypeChem7.52, could not be reliable. Except these three molecules, for the 18 remaining molecules the optimized geometries using the PM3/HypeChem7.52 method are plausible, having equal bond lengths and positive fundamental vibration. Therefore, their calculated geometries should correspond to stationary states. For the N<sub>6</sub> molecule PM3/MOPAC2009 leads to a deformed geometry, where at every two atoms the bonds are broken, and instead of a six-member homocycle, three N≡N bonds are formed. Although P<sub>3</sub>Bi<sub>3</sub> and As<sub>3</sub>Bi<sub>3</sub> have only positive vibrations their rings were deformed, and inside the rings three more Bi-Bi bonds were formed. The PM3/MOPAC2009 method generated also two deformed structures: P<sub>3</sub>Bi<sub>3</sub> and As<sub>3</sub>Bi<sub>3</sub>.

Excepting these three structures, the remaining molecules optimized with the PM3/MOPAC2009 method had plausible geometries with equal bonds and they belong to D<sub>3h</sub> point group, being identical with those given by PM3/HyperChem7.52. All the vibrations for the 18 correctly optimized rings were positive and consequently the optimized geometries should correspond to certain stationary states.

For the optimized molecules having all positive vibrations, one can observe some differences between the values of the Δ<sub>f</sub>H<sup>0</sup> calculated by using the PM3/HyperChem7.52, and PM3/MOPAC2009 respectively. We suppose these differences could be generated by the optimization algorithms used. In the PM3/HyperChem7.52 method the conjugated gradient Polak-Ribiere algorithm was used, while in PM3/MOPAC2009 the quasi-Newton Fletcher-Powell method was used.

The PM6/MOPAC2009 hamiltonian gives five deformed rings: N<sub>6</sub>, N<sub>3</sub>As<sub>3</sub>, Bi<sub>6</sub>, N<sub>3</sub>Sb<sub>3</sub> and N<sub>3</sub>Bi<sub>3</sub>, the last two with no-chemical significance. For N<sub>3</sub>Bi<sub>3</sub> a N-Bi bond is broken and a linear structure is formed. For N<sub>6</sub>, N<sub>3</sub>As<sub>3</sub> and Bi<sub>6</sub> the optimized geometries are planar but the bond lengths are alternated: d<sub>N-N</sub> = 1.2527Å, and 1.4098Å, d<sub>N-As</sub> = 1.5504Å, and 1.7768Å, d<sub>N-Bi</sub> = 2.8447Å, and 3.2315Å, respectively. These three molecules (N<sub>6</sub>, N<sub>3</sub>As<sub>3</sub> and Bi<sub>6</sub>) have at least one negative normal vibration and therefore the Δ<sub>f</sub>H<sup>0</sup> value is not reliable. All the other molecules optimized with the PM6/MOPAC2009 method have plausible geometries and all normal vibrations are positive. For these molecules we suppose that the calculated Δ<sub>f</sub>H<sup>0</sup> values might potentially be close to the

experimental values within the minimum limit of 8.0 kcal/mol (average unsigned error = AUE).<sup>13</sup>

To compare the calculated geometrical parameters and thermodynamic data we used the following available experimental data for benzene (gas phase): d<sub>C-C</sub> = 1.397Å, <C-C-C = 120°,<sup>21</sup> Δ<sub>f</sub>H<sup>0</sup> = 19.82±0.12 kcal/mol,<sup>22</sup> for *s*-triazine (gas phase): d<sub>C-N</sub> = 1.338Å, <C-N-C = 113.2°, <N-C-N = 126.8°,<sup>21</sup> Δ<sub>f</sub>H<sup>0</sup> = 53.98±0.21 kcal/mol,<sup>23</sup> and for 1,3,5-triphosphinine: d<sub>C-P</sub> = 1.724Å, <C-P-C = 109.3°, <P-C-P = 130.7°.<sup>4</sup>

Comparing the calculated geometrical data with the experimental data for C<sub>6</sub>H<sub>6</sub> (Table 1) one can see that, the calculated values for benzene (PM3/d<sub>C-C</sub> = 1.3911Å, <C-C-C = 120.00°; PM6/d<sub>C-C</sub> = 1.3986Å; <C-C-C = 120.00°) are close to the experimental ones. The PM3 method underestimates the bond lengths with 0.42%, and PM6 overestimates it with 0.11%, errors which are not significant. For *s*-triazine, the PM6 method overestimates the bond lengths with 2.21%, the angle <C-N-C is overestimated with 2.5% and the <N-C-N angle is underestimated with 2.24%. One can consider that the bond lengths calculated by the PM3/HyperChem7.52 method are almost identical with those calculated by the PM3/MOPAC2009 method (Table 1). Obviously, this is an expected result, because the semiempirical MO methods were developed especially for the optimization of geometries and Δ<sub>f</sub>H<sup>0</sup>. For all the molecules the bond lengths calculated with the PM3 method are smaller than those calculated with PM6, except for two geometries: As<sub>3</sub>Bi<sub>3</sub> and Sb<sub>3</sub>Bi<sub>3</sub> (Table 1). If the X heteroatom is constant and the Y heteroatom is variable (Table 1) one can observe that the bond lengths increase in the group for both PM3 and PM6 methods. There are some exceptions: P<sub>3</sub>Bi<sub>3</sub>, in the PM3 calculations and P<sub>3</sub>Bi<sub>3</sub> As<sub>3</sub>Bi<sub>3</sub> in the PM6 calculations. For them, the bond lengths are shorter than those of the precedent molecule P<sub>3</sub>Sb<sub>3</sub>, As<sub>3</sub>Sb<sub>3</sub>. If the Y heteroatom is constant and the X heteroatom is variable (Table 1) one can observe that the bond lengths increase in row, again both in the PM3 and PM6 methods.

The calculated Δ<sub>f</sub>H<sup>0</sup> of benzene is higher than the experimental one with 17.5% in the PM3 method and with 22.0% higher in the PM6 method. For *s*-triazine the calculated Δ<sub>f</sub>H<sup>0</sup> is 14.6% lower in the PM3 method and 9.4% higher in PM6 method (Table 1). Although the differences seem rather large, they are in the AUE limits of the method.<sup>13</sup> For seven structures (C<sub>6</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>, C<sub>3</sub>H<sub>3</sub>P<sub>3</sub>, N<sub>3</sub>P<sub>3</sub>, P<sub>6</sub>, P<sub>3</sub>As<sub>3</sub>, As<sub>3</sub>Sb<sub>3</sub>) with positive normal vibrations,

the  $\Delta_f H^\circ$  values given by the PM6/MOPAC2009 method are higher than those obtained with PM3/MOPAC2009. Nine structures ( $C_3H_3As_3$ ,  $C_3H_3Sb_3$ ,  $C_3H_3Bi_3$ ,  $P_3Sb_3$ ,  $P_3Bi_3$ ,  $As_6$ ,  $As_3Bi_3$ ,  $Sb_6$ ,  $Sb_3Bi_3$ ) with all normal vibrations positive have the  $\Delta_f H^\circ$ , calculated with PM6/MOPAC2009 method, lower than those obtained with the PM3/MOPAC2009 method (Table 1).

If the X heteroatom is constant and the Y heteroatom variable (Table 1) one can observe that  $\Delta_f H^\circ$  in the group, meaning that the ring stability decreases in group, for both methods PM3 and PM6, respectively. There are some exceptions:  $C_3H_3Sb_3$ ,  $P_3Bi_3$ ,  $As_3Bi_3$ ,  $Sb_3Bi_3$  for which the  $\Delta_f H^\circ$  values decrease in PM3 method, meaning that the ring stability increase compared to that of the previous ring. PM6 gives some exceptions:  $C_3H_3Sb_3$ ,  $P_3Sb_3$ ,  $P_3Bi_3$ ,  $As_3Bi_3$ ,  $Sb_3Bi_3$  for which the  $\Delta_f H^\circ$  values decrease in the group, and the ring stability increases compared to that of the previous ring (Table 1).

If the Y heteroatom is constant and the X heteroatom is variable (Table 1), one can observe that the  $\Delta_f H^\circ$  values decrease both in the PM3 and PM6 methods.  $P_3Sb_3$ ,  $As_3Sb_3$ ,  $Sb_3Bi_3$  are exceptions for which the PM3 calculations give increasing  $\Delta_f H^\circ$  values. In PM6 calculations the exceptions are  $P_3As_3$ ,  $As_3Sb_3$ , for which  $\Delta_f H^\circ$  values increase.

Based on the PM3 and PM6 estimations of  $\Delta_f H^\circ$  for all 21 heterocycles ( $(\lambda^3-X)_3-(\lambda^3-Y)_3$  (X, Y, = CH, N, P, As, Sb, Bi), on  $\Delta_f H^\circ$  variation in group and row, and on comparison of the data with those for benzene and *s*-triazine  $\Delta_f H^\circ$ , one can conclude that homoatomic 6-member rings, potentially aromatic ( $(\lambda^3-P)_6$ , ( $\lambda^3-As)_6$ , ( $\lambda^3-Sb)_6$ , ( $\lambda^3-Bi)_6$ , as well as the heteroatomic ones ( $(CH)_3-(\lambda^3-P)_3$ , ( $\lambda^3-N)_3-(\lambda^3-P)_3$ , ( $\lambda^3-N)_3-(\lambda^3-As)_3$ , ( $\lambda^3-P)_3-(\lambda^3-Sb)_3$ , ( $\lambda^3-P)_3-(\lambda^3-Bi)_3$ , ( $\lambda^3-As)_3-(\lambda^3-Bi)_3$ , ( $\lambda^3-Sb)_3-(\lambda^3-Bi)_3$ , have a comparable stability with that of benzene or *s*-triazine or even better. These results suggest that in normal conditions the 6-member rings: ( $\lambda^3-P)_6$ , ( $\lambda^3-As)_6$ , ( $\lambda^3-Sb)_6$ , ( $\lambda^3-Bi)_6$ , ( $CH-\lambda^3-P)_3$ , ( $\lambda^3-N)_3-(\lambda^3-P)_3$ , ( $\lambda^3-N)_3-(\lambda^3-As)_3$ , ( $\lambda^3-P)_3-(\lambda^3-Sb)_3$ , ( $\lambda^3-P)_3-(\lambda^3-Bi)_3$ , ( $\lambda^3-As)_3-(\lambda^3-Bi)_3$ , ( $\lambda^3-Sb)_3-(\lambda^3-Bi)_3$  are thermodynamically stable. For the *ab initio* calculations RHF or DFT, we chose the LACV3P\*\*++ basis set because it has all the elements of the 15<sup>th</sup> group.<sup>15</sup>

The results, *i.e.* geometric data (bond lengths and angles), standard enthalpies and free standard enthalpies (T=298,15, p = 1 atm), for all 21 rings ( $(\lambda^3-X)_3-(\lambda^3-Y)_3$  (X, Y = CH, N, P, As, Sb, Bi), are shown in Table 2 and 3.

The RHF optimizations using the LACV3P\*\*++ basis set give all normal vibrations positive for each of the 21 rings, which means the geometries are in stationary states and the thermodynamic calculated values should be reliable. By comparison, the DFT calculations using the hybrid functional B3LYP and the LACV3P\*\*++ basis set give for the  $N_6$ ,  $P_6$ ,  $As_6$ ,  $Sb_6$ ,  $As_3Sb_3$  rings geometries in non-stationary states having one or two negative normal vibrations. Therefore, the calculated thermodynamic data for these structures are not reliable. All the optimized geometries resulted from RHF/LACV3P\*\*++ and DFT/B3LYP/LACV3P\*\*++ are planar, corresponding to their theoretical point group, and in each molecule bond lengths of the same type are equal. For benzene the RHF/LACV3P\*\*++ calculations give a value of the bond length with 0.79% lower than the experimental one, for *s*-triazine a value with 1.57% lower and for 1,3,5-triphosphinine a value with 0.42% lower. The DFT/B3LYP/LACV3P\*\*++ calculations give for benzene a calculated bond length with 0.17% lower, for *s*-triazine with 0.27% lower, and 1,3,5-triphosphinine a value with 0.69% higher than the experimental values.

In the case of the *s*-triazine the calculated angles are: HF/LACV3P\*\*++  $\langle C-N-C \rangle = 114.45^\circ$ ,  $\langle N-C-N \rangle = 125.55^\circ$ , respectively DFT/B3LYP/LACV3P\*\*++  $\langle C-N-C \rangle = 114.25^\circ$ ,  $\langle N-C-N \rangle = 125.75^\circ$  compared to the experimental values which are:  $\langle C-N-C \rangle = 113.2^\circ$ ,  $\langle N-C-N \rangle = 126.8^\circ$ . HF/LACV3P\*\*++ overestimates the angle  $\langle C-N-C \rangle$  with 1.10%, while the angle  $\langle N-C-N \rangle$  is underestimated with 0.99%. DFT/B3LYP/LACV3P\*\*++ overestimates the angle  $\langle C-N-C \rangle$  with 0.93%, while the angle  $\langle N-C-N \rangle$  is underestimated with 0.83%.

In the case of the 1,3,5-triphosphinine the calculated angles are: HF/LACV3P\*\*++  $\langle C-P-C \rangle = 106.39^\circ$ ,  $\langle P-C-P \rangle = 133.61^\circ$ , respectively the DFT/B3LYP/LACV3P\*\*++  $\langle C-P-C \rangle = 105.52^\circ$ ,  $\langle P-C-P \rangle = 134.48^\circ$  compared to the experimental values which are:  $\langle C-P-C \rangle = 109.3^\circ$ ,  $\langle P-C-P \rangle = 130.7^\circ$ . HF/LACV3P\*\*++ underestimates the angle  $\langle C-P-C \rangle$  with 2.66%, while the angle  $\langle P-C-P \rangle$  is overestimated with 2.23%. DFT/B3LYP/LACV3P\*\*++ underestimates the angle  $\langle C-P-C \rangle$  with 3.46%, while the angle  $\langle P-C-P \rangle$  is overestimated with 2.89%. For these molecules there are small differences between the calculated and experimental values, proving that the chosen basis set (LACV3P\*\*++), in DFT calculation with B3LYP functional allows a good estimation of the geometry.

Table 2

Bond lengths and valence angles, calculated at RHF/LACV3P\*\*++ and DFT/B3LYP/LACV3P\*\*++ levels for the heterocycles  $(\lambda^3X)_3-(\lambda^3-Y)_3$  (X, Y = CH, N, P, As, Sb, Bi)

Heteroatom X	Y		CH	N	P	As	Sb	Bi	
	method	$d(\text{\AA})$ $\angle(^{\circ})$							
CH	LACV3P	$d_{X-Y}$	1.3860	1.3170	1.7167	1.8344	2.0192	2.0870	
		$\angle X-Y-X$	120.00	114.45	106.39	104.87	103.79	102.95	
		$\angle Y-X-Y$	120.00	125.55	133.61	135.13	136.21	137.05	
	B3LYP	$d_{X-Y}$	1.3946	1.3344	1.7359	1.8629	2.0486	2.1167	
		$\angle X-Y-X$	120.00	114.25	105.52	104.18	103.08	102.52	
		$\angle Y-X-Y$	120.00	125.75	134.48	135.82	136.92	137.42	
Symmetry			$D_{6h}$	$D_{3h}$	$D_{3h}$	$D_{3h}$	$D_{3h}$	$D_{3h}$	
N	LACV3P	$d_{X-Y}$		1.2835	1.6039	1.7412	1.9129	1.9887	
		$\angle X-Y-X$		120.00	109.11	107.28	105.16	105.79	
		$\angle Y-X-Y$		120.00	130.89	132.73	134.84	134.21	
	B3LYP	$d_{X-Y}$		1.3193*	1.6398	1.7934	1.9672	2.0473	
		$\angle X-Y-X$		120.00*	109.70	109.09	107.64	109.20	
		$\angle Y-X-Y$		120.00*	130.30	130.91	132.36	130.80	
Symmetry			$D_{6h}$	$D_{3h}$	$D_{3h}$	$D_{3h}$	$D_{3h}$		
P	LACV3P	$d_{X-Y}$			2.0950	2.2217	2.4088	2.4692	
		$\angle X-Y-X$			120.00	119.84	118.57	117.29	
		$\angle Y-X-Y$			120.00	120.18	121.43	122.72	
	B3LYP	$d_{X-Y}$			2.1334*	2.2740	2.4600	2.5165	
		$\angle X-Y-X$			120.00*	119.79	118.68	118.32	
		$\angle Y-X-Y$			120.00*	120.21	121.32	121.68	
Symmetry				$D_{6h}$	$D_{3h}$	$D_{3h}$	$D_{3h}$		
As	LACV3P	$d_{X-Y}$				2.3749	2.5549	2.6029	
		$\angle X-Y-X$				120.00	118.22	117.43	
		$\angle Y-X-Y$				120.00	121.78	122.57	
	B3LYP	$d_{X-Y}$				2.4298*	2.6085*	2.6528	
		$\angle X-Y-X$				120.00*	119.30*	119.11	
		$\angle Y-X-Y$				120.00*	120.70*	120.89	
Symmetry					$D_{6h}$	$D_{3h}$	$D_{3h}$		
Sb	LACV3P	$d_{X-Y}$					2.7424	2.7891	
		$\angle X-Y-X$					120.00	118.57	
		$\angle Y-X-Y$					120.00	121.43	
	B3LYP	$d_{X-Y}$					2.7933*	2.8342	
		$\angle X-Y-X$					120.00*	119.54	
		$\angle Y-X-Y$					120.00*	120.46	
Symmetry						$D_{6h}$	$D_{3h}$		
Bi	LACV3P	$d_{X-Y}$						2.8348	
		$\angle X-Y-X$						120.00	
		$\angle Y-X-Y$						120.00	
	B3LYP	$d_{X-Y}$							2.8748
		$\angle X-Y-X$							120.00
		$\angle Y-X-Y$							120.00
Symmetry								$D_{6h}$	

\* Non stationary states – negative vibrations.

If the X heteroatom is constant and Y heteroatom is variable (Table 2), one can observe that the bond length increases in the group, both at HF/LACV3P\*\*++ and DFT/B3LYP/LACV3P\*\*++ level. The valence angles predicted by the HF/LACV3P\*\*++ as well as by the DFT/B3LYP/LACV3P\*\*++ calculations are of 120°, for all the homorings  $X_6$  (X=CH, N, P, As, Sb, Bi). The  $\angle X-Y-X$  angle calculated with HF/LACV3P\*\*++ as well as with DFT/

B3LYP/LACV3P\*\*++ decreases in the group, while the  $\angle Y-X-Y$  angle increases (Table 2).

If the Y heteroatom is constant and the X heteroatom is variable, one can observe in Table 2 that the values of the X-Y bond length increase in period both for the HF/LACV3P\*\*++ and DFT/B3LYP/LACV3P\*\*++ methods.

If the X heteroatom is constant and Y heteroatom is variable (Table 2), one can observe that the bond length increases in the group, both at

HF/LACV3P\*\*++ and DFT/B3LYP/LACV3P\*\*++ level. The valence angles predicted by the HF/LACV3P\*\*++ as well as by the DFT/B3LYP/LACV3P\*\*++ calculations are of  $120^\circ$ , for all the homorings  $X_6$  ( $X=CH,N,P,As,Sb,Bi$ ). The  $\langle X-Y-X$  angle calculated with HF/LACV3P\*\*++ as well as with DFT/B3LYP/LACV3P\*\*++ decreases in the group, while the  $\langle Y-X-Y$  angle increases (Table 2).

If the Y heteroatom is constant and the X heteroatom is variable, one can observe in Table 2 that the values of the X-Y bond length increase in period both for the HF/LACV3P\*\*++ and DFT/B3LYP/LACV3P\*\*++ methods. As one can see from Table 2, geometry optimized at DFT/B3LYP/LACV3P\*\*++ level for  $N_6$ ,  $P_6$ ,  $As_6$ ,  $Sb_6$ ,  $As_3Sb_3$  rings are in non-stationary states, and therefore their standard thermodynamic values are not reliable.

Regarding the thermodynamic data, when the X heteroatom is constant and the Y heteroatom is

variable, the standard  $\Delta H^0$  values increase in the group, both for the HF/LACV3P\*\*++ and DFT/B3LYP/LACV3P\*\*++ calculations (Table 3).

When the Y heteroatom is constant and the X is variable the  $\Delta H^0$  increases in row both for the HF/LACV3P\*\*++ and DFT/B3LYP/LACV3P\*\*++ calculations (Table 3).

For all compounds, including those in non-stationary states,  $\Delta H^0 > 0$ . Thus, they have the ability to accumulate energy and could undergo endothermic reactions.

If the X heteroatom is constant and the Y heteroatom is variable the  $\Delta G^0$  values decrease in the group, both for the HF/LACV3P\*\*++ and DFT/B3LYP/LACV3P\*\*++ calculations (Table 3). If the Y heteroatom is constant and the X heteroatom is variable, including the non-stationary states, (Table 3) the  $\Delta G^0$  values decrease in row both for HF/LACV3P\*\*++ and DFT/B3LYP/LACV3P\*\*++ calculations.

Table 3

Standard enthalpies ( $\Delta H^0$ ) and standard free enthalpies ( $\Delta G^0$ ) calculated at RHF/LACV3P\*\*++ and DFT/B3LYP/LACV3P\*\*++ level for heterocycles  $(\lambda^3-X)_3-(\lambda^3-Y)_3$  ( $X,Y = CH,N,P,As,Sb,Bi$ )

Heteroatom X	Y		CH	N	P	As	Sb	Bi
	method	kcal/mol						
CH	LACV3P	$\Delta H^0$	3.181	3.014	4.068	4.703	5.251	5.598
		$\Delta G^0$	-15.679	-15.975	-17.945	-19.877	-21.463	-23.639
CH	B3LYP	$\Delta H^0$	3.348	3.180	4.290	4.698	5.517	5.850
		$\Delta G^0$	-15.761	-16.089	-18.155	-20.179	-21.809	-23.992
N	LACV3P	$\Delta H^0$		3.518	3.905	4.542	5.010	5.375
		$\Delta G^0$		-16.374	-18.944	-20.803	-22.283	-23.839
N	B3LYP	$\Delta H^0$		2.605*	4.329	5.052	5.440	5.757
		$\Delta G^0$		-15.380*	-19.722	-21.731	-23.054	-24.651
P	LACV3P	$\Delta H^0$			5.586	6.151	6.543	6.791
		$\Delta G^0$			-21.099	-24.076	-25.763	-27.248
P	B3LYP	$\Delta H^0$			4.625*	6.414	6.714	6.881
		$\Delta G^0$			-18.939*	-24.021	-25.482	-26.966
As	LACV3P	$\Delta H^0$				6.981	7.319	7.531
		$\Delta G^0$				-25.010	-26.787	-29.166
As	B3LYP	$\Delta H^0$				6.035*	6.350*	7.675
		$\Delta G^0$				-22.779*	-24.542*	-30.215
Sb	LACV3P	$\Delta H^0$					7.706	7.914
		$\Delta G^0$					-28.261	-31.032
Sb	B3LYP	$\Delta H^0$					6.679*	6.856
		$\Delta G^0$					-25.548*	-28.228
Bi	LACV3P	$\Delta H^0$						8.132
		$\Delta G^0$						-30.953
Bi	B3LYP	$\Delta H^0$						8.203
		$\Delta G^0$						-31.455

\* Non stationary states – negative vibrations.

Table 4

Ten highest occupied molecular orbitals and their symmetry for benzene, s-triazine, 1,3,5-triphosphinine, 1,3,5-triarsinine, 1,3,5-tristibine, 1,3,5-tribismuthine, calculated with the PM3 semiempirical MO method<sup>9</sup>

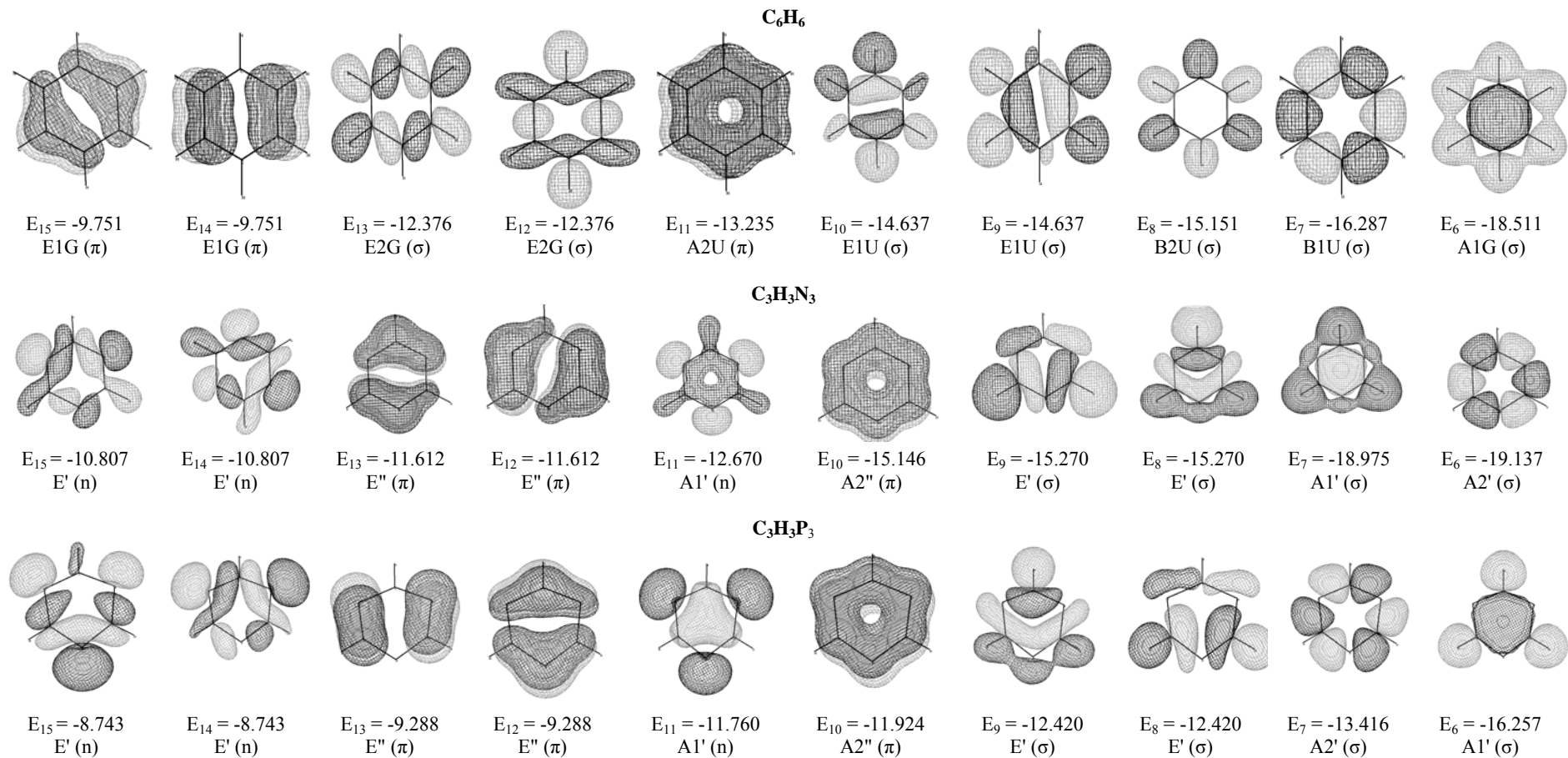
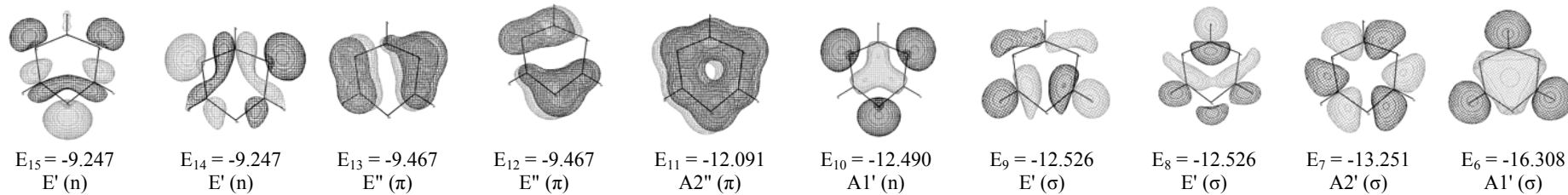


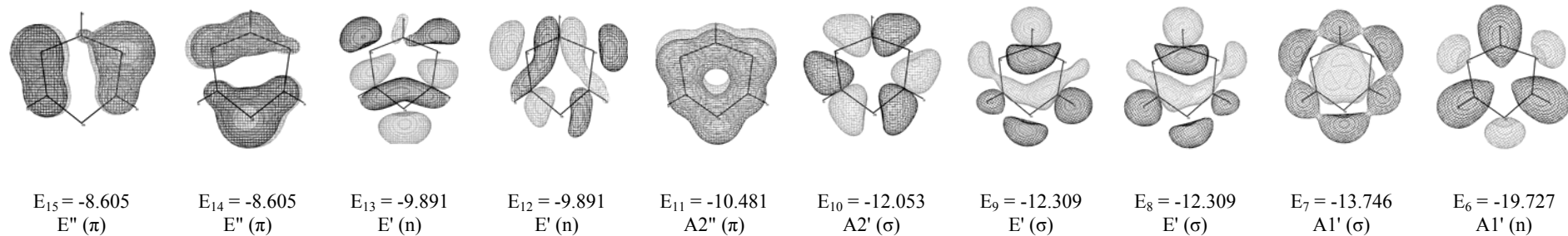


Table 4 (continued)

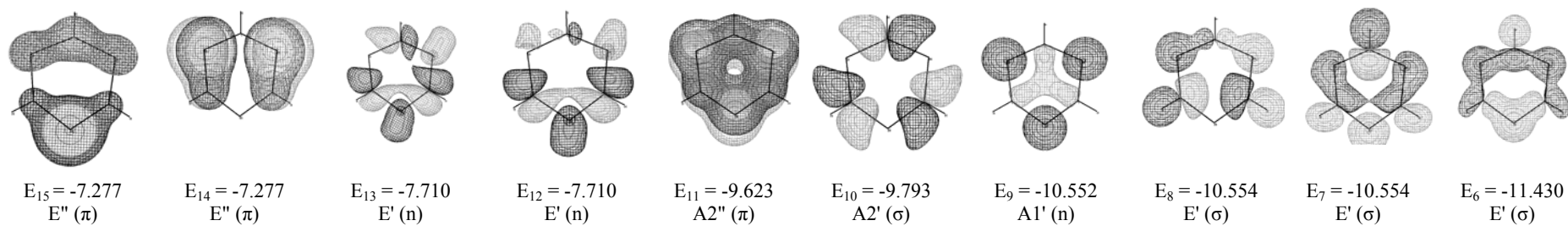
**C<sub>3</sub>H<sub>3</sub>As<sub>3</sub>**



**C<sub>3</sub>H<sub>3</sub>Sb<sub>3</sub>**



**C<sub>3</sub>H<sub>3</sub>Bi<sub>3</sub>**



A chemical system has a lower reaction potential as its chemical affinity,  $A$  is more negative ( $A < 0$ ), consequently its free enthalpy is increasingly positive  $\Delta G^0 > 0$ . The systems for which  $\Delta G^0 < 0$  have a high reaction potential. As the 21 molecules studied here have  $\Delta H^0 > 0$  and  $\Delta G^0 < 0$ , they ( $\lambda^3$ -X)<sub>3</sub>-( $\lambda^3$ -Y)<sub>3</sub> (X, Y = CH, N, P, As, Sb, Bi) have a strong tendency to undergo chemical reactions.

To evidence the potential aromatic character of C<sub>6</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>, C<sub>3</sub>H<sub>3</sub>P<sub>3</sub>, C<sub>3</sub>H<sub>3</sub>As<sub>3</sub>, C<sub>3</sub>H<sub>3</sub>Sb<sub>3</sub>, and C<sub>3</sub>H<sub>3</sub>Bi<sub>3</sub> their molecular orbitals were plotted. The first nine occupied molecular orbitals and symmetry assignments are presented comparatively in Fig. 4.<sup>9</sup> One can see that each heterocycle has (4+2) $\pi$  electrons suggesting they have aromatic character.

## CONCLUSIONS

It was shown through semiempirical MO methods (PM3, PM6) and ab initio at HF/LACV3P\*\*++ and DFT/B3LYP/LACV3P\*\*++ levels, that other unknown planar 6-membered rings ( $\lambda^3$ -X)<sub>3</sub>-( $\lambda^3$ -Y)<sub>3</sub> (X, Y = CH, N, P, As, Sb, Bi) with elements of the 15<sup>th</sup> group could exist. Some of those have a thermodynamic stability similar to that of benzene or s-triazine.

The results suggest that the 6-member rings ( $\lambda^3$ -P)<sub>6</sub>, ( $\lambda^3$ -As)<sub>6</sub>, ( $\lambda^3$ -Sb)<sub>6</sub>, ( $\lambda^3$ -Bi)<sub>6</sub>, (CH)<sub>3</sub>-( $\lambda^3$ -P)<sub>3</sub>, ( $\lambda^3$ -N)<sub>3</sub>-( $\lambda^3$ -P)<sub>3</sub>, ( $\lambda^3$ -N)<sub>3</sub>-( $\lambda^3$ -As)<sub>3</sub>, ( $\lambda^3$ -P)<sub>3</sub>-( $\lambda^3$ -Sb)<sub>3</sub>, ( $\lambda^3$ -P)<sub>3</sub>-( $\lambda^3$ -Bi)<sub>3</sub>, ( $\lambda^3$ -As)<sub>3</sub>-( $\lambda^3$ -Bi)<sub>3</sub>, ( $\lambda^3$ -Sb)<sub>3</sub>-( $\lambda^3$ -Bi)<sub>3</sub>, could be synthesizables.

It was proven that the bond lengths increase in the group, the angle X-Y-X decreases, and the angle Y-X-Y increases with the increase of the atomic radius.

All the studied compounds have positive standard enthalpy ( $\Delta H^0 > 0$ ) and a negative free standard enthalpy ( $\Delta G^0 < 0$ ) suggesting that these compounds have a high tendency to undergo chemical reactions.

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