# CHEMISTRY
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## Supporting Information

# Spherical Aromaticity of All-Metal $[Bi@In_8Bi_{12}]^{3-/5-}$ Clusters

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# Supporting Information

**Contents**

## 1. Distances of Bi-Bi, In-In and In-Bi for the different synthesized clusters.

**Table S1**. List of average bond lengths of corresponding Zintl clusters.

| cluster | Average Distance, Å | | |
|---|---|---|---|
| | Bi-Bi/Sb-Sb | In-Bi/In-Sb | In-In |
| $In_8Bi_{13}^{3-}$ | 3.011 | 2.893 / 3.068 (centre-Bi) | 3.542 |
| $In_8Sb_{13}^{3-}$ | 2.825 | 2.832 / 2.989 (centre-Sb) | 3.451 |
| $InBi_3^{2-}$ | | $3.013^a$ | |
| $In_4Bi_5^{3-}$ | 3.048 | 3.059 | 3.535 |
| $[(La@In_2Bi_{11})(\mu\text{-}Bi)_2(La@In_2Bi_{11})]^{6-}$ | 3.112 | 2.967 | 3.853 |
| $Bi_7^{3-}$ | 2.977 | | |
| $Bi_{11}^{3-}$ | 2.978 | | |

[a.] The atoms in $InBi_3^{2-}$ cluster are unordered

## 2. The selected bonds of the $C_s$ [Bi@In₈Bi₁₂]⁵⁻ cluster.



5c-2e
ON=1.71|e|

20c-2e
ON=2.00|e|
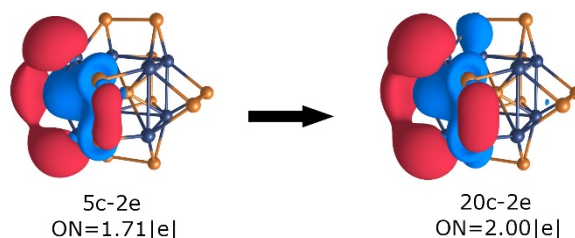
**Figure S1.** σ-bond found by the AdNDP analysis over five and twenty atomic centers.

### 3. The chemical bonding pattern of the $C_3$ [Bi@In$_8$Bi$_{12}$]$^{5-}$ cluster

Structure of
$C_3$ [Bi@In$_8$Bi$_{12}$]$^{5-}$

**a**

**b**

**c**

Twelve 1c-2e
lone pairs on Bi
ON=1.94-1.92|e|

Six 2c-2e
Bi-Bi σ–bonds
ON=1.94|e|

Twenty four 2c-2e
In-Bi σ–bonds
ON=1.95-1.86|e|

**e**

**f**

1c-2e
lone pair on In
ON=1.81|e|

8c-2e
ON=2.00|e|

**g**

**h**

**i**

Three 8c-2e
ON=1.95-1.93|e|
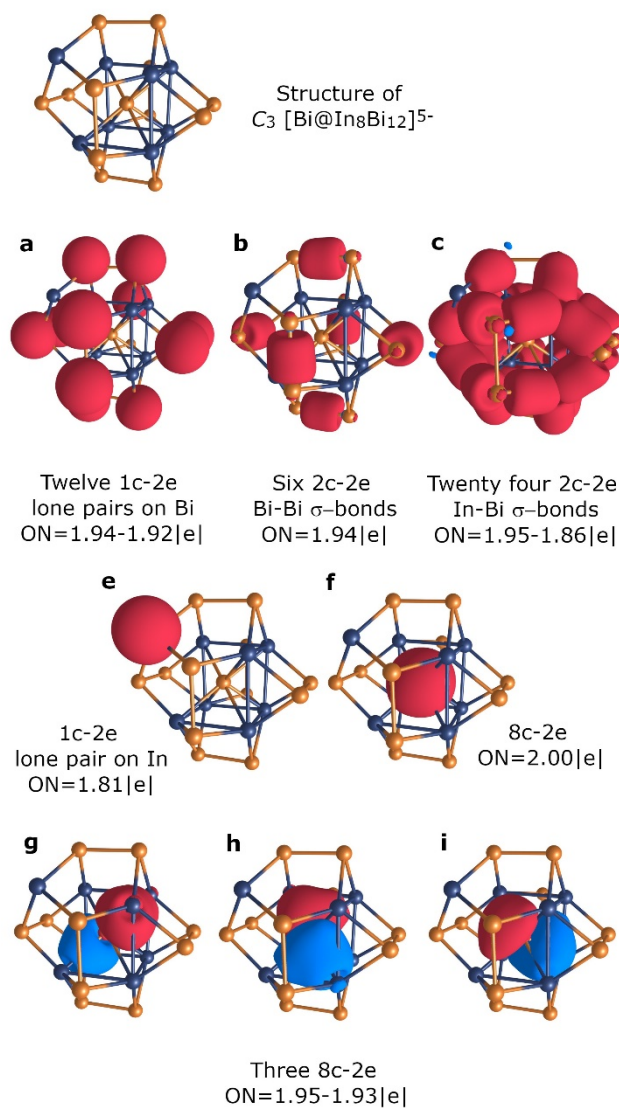
**Figure S2.** The chemical bonding pattern of the $C_3$ [Bi@In$_8$Bi$_{12}$]$^{5-}$ cluster.

### 4. The selected bonds of the $T_h$ [In$_8$Bi$_{12}$]$^{2-}$ cluster.

Structure of [In$_8$Bi$_{12}$]$^{2-}$

8c-2e
ON=1.86|e|

**Figure S3.** Structure of $T_h$ [In$_8$Bi$_{12}$]$^{2-}$ and spherically aromatic 8c-2e bond recovered by AdNDP method.

## 5. Experimental procedures
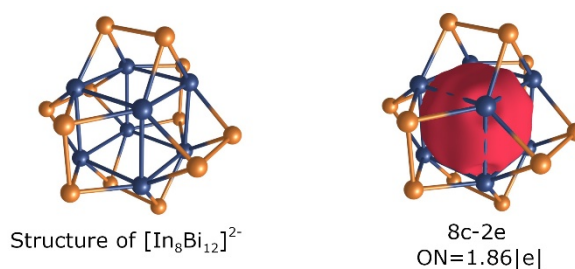
All manipulations and reactions were performed under a nitrogen atmosphere using standard Schlenk-line or glove box techniques. "$K_5In_2Bi_4$" was a nominal stoichiometric powder synthesized by heating a mixture of the elements at 600 °C for a week in a sealed niobium tube.[S1] $ZnMes_2$ is synthesized under anhydrous and anaerobic conditions according to the reported literature.[S2] 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane ([2,2,2]-crypt, Sigma-Aldirich 98%) were dried under vacuum for several hours and transfer to glove box for use. Pyridine (Aldrich, 99.8%) and toluene (Aldrich, 99.8%) were distilled by sodium in a nitrogen atmosphere and stored in a glove box prior to use.

***X-ray Diffraction.*** Suitable single crystals were selected for X-ray diffraction analyses. Crystallographic data were collected on Rigaku XtalAB Pro MM007 DW diffractometer with graphite monochromated Cu Kα radiation (λ = 1.54184 Å). Structures were solved using direct methods and then refined using SHELXL-2014 and Olex2 [S3-S5] to convergence, in which all the non-hydrogen atoms were refined anisotropically during the final cycles. All hydrogen atoms of the organic molecule were placed by geometrical considerations and were added to the structure factor calculation. Positional disorder was found in the cluster site in compound 1, and this was modeled accordingly (see Figure 3, 4). A summary of the crystallographic data for these complexes is listed in Table S2, and selected bond distances are given in Table S3.

***Energy Dispersive X-ray (EDX) Spectroscopy.*** EDX Analysis was performed using a scanning electron microscope (FE-SEM, JEOL JSM-7800F, Japan). Data acquisition was performed with an acceleration voltage of 15 kV and an accumulation time of 60 s.
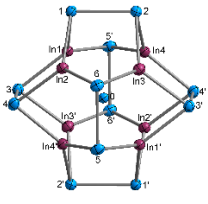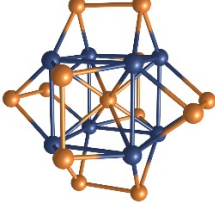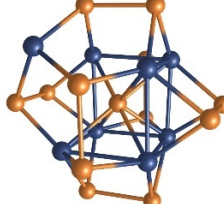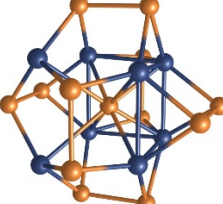
***Synthesis of [K(2,2,2-crypt)$_4$[Bi@In$_8$Bi$_{12}$] (1):*** The mixed powder of "$K_5In_2Bi_4$" (80mg) and [2,2,2]-crypt (80mg, 0.212mmol) were weighed in a reaction vial and dissolved in pyridine (2 mL). After stirring for 5 minutes, $ZnMes_2$ (50 mg, 0.164 mmol) was added into a pale yellow solution and stirring at 60 °C for 3 h. The resulting dark purple solution was filtered with a standard glass frit and layered with toluene (3 mL). Ten days later, a black strip-like crystal [K(2,2,2-crpyt)]$_4$[Bi@In$_8$Bi$_{12}$] (1) (13% yield based on the used "$K_5In_2Bi_4$") was obtained on the wall of the test tube.

## 6. Crystallographic supplementation

**Table S2.** X-ray measurements and structure solution of compounds.

| Compound | 1 |
|---|---|
| Empirical formula | $C_{72}H_{144}N_8O_{24}K_4In_8Bi_{13}$ |
| Formula weight | 5297.65 |
| Crystal system | triclinic |
| Space group | P -1 |
| a /Å | 15.6058(2) |
| b /Å | 16.0315(2) |
| c /Å | 17.1313(2) |
| α /° | 111.8670(10) |
| β /° | 115.3830(10) |
| γ /° | 96.2510(10) |
| *V* | 3404.31(7) |
| *Z* | 1 |
| $\rho$calc /g·cm–3 | 2.584 |
| $\mu$(CuK$\alpha$) /mm–1 | 44.319 |
| *F(000)* | 2371 |
| 2$\Theta$ range /° | 3.23 to 73.61 |
| Reflections collected / unique | 35593/13295 |
| Data / restraints / parameters | 13295/12/613 |
| R1/wR2 (I > 2$\sigma$(I))*a* | 0.0592/0.1606 |
| *R1/wR2 (all data)* | 0.0701/0.1653 |
| *GooF* (all data)*b* | 1.078 |
| Data completeness | 0.967 |
| Max. peak/hole /e–·Å–3 | 3.965 /-2.067 |

**Table S3.** Selected interatomic distances (in Å) and angles (in degrees) of the experimental and optimized structures of the clusters at the PBE0/Def2-TZVP level of theory.

| | Experimental | $T_h$ [Bi@In$_8$Bi$_{12}$]$^{3-}$ | $C_3$ [Bi@In$_8$Bi$_{12}$]$^{5-}$ | $C_s$ [Bi@In$_8$Bi$_{12}$]$^{5-}$ |
|---|---|---|---|---|
| |  |  |  |  |
| Bi1–Bi2 | 2.9991(8) | 3.00134 | 3.01973 | 3.01375 |
| Bi3–Bi4 | 3.0134(10) | 3.00134 | 3.01973 | 3.05903 |
| Bi5–Bi6 | 3.0028(9) | 3.00134 | 3.01973 | 2.98860 |
| In1–Bi1 | 2.8808(12) | 2.94000 | 2.92624 | 2.94646 |
| In1–Bi3 | 2.8947(5) | 2.94000 | 2.96234 | 2.96080 |
| In1–Bi5' | 2.8703(13) | 2.94000 | 3.01723 | 2.99210 |
| In2–Bi6 | 2.9022(14) | 2.94000 | 3.15084 | 3.07852 |
| In2–Bi4 | 2.8825(15) | 2.94000 | 3.15084 | 2.99479 |
| In2–Bi1 | 2.9028(16) | 2.94000 | 3.15084 | 3.06616 |
| In3–Bi2 | 2.9093(15) | 2.94000 | 2.96234 | 2.95922 |
| In3–Bi3' | 2.9038(8) | 2.94000 | 3.01723 | 2.97703 |
| In3–Bi6 | 2.9048(14) | 2.94000 | 2.92624 | 2.95180 |
| In4–Bi2 | 2.9139(11) | 2.94000 | 2.96309 | 2.98765 |
| In4–Bi4' | 2.9015(9) | 2.94000 | 2.96989 | 2.98448 |
| In4–Bi5' | 2.9009(14) | 2.94000 | 2.95631 | 2.97220 |
| Bi0–In1 | 3.0775(11) | 3.12421 | 3.11065 | 3.10692 |
| Bi0–In2 | 3.05965(8) | 3.12421 | 4.43194 | 3.73618 |
| Bi0–In3 | 3.0663(12) | 3.12421 | 3.11065 | 3.09107 |
| Bi0–In4 | 3.0679(14) | 3.12421 | 3.11246 | 3.08480 |
| In1–In4 | 3.5468(15) | 3.60753 | 3.66692 | 3.58076 |
| In1–In2 | 3.5385(18) | 3.60753 | 4.45620 | 4.03464 |
| In1–In3' | 3.5412(16) | 3.60753 | 3.61482 | 3.58286 |
| In2–In3 | 3.5390(18) | 3.60753 | 4.45620 | 4.04379 |
| In2–In4' | 3.5658(16) | 3.60753 | 4.45620 | 4.35588 |
| In3–In4 | 3.5231(18) | 3.60753 | 3.61482 | 3.48551 |
| Bi6–In3–Bi3' | 119.86 | 119.86 | 119.70 | 117.43 |
| Bi6–In3–Bi2 | 119.48 | 119.86 | 122.86 | 126.26 |
| Bi3'–In3–Bi2 | 119.88 | 119.86 | 117.14 | 118.32 |
| In2–In3–In1' | 89.76 | 90.00 | 100.43 | 94.96 |
| In2–In3–In4 | 90.18 | 90.00 | 101.27 | 96.80 |
| In1'–In3–In4 | 90.54 | 90.00 | 87.44 | 87.61 |
| In3–Bi0–In1' | 70.39 | 70.53 | 72.21 | 72.54 |
| Gap | - | 2.526 eV | 1.609 eV | 1.087 eV |
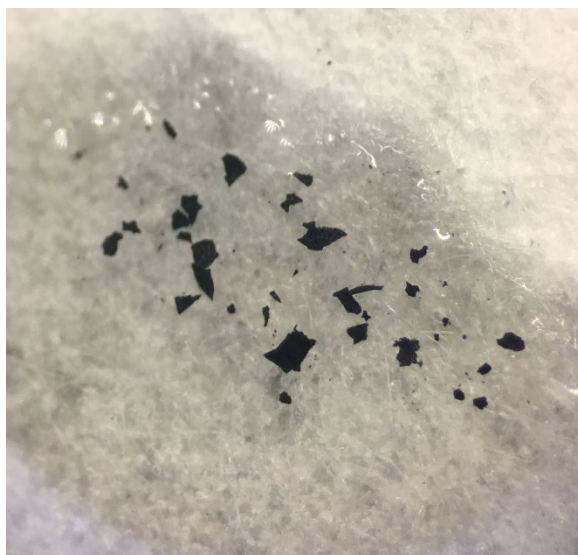
**Figure S4.** [K(2,2,2-crypt)]$_4$[In$_8$Bi$_{13}$] dispersed in silicon oil.
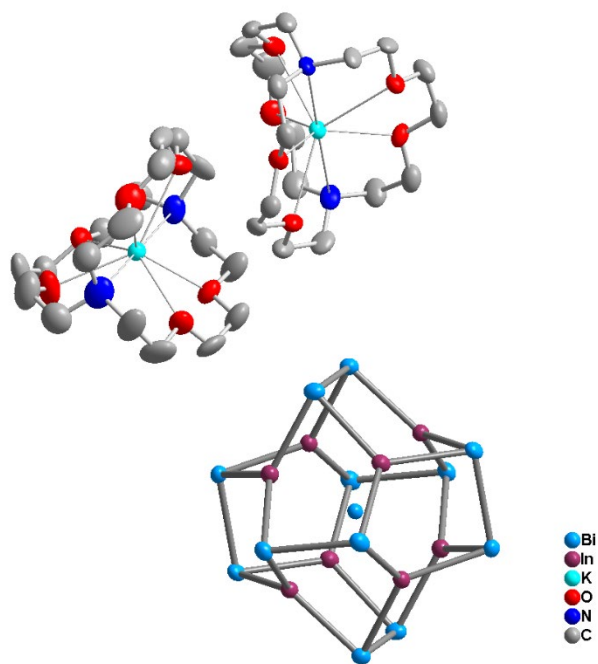


**Figure S5.** Asymmetric unit of 1 with the cluster fragment. Thermal ellipsoids are drawn at 50% probability. The minor components are omitted for clarity.
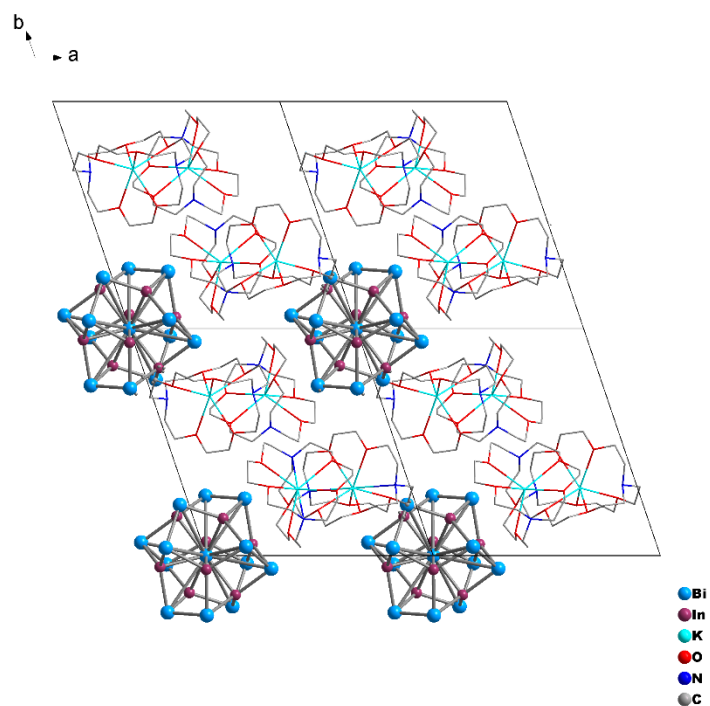
**Figure S6.** Unit cell of compound 1. Minor component in the cluster site are omitted for clarity.

## 7. Energy Dispersive X-ray (EDX) spectroscopic analysis

EDX analysis on $[K([2.2.2]crypt)]_4[In_8Bi_{13}]$ (Figure S8) was performed using a scanning electron microscope (FE-SEM, JEOL JSM-7800F, Japan). Data acquisition was performed with an acceleration voltage of 15 kV and an accumulation time of 60 s. The atomic ratio of In/Bi is 7.01:13.42, which is a little deviation but in a reasonable range of error with the experimental crystallographic data.
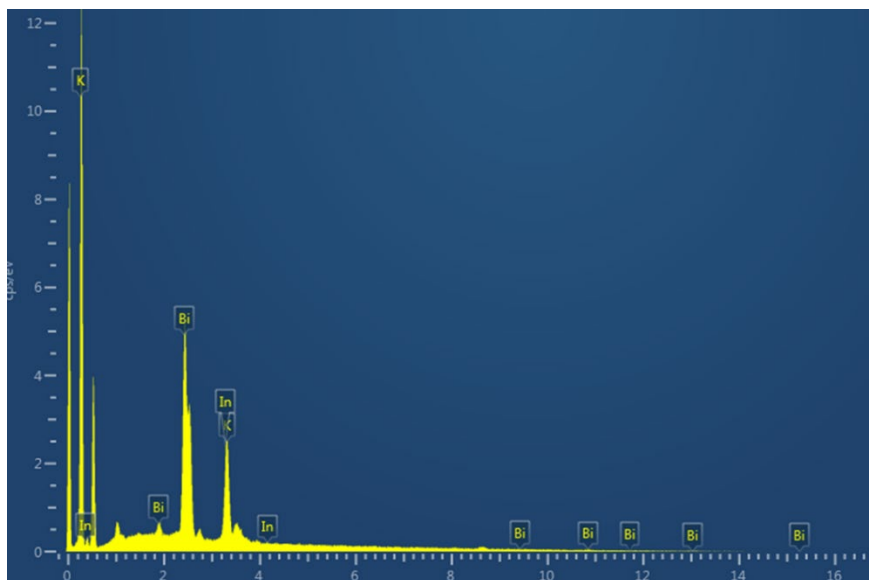


**Figure S7.** EDX analysis of $[K([2.2.2]crypt)]_4[In_8Bi_{13}]$.

## 8. The plot of induced magnetic field of $T_h$ $[Bi@In_8Bi_{12}]^{3-}$
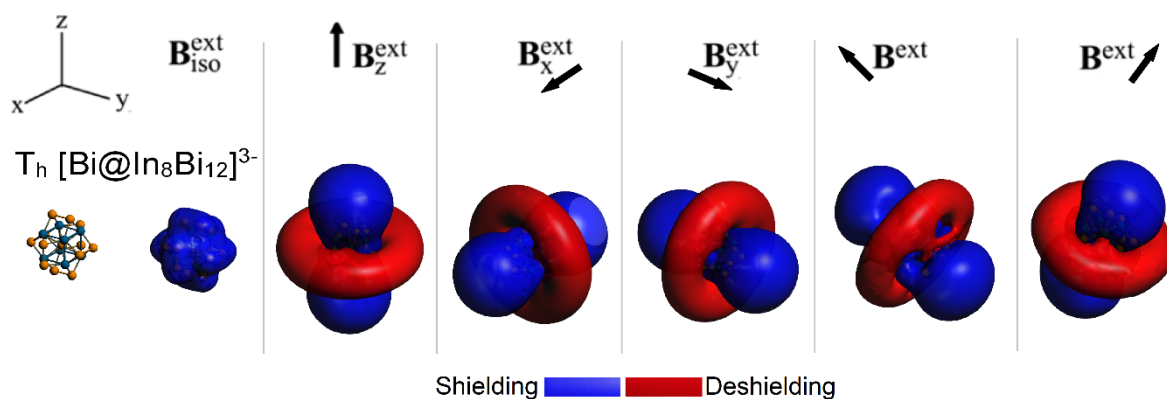


**Figure S8.** The induced magnetic field of $T_h$ $[Bi@In_8Bi_{12}]^{3-}$ under different orientations of the external field.

## 9. Optimized geometries of investigated molecules

**Table S4.** Coordinates of optimized geometries, total energies and ZPE corrections of investigated molecules [a.u.].

| $T_h$ [Bi@In$_8$Bi$_{12}$]$^{3-}$ (singlet) | PBE0/LANL2DZ (0 imaginary Frequencies, $E_{elec}$= -86.9480588633, ZPE correction= 0.011790) | | |
|---|---|---|---|
| | 49 | 1.828147000 | 1.828147000 | 1.828147000 |
| | 49 | 1.828147000 | -1.828147000 | 1.828147000 |
| | 49 | -1.828147000 | -1.828147000 | 1.828147000 |
| | 49 | -1.828147000 | 1.828147000 | 1.828147000 |
| | 49 | 1.828147000 | 1.828147000 | -1.828147000 |
| | 49 | -1.828147000 | 1.828147000 | -1.828147000 |
| | 49 | -1.828147000 | -1.828147000 | -1.828147000 |
| | 49 | 1.828147000 | -1.828147000 | -1.828147000 |
| | 83 | 4.146028000 | 0.000000000 | -1.516927000 |
| | 83 | 4.146028000 | 0.000000000 | 1.516927000 |
| | 83 | -4.146028000 | 0.000000000 | 1.516927000 |
| | 83 | -4.146028000 | 0.000000000 | -1.516927000 |
| | 83 | 1.516927000 | 4.146028000 | 0.000000000 |
| | 83 | -1.516927000 | 4.146028000 | 0.000000000 |
| | 83 | 1.516927000 | -4.146028000 | 0.000000000 |
| | 83 | -1.516927000 | -4.146028000 | 0.000000000 |
| | 83 | 0.000000000 | 1.516927000 | -4.146028000 |
| | 83 | 0.000000000 | -1.516927000 | -4.146028000 |
| | 83 | 0.000000000 | 1.516927000 | 4.146028000 |
| | 83 | 0.000000000 | -1.516927000 | 4.146028000 |
| | 83 | 0.000000000 | 0.000000000 | 0.000000000 |
| $C_1$ [Bi@In$_8$Bi$_{12}$]$^{3-}$ (triplet) | PBE0/LANL2DZ (0 imaginary Frequencies, $E_{elec}$= -86.8949707236, ZPE correction= 0.011338) | | |
| | 49 | 1.071264000 | 2.685380000 | 1.303273000 |
| | 49 | 2.582140000 | -0.603752000 | 1.641863000 |
| | 49 | -0.730767000 | -2.147764000 | 2.262447000 |
| | 49 | -2.259378000 | 1.162968000 | 1.744820000 |
| | 49 | 0.876070000 | 2.258095000 | -2.216561000 |
| | 49 | -3.386049000 | 0.728922000 | -1.981458000 |
| | 49 | -1.055074000 | -2.679891000 | -1.339211000 |
| | 49 | 2.333359000 | -1.218684000 | -1.841310000 |
| | 83 | 3.712852000 | 1.418469000 | -2.083284000 |
| | 83 | 3.920807000 | 1.934116000 | 0.904504000 |

| | | | | |
|---|---|---|---|---|
| | 83 | -3.603587000 | -1.451618000 | 2.121269000 |
| | 83 | -3.897512000 | -2.037685000 | -0.833012000 |
| | 83 | -0.348536000 | 4.431957000 | -0.641741000 |
| | 83 | -3.094468000 | 3.188618000 | -0.218490000 |
| | 83 | 3.172856000 | -3.146628000 | 0.250504000 |
| | 83 | 0.416019000 | -4.343476000 | 0.653278000 |
| | 83 | -0.971389000 | 0.646668000 | -3.828711000 |
| | 83 | 0.349995000 | -2.089515000 | -3.878951000 |
| | 83 | -0.291840000 | 2.000079000 | 3.827875000 |
| | 83 | 1.019391000 | -0.715088000 | 4.150412000 |
| | 83 | -0.049005000 | 0.054724000 | -0.172079000 |
| $C_3$ [Bi@In$_8$Bi$_{12}$]$^{5-}$ (singlet) | PBE0/LANL2DZ (0 imaginary Frequencies, E$_{elec}$= -86.4609468361, ZPE correction= 0.010945) | | | |
| | 49 | 0.000000000 | 0.000000000 | 3.101476000 |
| | 49 | -2.592935000 | 1.437767000 | 1.128520000 |
| | 49 | 0.000000000 | 2.904959000 | -1.103298000 |
| | 49 | 2.541611000 | 1.526664000 | 1.128520000 |
| | 49 | 0.051324000 | -2.964432000 | 1.128520000 |
| | 49 | 2.515768000 | -1.452479000 | -1.103298000 |
| | 49 | 0.000000000 | 0.000000000 | -4.488600000 |
| | 49 | -2.515768000 | -1.452479000 | -1.103298000 |
| | 83 | -2.904786000 | -2.926806000 | 1.554945000 |
| | 83 | -2.960102000 | -0.496800000 | 3.393911000 |
| | 83 | 2.967591000 | 2.978595000 | -1.454321000 |
| | 83 | 2.896315000 | 0.515952000 | -3.249407000 |
| | 83 | 1.910293000 | -2.315124000 | 3.393911000 |
| | 83 | 3.987081000 | -1.052215000 | 1.554945000 |
| | 83 | -4.063334000 | 1.080712000 | -1.454321000 |
| | 83 | -1.894985000 | 2.250306000 | -3.249407000 |
| | 83 | 1.095743000 | -4.059307000 | -1.454321000 |
| | 83 | -1.001329000 | -2.766258000 | -3.249407000 |
| | 83 | 1.049810000 | 2.811924000 | 3.393911000 |
| | 83 | -1.082295000 | 3.979021000 | 1.554945000 |
| | 83 | 0.000000000 | 0.000000000 | 0.038855000 |
| $C_s$ [Bi@In$_8$Bi$_{12}$]$^{5-}$ (singlet) | PBE0/LANL2DZ (1 imaginary Frequency -57.1719 cm$^{-1}$, E$_{elec}$= -86.4499525999, ZPE correction=0.010729) | | | |
| | 49 | 0.400491000 | 2.514060000 | 1.713733000 |
| | 49 | 0.400491000 | 2.514060000 | -1.713733000 |

| | | | | |
|---|---|---|---|---|
| | 49 | 2.511954000 | -0.464568000 | -1.802028000 |
| | 49 | 2.511954000 | -0.464568000 | 1.802028000 |
| | 49 | -2.462235000 | 0.433911000 | 1.847955000 |
| | 49 | -0.537773000 | -3.134790000 | 2.184992000 |
| | 49 | -0.537773000 | -3.134790000 | -2.184992000 |
| | 49 | -2.462235000 | 0.433911000 | -1.847955000 |
| | 83 | -3.590555000 | 2.530924000 | 0.000000000 |
| | 83 | -1.187332000 | 4.425704000 | 0.000000000 |
| | 83 | 3.834304000 | -2.444778000 | 0.000000000 |
| | 83 | 1.248706000 | -4.166780000 | 0.000000000 |
| | 83 | -0.863803000 | 1.342055000 | 4.198847000 |
| | 83 | 0.844854000 | -1.176496000 | 4.157215000 |
| | 83 | -0.863803000 | 1.342055000 | -4.198847000 |
| | 83 | 0.844854000 | -1.176496000 | -4.157215000 |
| | 83 | -3.469898000 | -2.342558000 | 1.503901000 |
| | 83 | -3.469898000 | -2.342558000 | -1.503901000 |
| | 83 | 3.396316000 | 2.418500000 | 1.514948000 |
| | 83 | 3.396316000 | 2.418500000 | -1.514948000 |
| | 83 | -0.016672000 | -0.058966000 | 0.000000000 |
| $C_2$ [Bi@In$_8$Bi$_{12}$]$^{5-}$ (triplet) | PBE0/LANL2DZ (0 imaginary Frequencies, E$_{elec}$= -86.4506364202, ZPE correction=0.010962) | | | |
| | 49 | -1.091975000 | 2.337221000 | -1.885611000 |
| | 49 | -2.271019000 | -1.028311000 | -1.712247000 |
| | 49 | 1.091975000 | -2.337221000 | -1.885611000 |
| | 49 | 2.271019000 | 1.028311000 | -1.712247000 |
| | 49 | -1.010223000 | 2.239685000 | 1.790858000 |
| | 49 | 2.950500000 | 1.367587000 | 2.240393000 |
| | 49 | 1.010223000 | -2.239685000 | 1.790858000 |
| | 49 | -2.950500000 | -1.367587000 | 2.240393000 |
| | 83 | -3.876083000 | 1.445248000 | 1.462460000 |
| | 83 | -3.947291000 | 1.455849000 | -1.589408000 |
| | 83 | 3.947291000 | -1.455849000 | -1.589408000 |
| | 83 | 3.876083000 | -1.445248000 | 1.462460000 |
| | 83 | 0.000000000 | 4.423719000 | -0.028528000 |
| | 83 | 2.874115000 | 3.416266000 | -0.047592000 |
| | 83 | -2.874115000 | -3.416266000 | -0.047592000 |
| | 83 | 0.000000000 | -4.423719000 | -0.028528000 |
| | 83 | 0.555340000 | 1.420623000 | 4.157431000 |

| | | | |
|---|---|---|---|
| | 83 | -0.555340000 | -1.420623000 | 4.157431000 |
| | 83 | 0.563632000 | 1.418023000 | -4.204922000 |
| | 83 | -0.563632000 | -1.418023000 | -4.204922000 |
| | 83 | 0.000000000 | 0.000000000 | -0.010599000 |

| $C_s$ [Bi@In$_8$Bi$_{12}$]$^{5-}$ (triplet) | PBE0/LANL2DZ (0 imaginary Frequencies, E$_{elec}$= -86.4467095963, ZPE correction=0.010844) |
|---|---|

| | | | |
|---|---|---|---|
| 49 | -0.402450000 | 2.501207000 | 1.721177000 |
| 49 | -0.402450000 | 2.501207000 | -1.721177000 |
| 49 | 2.510556000 | 0.414215000 | -1.806554000 |
| 49 | 2.510556000 | 0.414215000 | 1.806554000 |
| 49 | -2.490036000 | -0.411779000 | 1.870050000 |
| 49 | 0.451433000 | -3.062319000 | 2.235405000 |
| 49 | 0.451433000 | -3.062319000 | -2.235405000 |
| 49 | -2.490036000 | -0.411779000 | -1.870050000 |
| 83 | -4.214530000 | 1.225449000 | 0.000000000 |
| 83 | -2.529237000 | 3.764953000 | 0.000000000 |
| 83 | 4.291353000 | -1.176404000 | 0.000000000 |
| 83 | 2.439845000 | -3.588641000 | 0.000000000 |
| 83 | -1.239274000 | 0.998248000 | 4.194107000 |
| 83 | 1.206362000 | -0.813611000 | 4.179108000 |
| 83 | -1.239274000 | 0.998248000 | -4.194107000 |
| 83 | 1.206362000 | -0.813611000 | -4.179108000 |
| 83 | -2.462096000 | -3.353222000 | 1.552029000 |
| 83 | -2.462096000 | -3.353222000 | -1.552029000 |
| 83 | 2.456152000 | 3.419867000 | 1.526392000 |
| 83 | 2.456152000 | 3.419867000 | -1.526392000 |
| 83 | 0.008217000 | -0.068279000 | 0.000000000 |

| $C_3$ [Bi@In$_8$Bi$_{12}$]$^{5-}$ (triplet) | PBE0/LANL2DZ (0 imaginary Frequencies, E$_{elec}$= -86.4436727814, ZPE correction=0.010757) |
|---|---|

| | | | |
|---|---|---|---|
| 49 | -1.087718000 | -1.235108000 | -2.618491000 |
| 49 | -0.932454000 | -2.875738000 | 0.646709000 |
| 49 | 2.498223000 | -1.623231000 | 0.824053000 |
| 49 | 2.725851000 | 0.022363000 | -2.837419000 |
| 49 | -2.498223000 | 1.623231000 | -0.824053000 |
| 49 | 0.932454000 | 2.875738000 | -0.646709000 |
| 49 | 1.087718000 | 1.235108000 | 2.618491000 |
| 49 | -2.725851000 | -0.022363000 | 2.837419000 |
| 83 | -4.454808000 | -0.297202000 | 0.298126000 |

| | | | |
|---|---|---|---|
| | 83 | -3.305792000 | -2.713967000 | -1.150616000 |
| | 83 | 4.454808000 | 0.297202000 | -0.298126000 |
| | 83 | 3.305792000 | 2.713967000 | 1.150616000 |
| | 83 | -1.821238000 | 1.409834000 | -3.783432000 |
| | 83 | 1.019715000 | 2.481462000 | -3.581538000 |
| | 83 | -1.019715000 | -2.481462000 | 3.581538000 |
| | 83 | 1.821238000 | -1.409834000 | 3.783432000 |
| | 83 | -1.579619000 | 4.100182000 | 0.557865000 |
| | 83 | -1.390634000 | 2.724248000 | 3.265858000 |
| | 83 | 1.390634000 | -2.724248000 | -3.265858000 |
| | 83 | 1.579619000 | -4.100182000 | -0.557865000 |
| | 83 | 0.000000000 | 0.000000000 | 0.000000000 |

| $T_h$ [Bi@In$_8$Bi$_{12}$]$^{3-}$ (singlet) | PBE0/Def2TZVP (0 imaginary Frequencies, E$_{elec}$= -4312.64097148, ZPE correction= 0.011890) | | | |
|---|---|---|---|---|
| | 49 | 1.803764000 | 1.803764000 | 1.803764000 |
| | 49 | 1.803764000 | -1.803764000 | 1.803764000 |
| | 49 | -1.803764000 | -1.803764000 | 1.803764000 |
| | 49 | -1.803764000 | 1.803764000 | 1.803764000 |
| | 49 | 1.803764000 | 1.803764000 | -1.803764000 |
| | 49 | -1.803764000 | 1.803764000 | -1.803764000 |
| | 49 | -1.803764000 | -1.803764000 | -1.803764000 |
| | 49 | 1.803764000 | -1.803764000 | -1.803764000 |
| | 83 | 4.105537000 | 0.000000000 | -1.500672000 |
| | 83 | 4.105537000 | 0.000000000 | 1.500672000 |
| | 83 | -4.105537000 | 0.000000000 | 1.500672000 |
| | 83 | -4.105537000 | 0.000000000 | -1.500672000 |
| | 83 | 1.500672000 | 4.105537000 | 0.000000000 |
| | 83 | -1.500672000 | 4.105537000 | 0.000000000 |
| | 83 | 1.500672000 | -4.105537000 | 0.000000000 |
| | 83 | -1.500672000 | -4.105537000 | 0.000000000 |
| | 83 | 0.000000000 | 1.500672000 | -4.105537000 |
| | 83 | 0.000000000 | -1.500672000 | -4.105537000 |
| | 83 | 0.000000000 | 1.500672000 | 4.105537000 |
| | 83 | 0.000000000 | -1.500672000 | 4.105537000 |
| | 83 | 0.000000000 | 0.000000000 | 0.000000000 |

| $C_1$ [Bi@In$_8$Bi$_{12}$]$^{3-}$ (triplet) | PBE0/Def2TZVP (0 imaginary Frequencies, E$_{elec}$= -4312.59073560, ZPE correction= 0.011391) | | | |
|---|---|---|---|---|
| | 49 | 1.024724000 | 2.618303000 | 1.324606000 |

| | | | |
|---|---|---|---|
| 49 | 2.505881000 | -0.620679000 | 1.657657000 |
| 49 | -0.771117000 | -2.140809000 | 2.170898000 |
| 49 | -2.293994000 | 1.143829000 | 1.704129000 |
| 49 | 0.933470000 | 2.278503000 | -2.145630000 |
| 49 | -3.269286000 | 0.742404000 | -2.001180000 |
| 49 | -1.013339000 | -2.662506000 | -1.379164000 |
| 49 | 2.327615000 | -1.173986000 | -1.767926000 |
| 83 | 3.731159000 | 1.418605000 | -1.956999000 |
| 83 | 3.859993000 | 1.898469000 | 1.003459000 |
| 83 | -3.617943000 | -1.463092000 | 2.004831000 |
| 83 | -3.840773000 | -2.012902000 | -0.929332000 |
| 83 | -0.322236000 | 4.411121000 | -0.580879000 |
| 83 | -3.053196000 | 3.180338000 | -0.242609000 |
| 83 | 3.131729000 | -3.125982000 | 0.278055000 |
| 83 | 0.401431000 | -4.319658000 | 0.615936000 |
| 83 | -0.868539000 | 0.694480000 | -3.810585000 |
| 83 | 0.431170000 | -2.019314000 | -3.850342000 |
| 83 | -0.366728000 | 1.931616000 | 3.799187000 |
| 83 | 0.914831000 | -0.762196000 | 4.114018000 |
| 83 | -0.072631000 | 0.059263000 | -0.186983000 |

| $C_3$ [Bi@In$_8$Bi$_{12}$]$^{5-}$ (singlet) | PBE0/Def2TZVP (0 imaginary Frequencies, E$_{elec}$= -4312.16578473, ZPE correction= 0.011031) | | |
|---|---|---|---|
| 49 | 0.000000000 | 0.000000000 | 3.040492000 |
| 49 | 0.713579000 | 2.816582000 | 1.109341000 |
| 49 | 2.821668000 | 0.758393000 | -1.073807000 |
| 49 | 2.082442000 | -2.026269000 | 1.109341000 |
| 49 | -2.796022000 | -0.790313000 | 1.109341000 |
| 49 | -0.754046000 | -2.822832000 | -1.073807000 |
| 49 | 0.000000000 | 0.000000000 | -4.438442000 |
| 49 | -2.067622000 | 2.064439000 | -1.073807000 |
| 83 | -3.545067000 | 2.034310000 | 1.556771000 |
| 83 | -1.221678000 | 2.702450000 | 3.359232000 |
| 83 | 3.595590000 | -2.077815000 | -1.437742000 |
| 83 | 1.224196000 | -2.636163000 | -3.221974000 |
| 83 | -1.729551000 | -2.409229000 | 3.359232000 |
| 83 | 0.010770000 | -4.087273000 | 1.556771000 |
| 83 | 0.001646000 | 4.152780000 | -1.437742000 |
| 83 | 1.670886000 | 2.378266000 | -3.221974000 |

| | 83 | -3.597236000 | -2.074964000 | -1.437742000 |
|---|---|---|---|---|
| | 83 | -2.895082000 | 0.257897000 | -3.221974000 |
| | 83 | 2.951229000 | -0.293220000 | 3.359232000 |
| | 83 | 3.534298000 | 2.052964000 | 1.556771000 |
| | 83 | 0.000000000 | 0.000000000 | -0.006498000 |
| $C_s$ [Bi@In$_8$Bi$_{12}$]$^{5-}$ (singlet) | PBE0/Def2TZVP (1 imaginary Frequency -63.5722 cm$^{-1}$, $E_{elec}$= -4312.15496919, ZPE correction=0.010789) | | | |
| | 49 | 0.425614000 | 2.448725000 | 1.683104000 |
| | 49 | 0.425614000 | 2.448725000 | -1.683104000 |
| | 49 | 2.488025000 | -0.476434000 | -1.791429000 |
| | 49 | 2.488025000 | -0.476434000 | 1.791429000 |
| | 49 | -2.446441000 | 0.479231000 | 1.828699000 |
| | 49 | -0.566474000 | -3.083910000 | 2.177940000 |
| | 49 | -0.566474000 | -3.083910000 | -2.177940000 |
| | 49 | -2.446441000 | 0.479231000 | -1.828699000 |
| | 83 | -3.523399000 | 2.566981000 | 0.000000000 |
| | 83 | -1.104788000 | 4.380606000 | 0.000000000 |
| | 83 | 3.737571000 | -2.475367000 | 0.000000000 |
| | 83 | 1.184573000 | -4.160561000 | 0.000000000 |
| | 83 | -0.837308000 | 1.346047000 | 4.155994000 |
| | 83 | 0.825897000 | -1.167008000 | 4.124252000 |
| | 83 | -0.837308000 | 1.346047000 | -4.155994000 |
| | 83 | 0.825897000 | -1.167008000 | -4.124252000 |
| | 83 | -3.456805000 | -2.274038000 | 1.494298000 |
| | 83 | -3.456805000 | -2.274038000 | -1.494298000 |
| | 83 | 3.390834000 | 2.361213000 | 1.499265000 |
| | 83 | 3.390834000 | 2.361213000 | -1.499265000 |
| | 83 | -0.021975000 | -0.097413000 | 0.000000000 |
| $C_2$ [Bi@In$_8$Bi$_{12}$]$^{5-}$ (triplet) | PBE0/Def2TZVP (0 imaginary Frequencies, $E_{elec}$= -4312.15133297, ZPE correction=0.010962) | | | |
| | 49 | 1.064542000 | 2.284739000 | 1.841310000 |
| | 49 | 2.249032000 | -1.018524000 | 1.712339000 |
| | 49 | -1.064542000 | -2.284739000 | 1.841310000 |
| | 49 | -2.249032000 | 1.018524000 | 1.712339000 |
| | 49 | 1.021385000 | 2.266517000 | -1.791175000 |
| | 49 | -2.890452000 | 1.341463000 | -2.190796000 |
| | 49 | -1.021385000 | -2.266517000 | -1.791175000 |
| | 49 | 2.890452000 | -1.341463000 | -2.190796000 |

| | | | | |
|---|---|---|---|---|
| | 83 | 3.846760000 | 1.433348000 | -1.445351000 |
| | 83 | 3.901902000 | 1.444664000 | 1.574897000 |
| | 83 | -3.901902000 | -1.444664000 | 1.574897000 |
| | 83 | -3.846760000 | -1.433348000 | -1.445351000 |
| | 83 | 0.000000000 | 4.386355000 | 0.037148000 |
| | 83 | -2.846134000 | 3.382334000 | 0.052034000 |
| | 83 | 2.846134000 | -3.382334000 | 0.052034000 |
| | 83 | 0.000000000 | -4.386355000 | 0.037148000 |
| | 83 | -0.554470000 | 1.409125000 | -4.116592000 |
| | 83 | 0.554470000 | -1.409125000 | -4.116592000 |
| | 83 | -0.552691000 | 1.404159000 | 4.161538000 |
| | 83 | 0.552691000 | -1.404159000 | 4.161538000 |
| | 83 | 0.000000000 | 0.000000000 | -0.021621000 |
| $C_s$ [Bi@In$_8$Bi$_{12}$]$^{5-}$ (triplet) | PBE0/Def2TZVP (0 imaginary Frequencies, $E_{elec}$= -4312.14916985, ZPE correction=0.010888) | | | |
| | 49 | 0.409351000 | -2.445572000 | 1.693948000 |
| | 49 | 0.409351000 | -2.445572000 | -1.693948000 |
| | 49 | -2.483086000 | -0.443604000 | -1.790515000 |
| | 49 | -2.483086000 | -0.443604000 | 1.790515000 |
| | 49 | 2.478552000 | 0.414921000 | 1.848752000 |
| | 49 | -0.474808000 | 3.016784000 | 2.216878000 |
| | 49 | -0.474808000 | 3.016784000 | -2.216878000 |
| | 49 | 2.478552000 | 0.414921000 | -1.848752000 |
| | 83 | 4.189652000 | -1.191520000 | 0.000000000 |
| | 83 | 2.517467000 | -3.696209000 | 0.000000000 |
| | 83 | -4.251953000 | 1.124868000 | 0.000000000 |
| | 83 | -2.452058000 | 3.542788000 | 0.000000000 |
| | 83 | 1.235530000 | -0.980060000 | 4.150145000 |
| | 83 | -1.202441000 | 0.791830000 | 4.142300000 |
| | 83 | 1.235530000 | -0.980060000 | -4.150145000 |
| | 83 | -1.202441000 | 0.791830000 | -4.142300000 |
| | 83 | 2.410724000 | 3.337976000 | 1.538212000 |
| | 83 | 2.410724000 | 3.337976000 | -1.538212000 |
| | 83 | -2.397563000 | -3.411607000 | 1.510390000 |
| | 83 | -2.397563000 | -3.411607000 | -1.510390000 |
| | 83 | -0.012969000 | 0.103220000 | 0.000000000 |
| $C_3$ [Bi@In$_8$Bi$_{12}$]$^{5-}$ (triplet) | PBE0/Def2TZVP (1 imaginary Frequency -3.8214 cm$^{-1}$, $E_{elec}$= -4312.14656528, ZPE correction=0.010733) | | | |

| | 49 | 0.000000000 | 2.872789000 | 1.099618000 |
|---|---|---|---|---|
| | 49 | 2.487867000 | 1.436353000 | -1.099656000 |
| | 49 | 2.487908000 | -1.436394000 | 1.099618000 |
| | 49 | 0.000000000 | 0.000000000 | 3.815865000 |
| | 49 | -2.487852000 | 1.436379000 | -1.099656000 |
| | 49 | -2.487908000 | -1.436394000 | 1.099618000 |
| | 49 | -0.000015000 | -2.872733000 | -1.099656000 |
| | 49 | 0.000000000 | 0.000000000 | -3.815892000 |
| | 83 | -1.034524000 | 2.803139000 | -3.264572000 |
| | 83 | 1.066745000 | 4.002740000 | -1.466557000 |
| | 83 | 1.034566000 | -2.803130000 | 3.264587000 |
| | 83 | -1.066682000 | -4.002743000 | 1.466547000 |
| | 83 | -2.933136000 | 2.925145000 | 1.466547000 |
| | 83 | -2.944865000 | 0.505605000 | 3.264587000 |
| | 83 | 2.944852000 | -0.505645000 | -3.264572000 |
| | 83 | 2.933102000 | -2.925199000 | -1.466557000 |
| | 83 | -3.999848000 | -1.077542000 | -1.466557000 |
| | 83 | -1.910328000 | -2.297494000 | -3.264572000 |
| | 83 | 1.910299000 | 2.297526000 | 3.264587000 |
| | 83 | 3.999818000 | 1.077598000 | 1.466547000 |
| | 83 | 0.000000000 | 0.000000000 | 0.000068000 |

| $T_h$ [In$_8$Bi$_{12}$] (singlet) | PBE0/Def2TZVP (0 imaginary Frequencies, $E_{elec}$= -4097.88336929, ZPE correction=0.011527) | | |
|---|---|---|---|
| | 49 | 1.887534000 | 1.887534000 | 1.887534000 |
| | 49 | 1.887534000 | -1.887534000 | 1.887534000 |
| | 49 | -1.887534000 | -1.887534000 | 1.887534000 |
| | 49 | -1.887534000 | 1.887534000 | 1.887534000 |
| | 49 | 1.887534000 | 1.887534000 | -1.887534000 |
| | 49 | -1.887534000 | 1.887534000 | -1.887534000 |
| | 49 | -1.887534000 | -1.887534000 | -1.887534000 |
| | 49 | 1.887534000 | -1.887534000 | -1.887534000 |
| | 83 | 4.042356000 | 0.000000000 | -1.497283000 |
| | 83 | 4.042356000 | 0.000000000 | 1.497283000 |
| | 83 | -4.042356000 | 0.000000000 | 1.497283000 |
| | 83 | -4.042356000 | 0.000000000 | -1.497283000 |
| | 83 | 1.497283000 | 4.042356000 | 0.000000000 |
| | 83 | -1.497283000 | 4.042356000 | 0.000000000 |
| | 83 | 1.497283000 | -4.042356000 | 0.000000000 |

| | 83 | -1.497283000 | -4.042356000 | 0.000000000 |
| | 83 | 0.000000000 | 1.497283000 | -4.042356000 |
| | 83 | 0.000000000 | -1.497283000 | -4.042356000 |
| | 83 | 0.000000000 | 1.497283000 | 4.042356000 |
| | 83 | 0.000000000 | -1.497283000 | 4.042356000 |
| $T_h$ [In$_8$Bi$_{12}$]$^{2-}$ (singlet) | PBE0/Def2TZVP (4 imaginary Frequencies: $T_u$ = -14.4921 cm$^{-1}$, $A_u$ = -14.2521 cm$^{-1}$ $E_{elec}$= -4097.96122377, ZPE correction=0.010598) | | | |
| | 49 | 1.731542000 | 1.731542000 | 1.731542000 |
| | 49 | 1.731542000 | -1.731542000 | 1.731542000 |
| | 49 | -1.731542000 | -1.731542000 | 1.731542000 |
| | 49 | -1.731542000 | 1.731542000 | 1.731542000 |
| | 49 | 1.731542000 | 1.731542000 | -1.731542000 |
| | 49 | -1.731542000 | 1.731542000 | -1.731542000 |
| | 49 | -1.731542000 | -1.731542000 | -1.731542000 |
| | 49 | 1.731542000 | -1.731542000 | -1.731542000 |
| | 83 | 4.059436000 | 0.000000000 | -1.494966000 |
| | 83 | 4.059436000 | 0.000000000 | 1.494966000 |
| | 83 | -4.059436000 | 0.000000000 | 1.494966000 |
| | 83 | -4.059436000 | 0.000000000 | -1.494966000 |
| | 83 | 1.494966000 | 4.059436000 | 0.000000000 |
| | 83 | -1.494966000 | 4.059436000 | 0.000000000 |
| | 83 | 1.494966000 | -4.059436000 | 0.000000000 |
| | 83 | -1.494966000 | -4.059436000 | 0.000000000 |
| | 83 | 0.000000000 | 1.494966000 | -4.059436000 |
| | 83 | 0.000000000 | -1.494966000 | -4.059436000 |
| | 83 | 0.000000000 | 1.494966000 | 4.059436000 |
| | 83 | 0.000000000 | -1.494966000 | 4.059436000 |

## 10. Coordinates of chosen points for NICS calculation

**Table S5.** Coordinates of points for NICS calculation.

| $T_h$ [Bi@In$_8$Bi$_{12}$]$^{3-}$ | 49 | 1.803764000 | 1.803764000 | 1.803764000 |
| | 49 | 1.803764000 | -1.803764000 | 1.803764000 |
| | 49 | -1.803764000 | -1.803764000 | 1.803764000 |
| | 49 | -1.803764000 | 1.803764000 | 1.803764000 |
| | 49 | 1.803764000 | 1.803764000 | -1.803764000 |
| | 49 | -1.803764000 | 1.803764000 | -1.803764000 |
| | 49 | -1.803764000 | -1.803764000 | -1.803764000 |

| | | | |
|---|---|---|---|
| | 49 | 1.803764000 | -1.803764000 | -1.803764000 |
| | 83 | 4.105537000 | 0.000000000 | -1.500672000 |
| | 83 | 4.105537000 | 0.000000000 | 1.500672000 |
| | 83 | -4.105537000 | 0.000000000 | 1.500672000 |
| | 83 | -4.105537000 | 0.000000000 | -1.500672000 |
| | 83 | 1.500672000 | 4.105537000 | 0.000000000 |
| | 83 | -1.500672000 | 4.105537000 | 0.000000000 |
| | 83 | 1.500672000 | -4.105537000 | 0.000000000 |
| | 83 | -1.500672000 | -4.105537000 | 0.000000000 |
| | 83 | 0.000000000 | 1.500672000 | -4.105537000 |
| | 83 | 0.000000000 | -1.500672000 | -4.105537000 |
| | 83 | 0.000000000 | 1.500672000 | 4.105537000 |
| | 83 | 0.000000000 | -1.500672000 | 4.105537000 |
| | 83 | 0.000000000 | 0.000000000 | 0.000000000 |
| | Point 1 | 0.901879000 | 0.901879000 | 0.901879000 |
| | Point 2 | 0.000000000 | 0.901882000 | 0.901882000 |
| | Point 3 | 0.000000000 | 0.000000000 | 0.901882000 |
| | Point 4 | 0.000000000 | 0.000000000 | 1.803764000 |
| $C_3$ [Bi@In$_8$Bi$_{12}$]$^{5-}$ | 49 | 3.040492000 | 0.000000000 | -0.000002000 |
| | 49 | 1.109342000 | 0.917092000 | 2.757039000 |
| | 49 | -1.073806000 | 2.869464000 | 0.550589000 |
| | 49 | 1.109340000 | 1.929120000 | -2.172747000 |
| | 49 | 1.109340000 | -2.846214000 | -0.584295000 |
| | 49 | -1.073808000 | -0.957908000 | -2.760322000 |
| | 49 | -4.438442000 | 0.000001000 | 0.000002000 |
| | 49 | -1.073806000 | -1.911556000 | 2.209734000 |
| | 83 | 1.556771000 | -3.387264000 | 2.287434000 |
| | 83 | 3.359233000 | -1.021335000 | 2.784349000 |
| | 83 | -1.437743000 | 3.434480000 | -2.334508000 |
| | 83 | -3.221975000 | 1.028681000 | -2.718423000 |
| | 83 | 3.359231000 | -1.900651000 | -2.276679000 |
| | 83 | 1.556769000 | -0.287344000 | -4.077175000 |
| | 83 | -1.437740000 | 0.304505000 | 4.141602000 |
| | 83 | -3.221973000 | 1.839884000 | 2.250076000 |
| | 83 | -1.437743000 | -3.738984000 | -1.807091000 |
| | 83 | -3.221974000 | -2.868564000 | 0.468350000 |
| | 83 | 3.359232000 | 2.921985000 | -0.507674000 |

| | | | |
|---|---|---|---|
| | 83 | 1.556772000 | 3.674609000 | 1.789739000 |
| | 83 | -0.006498000 | 0.000000000 | 0.000000000 |
| | Point 1 | 1.523490000 | 0.000000000 | 0.000000000 |
| | Point 2 | 1.032976000 | 0.225458000 | 0.677789000 |
| | Point 3 | 0.488190000 | -0.477731000 | 0.552251000 |
| | Point 4 | 0.983250000 | -0.955821000 | 1.104916000 |
| $C_s$ [Bi@In$_8$Bi$_{12}$]$^{5-}$ | 49 | 0.425614000 | 2.448725000 | 1.683104000 |
| | 49 | 0.425614000 | 2.448725000 | -1.683104000 |
| | 49 | 2.488025000 | -0.476434000 | -1.791429000 |
| | 49 | 2.488025000 | -0.476434000 | 1.791429000 |
| | 49 | -2.446441000 | 0.479231000 | 1.828699000 |
| | 49 | -0.566474000 | -3.083910000 | 2.177940000 |
| | 49 | -0.566474000 | -3.083910000 | -2.177940000 |
| | 49 | -2.446441000 | 0.479231000 | -1.828699000 |
| | 83 | -3.523399000 | 2.566981000 | 0.000000000 |
| | 83 | -1.104788000 | 4.380606000 | 0.000000000 |
| | 83 | 3.737571000 | -2.475367000 | 0.000000000 |
| | 83 | 1.184573000 | -4.160561000 | 0.000000000 |
| | 83 | -0.837308000 | 1.346047000 | 4.155994000 |
| | 83 | 0.825897000 | -1.167008000 | 4.124252000 |
| | 83 | -0.837308000 | 1.346047000 | -4.155994000 |
| | 83 | 0.825897000 | -1.167008000 | -4.124252000 |
| | 83 | -3.456805000 | -2.274038000 | 1.494298000 |
| | 83 | -3.456805000 | -2.274038000 | -1.494298000 |
| | 83 | 3.390834000 | 2.361213000 | 1.499265000 |
| | 83 | 3.390834000 | 2.361213000 | -1.499265000 |
| | 83 | -0.021975000 | -0.097413000 | 0.000000000 |
| | Point 1 | 0.200020000 | 1.165421000 | 0.834786000 |
| | Point 2 | 0.196392000 | 1.144780000 | 0.000000000 |
| | Point 3 | -0.527144000 | 0.675669000 | 0.000000000 |
| | Point 4 | -1.032284000 | 1.448705000 | 0.000000000 |

## 11. References

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