SUPPLEMENTARY INFORMATION

**Figure 1.** Plot of ΔE (kJ/mol) versus $d$ (Å) with for the complex $[B_4(CH_2)_6]\cdots H_2$ for a range of distances 1.25 Å ≤ $d$ ≤ 4.0 Å and a step $\Delta d$ = 0.25 Å. MP2/aug-cc-pVDZ (red solid line) and MP2/aug-cc-pVTZ (green dashed line) computations.

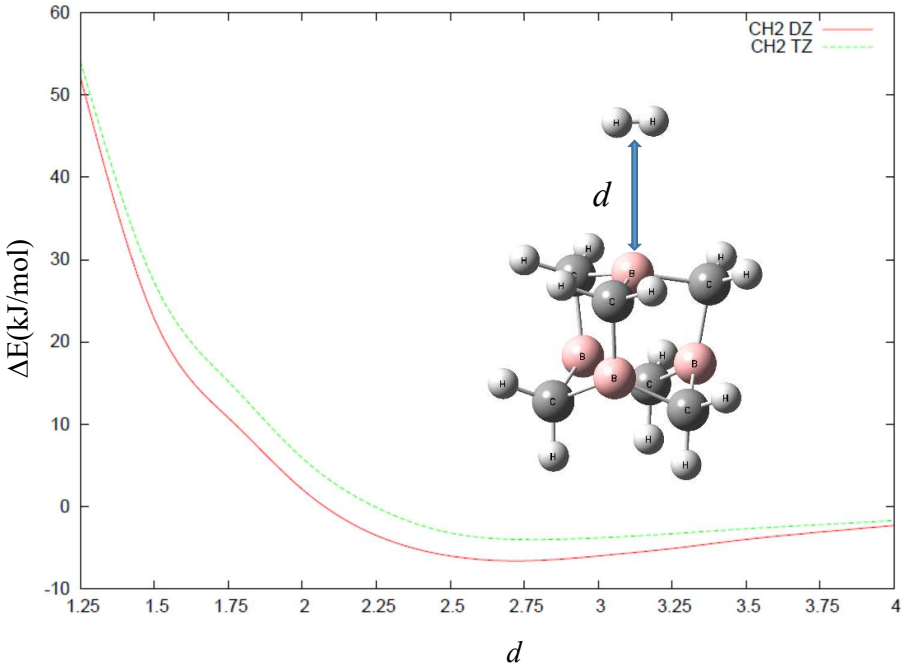
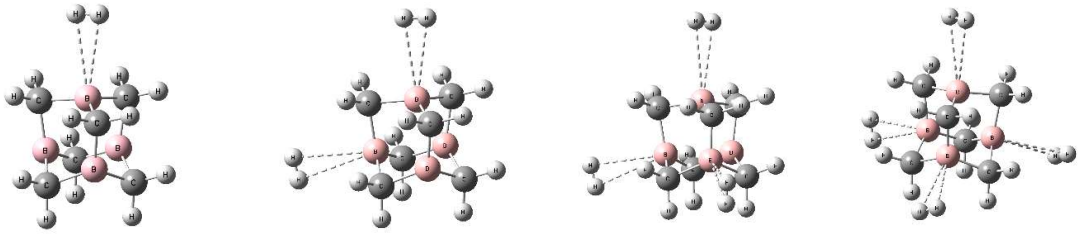


**Figure 2.** Optimized structures of the $B_4X_6{:}nH_2$ complexes ($n$ = 1-4), X = {$CH_2$ ; NH, PH; S} with MP2/aug-cc-pVDZ computations. All geometries corrrespond to energy minima.

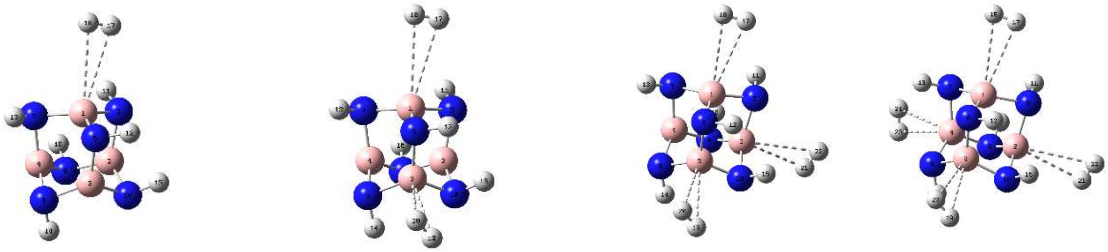
CARBON

(1:1) (1:2) (1:3) (1:4)



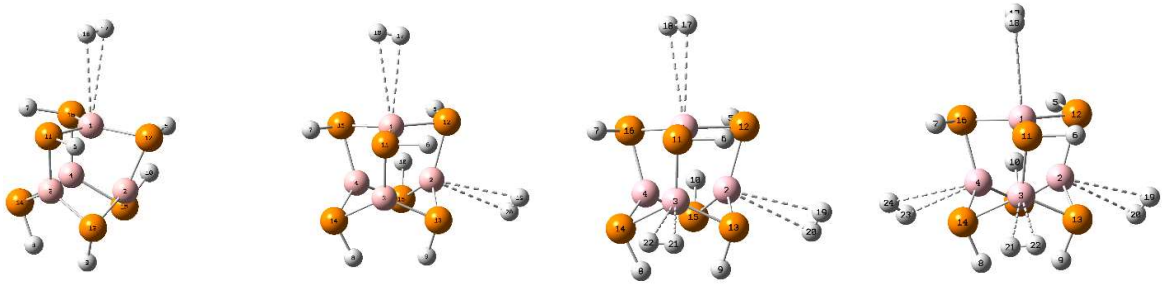
NITROGEN

(1:1) (1:2) (1:3) (1:4)



PHOSPHORUS

(1:1) (1:2) (1:3) (1:4)



SULPHUR

(1:1) (1:2) (1:3) (1:4)

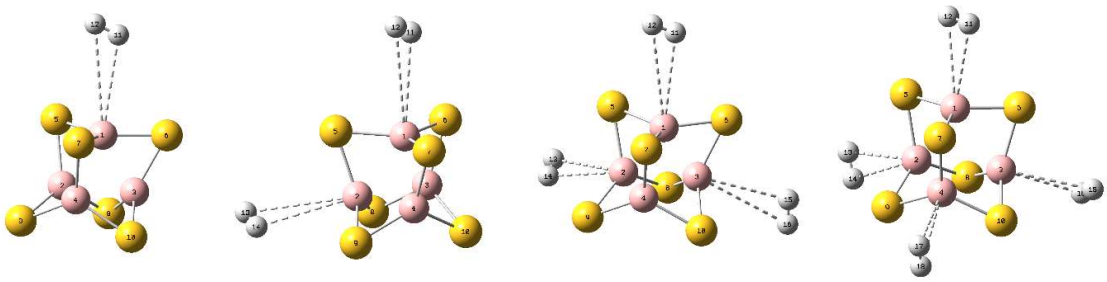


**Table 1.** Cartesian coordinates (Å) of MP2/aug-cc-pVDZ (left column) and MP2/aug-cc-pVTZ (right column) optimized geometries corresponding to energy minima of the adamantane analogue systems $B_4X_6$ with X = {$CH_2$, $SiH_2$; NH, PH; O, S}. All molecules have $T_d$ symmetry except $B_4X_6$ with X = {NH, PH} which have $C_1$ symmetry.

| $B_4(CH_2)_6$ (MP2/aug-cc-pVDZ) E = -334.198263 au | | | | $B_4(CH_2)_6$ (MP2/aug-cc-pVTZ) E = -334.498131 au | | | |
|---|---|---|---|---|---|---|---|
| Atom | X | Y | Z | Atom | X | Y | Z |
| B | -1.136610 | 0.656222 | -0.464019 | B | -1.126811 | 0.650564 | -0.460018 |
| B | 0.000000 | 0.000000 | 1.392057 | B | 0.000000 | 0.000000 | 1.380056 |
| B | 0.000000 | -1.312444 | -0.464019 | B | 0.000000 | -1.301129 | -0.460018 |
| B | 1.136610 | 0.656222 | -0.464019 | B | 1.126811 | 0.650564 | -0.460018 |
| C | 0.000000 | -1.573495 | 1.112629 | C | 0.000000 | -1.562461 | 1.104827 |
| C | -1.362686 | 0.786747 | 1.112629 | C | -1.353131 | 0.781230 | 1.104827 |
| C | -1.362686 | -0.786747 | -1.112629 | C | -1.353131 | -0.781230 | -1.104827 |
| C | 1.362686 | 0.786747 | 1.112629 | C | 1.353131 | 0.781230 | 1.104827 |
| C | 0.000000 | 1.573495 | -1.112629 | C | 0.000000 | 1.562461 | -1.104827 |
| C | 1.362686 | -0.786747 | -1.112629 | C | 1.353131 | -0.781230 | -1.104827 |
| H | 0.913880 | -2.074432 | 1.466845 | H | 0.904696 | -2.057529 | 1.454893 |
| H | -0.913880 | -2.074432 | 1.466845 | H | -0.904696 | -2.057529 | 1.454893 |
| H | -2.253451 | 0.245772 | 1.466845 | H | -2.234221 | 0.245274 | 1.454893 |
| H | -1.339571 | 1.828660 | 1.466845 | H | -1.329524 | 1.812254 | 1.454893 |
| H | -1.339571 | -0.773401 | -2.213025 | H | -1.329524 | -0.767601 | -2.193574 |
| H | -2.253451 | -1.301030 | -0.720665 | H | -2.234221 | -1.289928 | -0.716211 |
| H | 1.339571 | -0.773401 | -2.213025 | H | 1.329524 | -0.767601 | -2.193574 |
| H | 2.253451 | -1.301030 | -0.720665 | H | 2.234221 | -1.289928 | -0.716211 |
| H | 2.253451 | 0.245772 | 1.466845 | H | 2.234221 | 0.245274 | 1.454893 |
| H | 1.339571 | 1.828660 | 1.466845 | H | 1.329524 | 1.812254 | 1.454893 |
| H | 0.000000 | 1.546803 | -2.213025 | H | 0.000000 | 1.535203 | -2.193574 |
| H | 0.000000 | 2.602061 | -0.720665 | H | 0.000000 | 2.579856 | -0.716211 |
| $B_4(SiH_2)_6$ (MP2/aug-cc-pVDZ) E = -1840.120753 au | | | | $B_4(SiH_2)_6$ (MP2/aug-cc-pVTZ) E = -1840.397176 au | | | |
| Atom | X | Y | Z | Atom | X | Y | Z |
| B | -1.426555 | 0.823622 | -0.582388 | B | -1.413585 | 0.816133 | -0.577093 |
| B | 0.000000 | 0.000000 | 1.747166 | B | 0.000000 | 0.000000 | 1.731281 |
| B | 0.000000 | -1.647244 | -0.582388 | B | 0.000000 | -1.632267 | -0.577093 |
| B | 1.426555 | 0.823622 | -0.582388 | B | 1.413585 | 0.816133 | -0.577093 |
| H | 1.224976 | -2.707777 | 1.914687 | H | 1.217149 | -2.685999 | 1.899288 |
| H | -1.224976 | -2.707777 | 1.914687 | H | -1.217149 | -2.685999 | 1.899288 |
| H | -2.957491 | 0.293027 | 1.914687 | H | -2.934718 | 0.288916 | 1.899288 |
| H | -1.732515 | 2.414749 | 1.914687 | H | -1.717568 | 2.397082 | 1.899288 |
| H | -1.732515 | -1.000268 | -2.914876 | H | -1.717568 | -0.991638 | -2.893087 |
| H | -2.957491 | -1.707508 | -0.914498 | H | -2.934718 | -1.694360 | -0.905489 |
| H | 1.732515 | -1.000268 | -2.914876 | H | 1.717568 | -0.991638 | -2.893087 |
| H | 2.957491 | -1.707508 | -0.914498 | H | 2.934718 | -1.694360 | -0.905489 |
| H | 2.957491 | 0.293027 | 1.914687 | H | 2.934718 | 0.288916 | 1.899288 |
| H | 1.732515 | 2.414749 | 1.914687 | H | 1.717568 | 2.397082 | 1.899288 |
| H | 0.000000 | 2.000536 | -2.914876 | H | 0.000000 | 1.983277 | -2.893087 |
| H | 0.000000 | 3.415017 | -0.914498 | H | 0.000000 | 3.388721 | -0.905489 |
| Si | 0.000000 | -2.010143 | 1.421386 | Si | 0.000000 | -1.993206 | 1.409410 |
| Si | -1.740835 | 1.005071 | 1.421386 | Si | -1.726167 | 0.996603 | 1.409410 |
| Si | 1.740835 | 1.005071 | 1.421386 | Si | 1.726167 | 0.996603 | 1.409410 |
| Si | 0.000000 | 2.010143 | -1.421386 | Si | 0.000000 | 1.993206 | -1.409410 |
| Si | 1.740835 | -1.005071 | -1.421386 | Si | 1.726167 | -0.996603 | -1.409410 |
| Si | -1.740835 | -1.005071 | -1.421386 | Si | -1.726167 | -0.996603 | -1.409410 |
| $B_4(NH)_6$ (MP2/aug-cc-pVDZ) E = -430.581755 au | | | | $B_4(NH)_6$ (MP2/aug-cc-pVTZ) E = -430.950451 au | | | |
| Atom | X | Y | Z | Atom | X | Y | Z |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| B | 0.428828 | 0.868120 | 0.867229 | B | -0.421400 | -0.865243 | 0.864084 |
| B | -0.255164 | 0.543985 | -1.139263 | B | 0.251968 | -0.539565 | -1.133825 |
| B | 0.914321 | -0.931094 | -0.127376 | B | -0.913615 | 0.923466 | -0.123734 |
| B | -1.113359 | -0.567493 | 0.437212 | B | 1.108205 | 0.568894 | 0.431742 |
| N | 0.196881 | 1.739837 | -0.349048 | N | -0.187641 | -1.728615 | -0.345029 |
| N | 1.610113 | -0.038300 | 0.871548 | N | -1.598188 | 0.031577 | 0.868567 |
| N | -0.759737 | 0.331365 | 1.577572 | N | 0.759607 | -0.324822 | 1.565457 |
| N | -0.259514 | -1.759171 | 0.271759 | N | 0.253250 | 1.748699 | 0.267159 |
| N | -1.632776 | 0.034563 | -0.828728 | N | 1.620004 | -0.030222 | -0.827448 |
| N | 0.833906 | -0.426760 | -1.529083 | N | -0.836653 | 0.419261 | -1.515463 |
| H | -0.592499 | 2.363101 | -0.154899 | H | 0.596001 | -2.348049 | -0.156128 |
| H | 2.384061 | 0.434506 | 0.394590 | H | -2.370516 | -0.437844 | 0.402357 |
| H | -0.443606 | -0.235475 | 2.369867 | H | 0.450806 | 0.233107 | 2.357143 |
| H | -0.569568 | -2.271185 | -0.559643 | H | 0.556154 | 2.264014 | -0.555404 |
| H | 1.656990 | 0.141025 | -1.752872 | H | -1.652534 | -0.144890 | -1.739629 |
| H | -2.230615 | 0.829700 | -0.584192 | H | 2.221658 | -0.815238 | -0.592380 |

$B_4(PH)_6$ (MP2/aug-cc-pVDZ) E =-2147.787104 au

| Atom | X | Y | Z |
|---|---|---|---|
| B | 1.099006 | -0.667265 | 0.795708 |
| B | 0.693220 | 0.833045 | -0.970552 |
| B | -0.885016 | -1.006592 | -0.629905 |
| B | -0.890524 | 0.813190 | 0.868851 |
| H | 2.610400 | 1.385865 | 0.587744 |
| H | 1.216579 | -2.485568 | -0.999629 |
| H | -0.631917 | -0.949429 | 2.714271 |
| H | -2.883374 | 0.555435 | -0.704491 |
| H | -1.367731 | 0.630138 | -2.532482 |
| H | 0.753595 | 2.806646 | 0.646892 |
| P | 0.373915 | -2.302960 | 0.143231 |
| P | 2.421837 | 0.267180 | -0.281046 |
| P | -0.299802 | -0.290715 | -2.297989 |
| P | -2.408852 | -0.271275 | 0.359987 |
| P | -0.264175 | 2.328422 | -0.234719 |
| P | 0.191678 | 0.149015 | 2.308349 |

$B_4(PH)_6$ (MP2/aug-cc-pVTZ) E = -2148.103969 au

| Atom | X | Y | Z |
|---|---|---|---|
| B | 1.068570 | -0.703575 | 0.768142 |
| B | 0.717337 | 0.852451 | -0.891808 |
| B | -0.875588 | -0.946149 | -0.675723 |
| B | -0.892725 | 0.766889 | 0.870200 |
| H | 2.594540 | 1.320397 | 0.702885 |
| H | 1.199837 | -2.420571 | -1.097570 |
| H | -0.697645 | -1.074385 | 2.616559 |
| H | -2.849685 | 0.609581 | -0.727802 |
| H | -1.294373 | 0.762973 | -2.501773 |
| H | 0.759509 | 2.740759 | 0.791852 |
| P | 0.351986 | -2.281298 | 0.031728 |
| P | 2.418531 | 0.255563 | -0.213605 |
| P | -0.256854 | -0.176039 | -2.281994 |
| P | -2.406438 | -0.257961 | 0.299716 |
| P | -0.227963 | 2.314500 | -0.128975 |
| P | 0.134063 | 0.026113 | 2.283916 |

$B_4O_6$ (MP2/aug-cc-pVDZ) E = -549.777243 au

| Atom | X | Y | Z |
|---|---|---|---|
| B | 0.000000 | 0.000000 | 1.262242 |
| B | -1.030616 | 0.595026 | -0.420747 |
| B | 1.030616 | 0.595026 | -0.420747 |
| B | 0.000000 | -1.190053 | -0.420747 |
| O | -1.212041 | 0.699772 | 0.989627 |
| O | 1.212041 | 0.699772 | 0.989627 |
| O | 0.000000 | -1.399544 | 0.989627 |
| O | 0.000000 | 1.399544 | -0.989627 |
| O | -1.212041 | -0.699772 | -0.989627 |
| O | 1.212041 | -0.699772 | -0.989627 |

$B_4O_6$ (MP2/aug-cc-pVTZ) E = -550.250527 au

| Atom | X | Y | Z |
|---|---|---|---|
| B | 0.000000 | 0.000000 | 1.257649 |
| B | -1.026866 | 0.592861 | -0.419216 |
| B | 1.026866 | 0.592861 | -0.419216 |
| B | -0.000000 | -1.185722 | -0.419216 |
| O | -1.199450 | 0.692503 | 0.979347 |
| O | 1.199450 | 0.692503 | 0.979347 |
| O | 0.000000 | -1.385006 | 0.979347 |
| O | 0.000000 | 1.385006 | -0.979347 |
| O | -1.199450 | -0.692503 | -0.979347 |
| O | 1.199450 | -0.692503 | -0.979347 |

$B_4S_6$ (MP2/aug-cc-pVDZ) E = -2485.309501 au

| Atom | X | Y | Z |
|---|---|---|---|
| B | 0.000000 | 0.000000 | 1.255644 |
| B | -1.025229 | 0.591916 | -0.418548 |
| B | 1.025229 | 0.591916 | -0.418548 |
| B | 0.000000 | -1.183832 | -0.418548 |

$B_4S_6$ (MP2/aug-cc-pVTZ) E = -2485.678123 au

| Atom | X | Y | Z |
|---|---|---|---|
| B | 0.000000 | 0.000000 | 1.252465 |
| B | -1.022633 | 0.590417 | -0.417488 |
| B | 1.022633 | 0.590417 | -0.417488 |
| B | 0.000000 | -1.180835 | -0.417488 |

| | | | |
|---|---|---|---|
| S | -1.583624 | 0.914305 | 1.293023 |
| S | 1.583624 | 0.914305 | 1.293023 |
| S | 0.000000 | -1.828611 | 1.293023 |
| S | 0.000000 | 1.828611 | -1.293023 |
| S | -1.583624 | -0.914305 | -1.293023 |
| S | 1.583624 | -0.914305 | -1.293023 |

| | | | |
|---|---|---|---|
| S | -1.564782 | 0.903427 | 1.277639 |
| S | 1.564782 | 0.903427 | 1.277639 |
| S | 0.000000 | -1.806855 | 1.277639 |
| S | 0.000000 | 1.806855 | -1.277639 |
| S | -1.564782 | -0.903427 | -1.277639 |
| S | 1.564782 | -0.903427 | -1.277639 |