**Electronic Supporting Information**

# Substitution of the Laser Borane *anti*-$B_{18}H_{22}$ with Pyridine: A Structural and Photophysical Study of some Unusually Structured Macropolyhedral Boron Hydrides

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**Content**



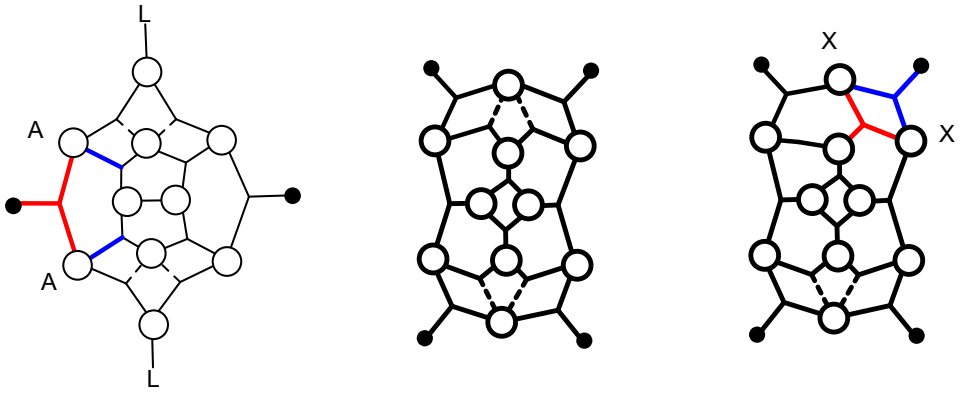
**References**

**SI 1**. Selected crystallographically determined interatomic distances for the molecular structure of $B_{18}H_{20}Py_2$ **2**; additional values may be found in the crystallographic cif file.

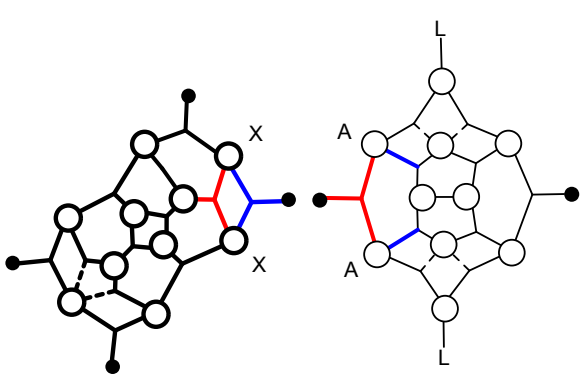
| | | | |
|---|---|---|---|
| B5-B6 | 1.870(2) | B6′-N61 | 1.566(2) |
| B5-B10 | 2.007(2) | B9′-N91 | 1.568(2) |
| B6-B7 | 1.851(2) | B5-B9′ | 1.935(2) |
| B7-B8 | 1.919(2) | B8′-B9′ | 1.851(2) |
| B8-B9 | 1.814(3) | B7′-B8′ | 1.880(2) |
| B9-B10 | 1.797(2) | B6′-B7′ | 1.835(2) |
| | | B6-B6′ | 1.899(2) |

**SI 2**. Simple factorisation of the electronic structure of compound **2**.

Rationalisation of the overall electronic structure of compound **2** can be found by reference to simple Lipscomb-type semi-localised bonding schemes[a,b] of its constituent conjoined two subclusters. Such representations for compound **5** and $B_{10}H_{14}$ are in *schematic bonding diagrams* **V** and **VI** respectively. For the two-atoms-in-common cluster fusion mode, a common instance is when the B-H-B three-centre bridge of one subcluster model mimics the B-B-B three-centre bond in the other subcluster model, and the latter formally replaces the former.[c,d] In order to accommodate this, the partial three-centre bonding character within the *nido*-decaboranyl subcluster **VI** needs to be localised into one two-centre and one three-centre bond (schematic **VII**). This breaks the bonding symmetry and thence significantly perturbs the internal molecular orbital structure; this change in internal 'intracluster' bonding will change the chemical properties of the cluster. The formal B-B-B fusion replacement of B-H-B then models a bonding description for compound **5** (Schematics **VIII** and **IX**). It can be seen that the electronic structure of the *arachno* subcluster retains its single-cluster characteristics, in contrast to that of the *nido* residue, which is perturbed near the site of fusion.

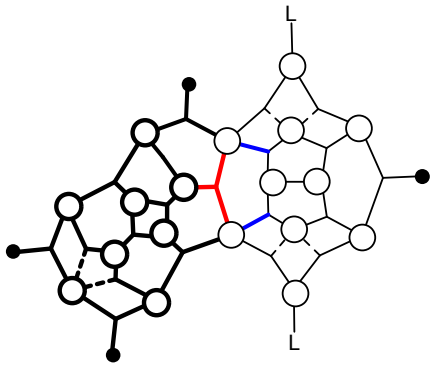


**V** **VI** **VII**









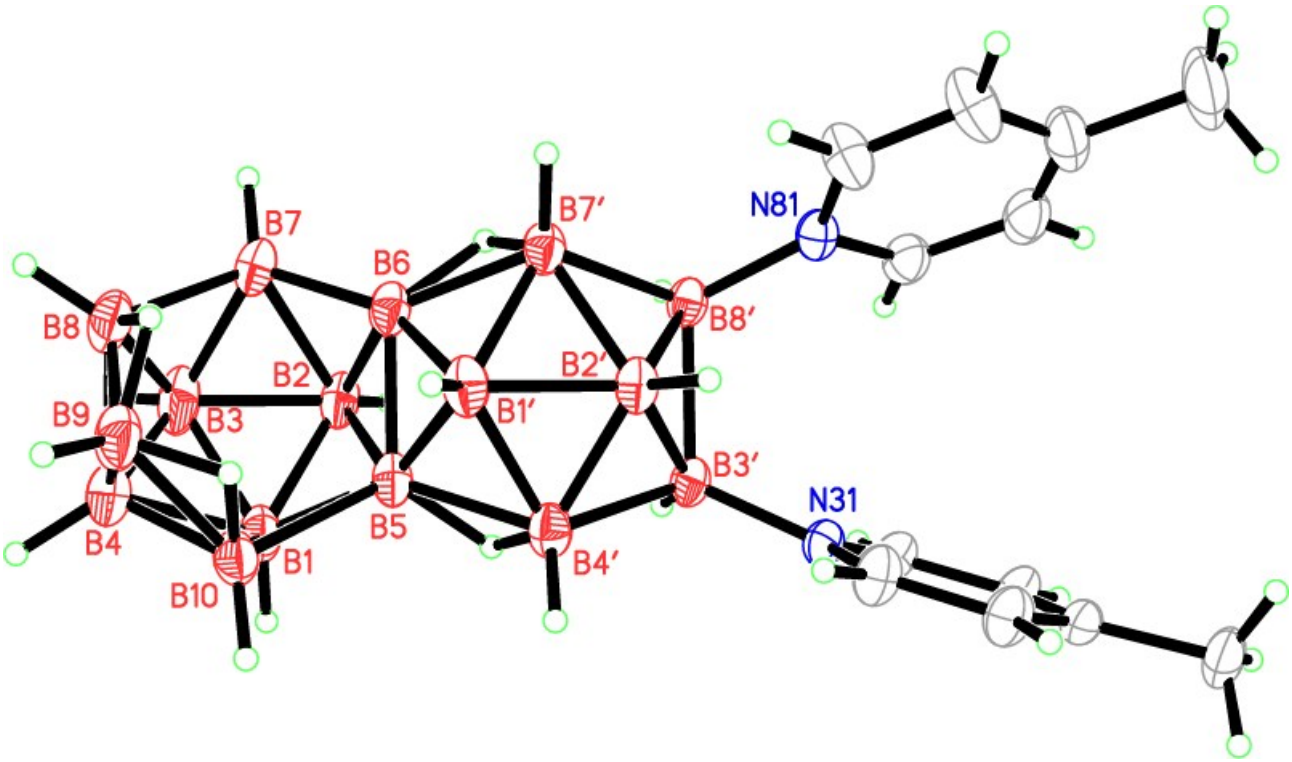

**VIII** **IX**

**SI 3**. Selected crystallographically determined interatomic distances for the molecular structure of $B_{16}H_{18}Py_2$ **3a** and $B_{16}H_{18}Pic_2$ **3b**; additional values may be found in the crystallographic cif files.

| | **3a** | **3b** | | **3a** | **3b** |
|---|---|---|---|---|---|
| B5-B6 | 1.777(4) | 1.781(3) | B3′-N31 | 1.566(3) | 1.563(2) |
| B5-B10 | 1.899(4) | 1.942(4) | B8′-N81 | 1.571(3) | 1.565(2) |
| B6-B7 | 1.658(5) | 1.692(3) | B5-B4′ | 1.830(3) | 1.832(3) |
| B7-B8 | 1.850(6) | 1.819(4)* | B7′-B8′ | 1.894(3) | 1.885(3) |
| B8-B9 | 1.800(7) | 1.856(7)* | B3′-B4′ | 1.882(3) | 1.874(3) |
| B9-B10 | 1.774(5) | 1.785(6) | B3′-B8′ | 1.885(4) | 1.911(3) |
| | | | B6-B7′ | 1.806(4) | 1.807(3) |

*these crystallographically derived distances for **3b** severely affected by crystallographic disorder.

**SI 4**. Molecular structure of **3b**.



**SI 5**. Selected measured $^{11}B$ and $^{1}H$ NMR parameters for $B_{16}H_{18}(NC_6H_4\text{-}4\text{-}isoPr)_2$ (compound **3c**) and $B_{16}H_{18}(NC_6H_4\text{-}4\text{-}Me)_2$ (compound **3b**) in $(CD_3)_2CO$ solution at *ca*. 293 K, together with their tentative assignments.

| | $B_{16}H_{18}(NC_6H_4\text{-}4\text{-}isoPr)_2$ **3c** | | $B_{16}H_{18}(NC_6H_4\text{-}4\text{-}Me)_2$ **3b** | |
|---|---|---|---|---|
| Assignment | $\delta(^{11}B)$/ppm | $\delta(^{1}H)$/ppm | $\delta(^{11}B)$/ppm | $\delta(^{1}H)$/ppm |
| B(6) | +21.8 | *conjuncto* site | +21.7 | *conjuncto* site |
| BH(3) | +4.1 | +2.94 | +4.0 | +2.95 |
| BH(10) | +1.1 | +3.13 | ca. +0.9 | +3.13 |
| BH(2′) | +0.2 | +3.21 | –0.12 | +3.25 |
| B(5) | –6.5 | *conjuncto* site *ca*. | –7.0 | *conjuncto* site |
| BH(1)(8) and (9) | *ca.* –8.5 | +2.62 | *ca*. –8.5 | +2.59 |
| | *ca.* –8.5 | +2.11 | *ca*. –8.5 | +2.28 |
| | *ca.* –8.5 | +2.56 | *ca.* –8.5 | +2.59 |
| BH(7) | –10.1 | +2.48 | –10.1 | +2.50 |
| BH(8′) | –15.4 | +2.28 | –15.5 | +2.34 |
| BH(3′) | –18.6 | +1.98 | –18.7 | +2.00 |
| BH(7) | –23.8 | +2.02 | –23.9 | +2.00 |
| BH(4′) | –26.9 | +1.60 | –27.0 | +1.58 |
| BH(2) | –27.8 | -0.63 | –27.7 | -0.62 |
| BH(4) | –43.2 | +0.19 | –43.3 | +0.20 |
| BH(1’) | –46.0 | –1.25 | –46.1 | –1.23 |
| mH(6,7′) | - | –1.74 | | –1.71 |
| mH(9,10) | - | –1.74 | | –1.71 |
| mH(8,9) | - | –2.86 | | –2.84 |
| mH(5,4′) | - | +0.82 | | +0.85 |
| C6H4 | - | +7.6 (4H), +8.6 (4H) | | +7.6 (4H), +8.6 (4H) |
| CH | | +2.92 (2H) | | - |
| Me | | +1.27 (12H) | | +2.54(6H) |

**SI 6**. Selected crystallographically determined interatomic distances for the molecular structure of $B_{18}H_{20}$Py **4**; additional values may be found in the crystallographic cif file.

| | | | |
|---|---|---|---|
| B5-B6 | 1.807(2) | B8′-N81 | 1.549(2) |
| B5-B10 | 1.969(2) | B5′-B10′ | 2.037(3) |
| B6-B7 | 1.834(2) | B5-B5′ | 1.814(2) |
| B7-B8 | 1.950(2) | B6-B8′ | 1.831(2) |
| B8-B9 | 1.807(2) | B8′-B9′ | 1.650(2) |
| B9-B10 | 1.782(2) | B9′-B10′ | 1.784(2) |

**SI 7**. Measured $^{11}$B and $^{1}$H NMR chemical shifts and tentative assignments for *anti*-$B_{18}H_{20}$-8′-Py (compound **4**); $CD_2Cl_2$ solution.

| Provisional assignment | δ($^{11}$B) | δ($^{1}$H) | correlations with μH |
|---|---|---|---|
| BH(4) | –42.9 | +0.18 | |
| BH(4′) | –35.8 | –0.06 [#] | |
| BH(2) | –32.1 | –0.06 [#] | |
| BH(2′) | –30.0 | +0.61 | |
| BH | –20.2 | +2.20 | μH –1.44 |
| BH(7) | –17.0 | +2.56 | μH –0.42 |
| BH | –15.5 | +1.99 | |
| BH | –6.9 | – | μH –1.44 |
| B | –4.4 | – | μH –2.77 |
| BH(1) | –0.6 | +3.05 | |
| BH(9) | +0.3 | +3.41 | μH –2.77, +0.01 |
| BH | +1.4 | +3.78 | μH –2.43 |
| B, BH (10), BH(6) | ca. +6.7 [*] | –, +3.83, +3.41 | μH –0.42, +0.01 |
| B | +9.4 | – | |
| BH(3) | +10.7 | –3.62 | |
| BH(5) | +11.3 | – | |

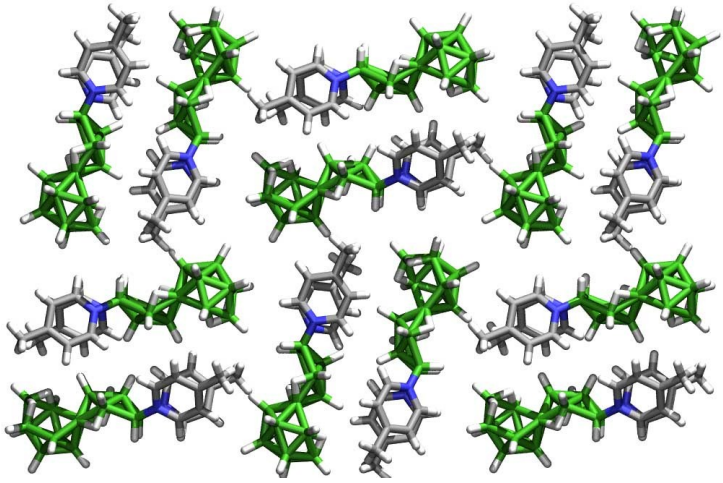
*Notes:* [#] two $^{1}$H resonances by chance coincident. [*] Three $^{11}$B resonances by chance coincident.

**SI 8**. Comparison $^{11}B$ and $^{1}H$ NMR chemical shifts and assignments for neutral [5′-{(MeNH)$C_3N_2HMe_2$}-*anti*-$B_{18}H_{20}$] (data from reference 6) and for the [*anti*-$B_{18}H_{21}$]- anion (data from reference 16).

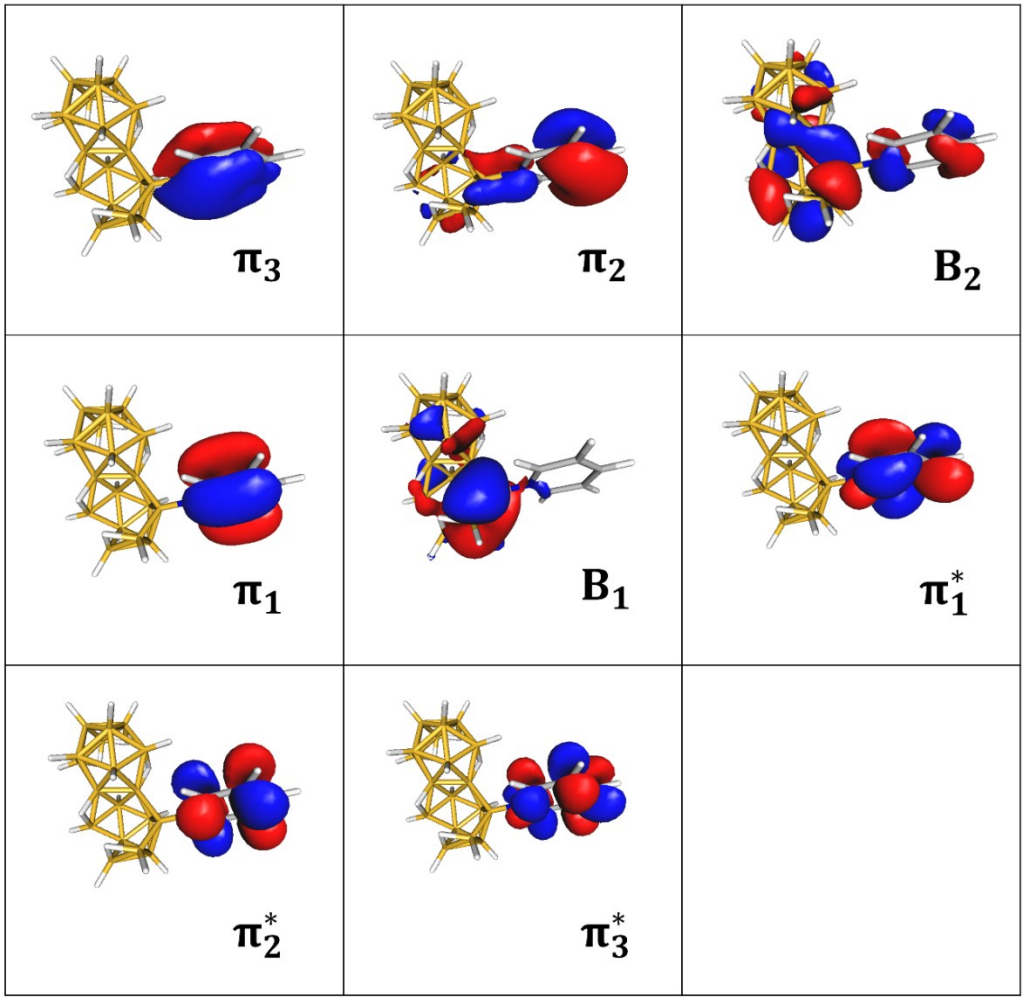
| | [{(MeNH)$C_3N_2HMe_2$}$B_{18}H_{20}$] [#] | | [*anti*-$B_{18}H_{21}$]$^-$ anion [*] | |
|---|---|---|---|---|
| Assignment [6,16] | δ($^{11}B$)/ppm | δ($^{1}H$)/ppm | δ($^{11}B$)/ppm | d($^{1}H$)/ppm |
| BH(1) | –3.4 | +2.72 | –4.5 | +2.64 |
| BH(2) | –29.5 | –0.89 | –29.2 | -0.92 |
| BH(3) | +13.5 | +3.55 | +13.4 | +3.50 |
| BH(4) | –38.9 | +0.19 | –41.1 | +0.17 |
| BH(5/6′) | +15.3 | *conjuncto* site | +17.0 | *conjuncto* site |
| BH(6,7′) | -0.2 | *conjuncto* site | +0.1 | *conjuncto* site |
| BH(7) | –12.0 | +2.80 | –13.6 | +2.62 |
| BH(8) | –9.2 | +2.55 | –10.0 | +2.44 |
| BH(9) | –0.2 | +2.90 | –1.2 | +2.94 |
| BH(10) | +8.3 | +3.20 | +9.3 | +3.73 |
| BH(1′) | +5.5 | +3.21 | +5.1 | +2.98 |
| BH(2′) | –24.2 | –0.01 | –24.1 | -0.42 |
| BH(3′) | –12.0 | +1.90 or +2.20 | –10.6 | +2.11 |
| BH(4′) | –41.6 | +0.32 | –39.2 | +0.19 |
| BH(5′) | –5.1 | ligand site | –3.4 | +2.76 |
| BH(8′) | +4.1 | +3.65 | +3.2 | +3.51 |
| BH(9′’) | –7.6 | +2.65 | –7.7 | +2.55 |
| BH(10′) | –12.0 | +1.90 or +2.20 | –13.0 | +1.86 |
| μH(8,9) | | –2.92 | | –3.31 |
| μH(9,10) | | –1.23 | | –1.03 |
| μH(6/7′,7) | | –1.80 | | –1.88 |
| μH(8′,9′) | | –1.38 | | –1.59 |
| μH(9′,10′) | | –3.60 | | –3.90 |

*Notes:* [#] Ligand species: $(CD_3)_2CO$ solution. [*] Anion: $CD_2Cl_2$ solution; $[C_{10}H_6(NMe_2)_2H]^+$ salt.

**SI 9.** Crystal structure diagram for compound **3b**.



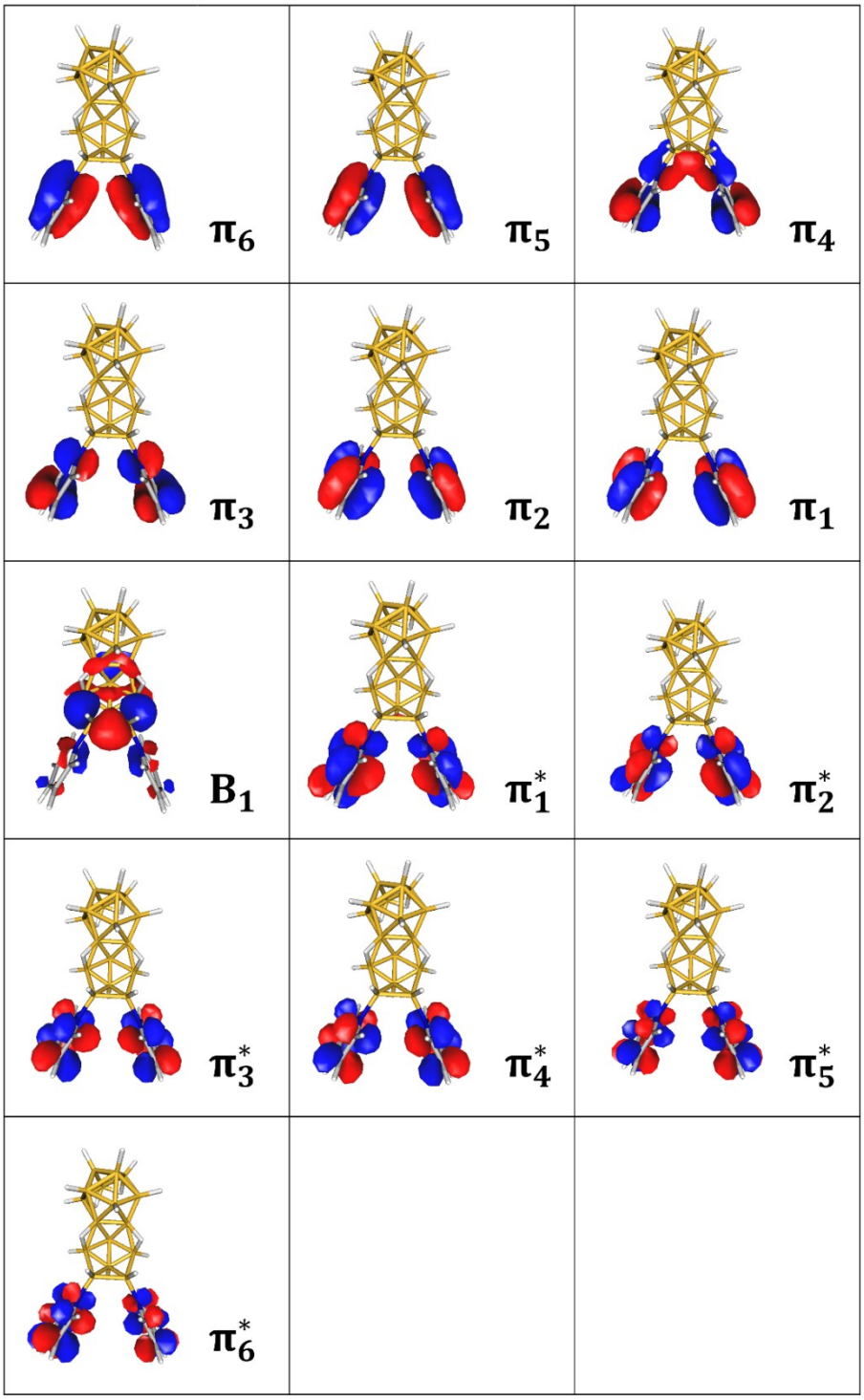
**SI 10**. CASSCF natural orbitals that compose the CAS active space of $B_{18}H_{20}Py$, compound **4**, at the $(S_0)_{min}$ structure.



**SI 11**. Full rationale for the absorption characteristics of compound **4**.

The CASPT2(IPEA=0.25) calculated energy for the most probable electronic transition, 4.54 eV (273 nm), with an *f* of 0.2265, has a high value as compared to the experimentally measured absorption band with a band maximum recorded at 320 nm (see Figure 7). The lowest-energy transition computed at 3.69 eV (336 nm) has a much lower *f* value (0.0082). The calculation of more states (up to eight) and the use of the multi-state CASPT2 method,[e] which provides more correlated wave functions, do not change the scenario. CASPT2(IPEA=0.00) computations have been also carried out giving rise to vertical transition energies of 3.27 and 3.95 eV (379 and 314 nm) for the excitations to $S_1$ and $S_2$, respectively. The *f* values are 0.0073 and 0.1972, respectively. Taking into account both group of values, we can assign the $S_0 \rightarrow S_2$ electronic transition to the band maximum and the $S_0 \rightarrow S_1$ one to the broad curve of the band appearing at lower energies. Meanwhile, transitions related to $S_3$ and $S_4$ might be responsible for the absorbance appearing in the 250-300 nm range. To be consistent with our previous work,[f] we continue the theoretical analysis on the photophysics of the system using the CASPT2(IPEA=0.25) level of theory. Even though this level shows a worse agreement with the experimental data as compared to the outcomes of the CASPT2(IPEA=0.00) level, the IPEA parameter only provides with a systematic shift of the energies and then the qualitative behavior is maintained.

**SI 12**. CASSCF natural orbitals that compose the CAS active space of $B_{16}H_{18}Py_2$, compound **4**, at the $(S_0)_{min}$ structure.



**References**


a. See, for example, page 71 in W. N. Lipscomb, *Boron Hydrides*, Benjamin, New York and Amsterdam, 1963.

b. See, for example, page 59 in E. L. Muetterties (Ed), *Boron Hydride Chemsitry*, Academic, New York, San Francisco and London, 1975.

c. L. Barton, J. Bould, J. D. Kennedy and N. P. Rath, *J. Chem. Soc., Dalton Trans.,* 1996, 3145-3149.

d. S. L. Shea, P. I. MacKinnon, M. Thornton-Pett and J. D. Kennedy, *Inorg. Chim. Acta, Special Issue for Gordon Stone*, 2005, **358**, 1709-1714.

e. J. Finley, P.-Å. Malmqvist, B. O. Roos, and L. Serrano-Andrés, *Chem. Phys. Lett.,* 1998, **228**, 299.

f. M. G. S. Londesborough, J. Dolanský, L. Cerdán, K. Lang, T. Jelínek, I. Garcia-Moreno, J. M. Oliva, D. Hnyk, D. Roca-Sanjuán, J. Martinčík, M. Nikl, and J. D. Kennedy, *Adv. Opt. Mater.,* 2017, **5**, 1600694.