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Substitution of the Laser Borane *anti*-B₁₈H₂₂ with Pyridine: A Structural and Photophysical Study of some Unusually Structured Macropolyhedral Boron Hydrides

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Reaction of *anti*-B₁₈H₂₂ **1** with pyridine in neutral solvents gives sparingly soluble B₁₆H₁₈-3',8'-Py₂ **3a** as the major product (ca. 53 %) and B₁₈H₂₀-6',9'-Py₂ **2** (ca. 15 %) as the minor product, with small quantities of B₁₈H₂₀-8'-Py **4** (ca. 1 %) also being formed. The three new compounds **2**, **3a** and **4** are characterised by single-crystal X-ray diffraction analyses and by multinuclear multiple-resonance NMR spectroscopy. Compound **2** is of ten-vertex *nido* : ten-vertex *arachno* two-atoms-in-common architecture, long postulated for a species with borons-only cluster constitution, but previously elusive. Compound **3a** is of unprecedented ten-vertex *nido* : eight-vertex *arachno* two-atoms-in-common architecture. The single-crystal X-ray diffraction analysis for the picoline derivative B₁₆H₁₈(NC₅H₄Me)₂ **3b**, similarly obtained, is also presented. B₁₈H₂₀Py **4** is also previously unreported but is of known ten-vertex *nido* : ten-vertex *nido* two-atoms-in-common architecture of *anti* configuration, but now with the pyridine ligand positioned differently to other reported examples of B₁₈H₂₀L compounds. Factors behind the remarkably low solubility of **3a** and **3b** are elucidated in terms of electrostatic potential (ESP) calculations, polarity, and Van-der-Waals complementarities. In view of contemporary developing high interest in the fluorescent properties of macropolyhedral boron-containing species, a detailed assessment of the photophysical characteristics of **3a** and **4** is also presented. In contrast to the thermochromic fluorescence of **2** (from 620 nm brick-red at room-temperature to 585 nm yellow at 8 K, quantum yield 0.15), compound **3a** is only weakly phosphorescent in the yellow region (590 nm, quantum yield 0.01), whereas compound **4** exhibits no luminescence. The far more photoactive nature of compound **2** is associated with S₁ excited-state minima structures that differ from each other only by the relative rotational positions of the pyridine substituents on its disubstituted ten-vertex {*arachno*-B₁₀Py₂}-subcluster. The wavelength and relative intensity of fluorescence from these structures depends on the rotational positions of the pyridine ligands, which in turn are influenced by temperature and/or rotational inhibition in the solid-state.

Introduction

Boron, like carbon, forms an extensive series of hydrides and heteroatom derivatives of hydrides. Organic chemistry builds upon the ability of smaller hydrocarbon-based units to join together to form chains and rings. Otherwise equivalent smaller boron hydride units are of polyhedral cage constitution rather than chains and rings, and the study and usage of these as single-cage species dominates the area. A comprehensive monograph on polyhedral boron-containing cluster chemistry is lacking, but a recently compiled survey¹ of the subdiscipline of carborane chemistry well illustrates the single-cluster

dominance. For the extent of boron-hydride-based chemistry to compete with that of organic chemistry, at least in structural terms, individual cage units need to join together to give larger molecular assemblies. Here the term 'macropolyhedral' has been coined² to categorize compounds that (*a*) contain more than one boron-hydride-based cage and in which (*b*) individual cages fuse to each other with two or more cage atoms held in common so that the cluster multicentre bonding characteristics extend through, and are part of, the inter-cage link. One way of developing this area is to examine the chemistry of pre-formed macropolyhedral compounds. In a seminal report, over 40 years ago now, Siedle and Todd examined some reaction chemistry of the two most readily available macropolyhedral binary boron hydrides, the *anti* and *syn* isomers of B₁₈H₂₂ (also known as *n*-B₁₈H₂₂ and *iso*-B₁₈H₂₂ respectively).³ Their work tentatively identified a macropolyhedral carbaborane and a macropolyhedral metallacarborane, as well as several macropolyhedral metallaboranes, but no definitive molecular structural work was presented. Aspects of these chemistries have subsequently been developed by others, often by us in our own laboratories.⁴ Particularly interesting is the utilisation of *anti*-B₁₈H₂₂ itself as the optical gain medium in a non-organic

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borane-based laser device.⁵ This seems to be a rare incidence of photoactive behaviour from a binary borane system. Indeed, with regards to the boron hydrides – or boranes – as luminescent materials,⁶ the general focus of work has been instead on the isomers of *closo*-dicarbododecaborane (conveniently referred to here as ‘carborane’), $C_2B_{10}H_{12}$, as enhancers of the fluorescent properties of various luminescent organic polymers or fluorophores.⁷ Additionally, the principle of aggregation-induced-emission (AIE) claims enhanced luminescence of π -conjugated organic systems that are connected to *ortho*-carborane, $1,2-C_2B_{10}H_{12}$.^{8,9} Here the advantage of the carboranyl moieties being their suppression of intermolecular interaction between the luminescent π -conjugated organic ligands owing to the three-dimensional structure of the icosahedral cluster. Carborane-based dyads and triads that participate in photon-induced electron transfer¹⁰ have also been made and studied,¹¹ and, more recently, multiple emissions from single-molecules have led to efficient white-light production from *o*-carborane-based luminophors.¹² By itself, however, *ortho*-carborane shows no photoluminescence in solution¹³ and just a blue-green phosphorescence in the solid-state at temperatures of 77 K.¹³ Indeed, of all the known binary boranes (compounds consisting only of boron and hydrogen), *anti*- $B_{18}H_{22}$ – the centrosymmetric isomer of octadecaborane(22) – is the only one known to have the property of fluorescence. This attribute was first noticed by Hawthorne *et al.* some years ago,¹⁴ and subsequently described comprehensively, including a full consideration of all transitions between ground and excited electronic states of the molecule.¹⁵ In this latter study, *anti*- $B_{18}H_{22}$ was revealed to exhibit an intense blue fluorescence at 406 nm with a quantum yield approaching unity ($\Phi_F = 0.97$).¹⁵ With respect to the successful combination of carborane cluster and π -delocalised organic systems in one molecule, as mentioned above, we became interested in such a combination with the macropolyhedral borane species *anti*- $B_{18}H_{22}$.

From the reaction of *anti*- $B_{18}H_{22}$ **1** with pyridine (abbreviated as Py in formulae in this present report) Siedle and Todd identified an orange-red species, of proposed formulation $B_{18}H_{20}Py_2$ and of asymmetric constitution, as well as noting a pale-yellow crystalline material **3** that dissolved only in polar solvents.³ No definitive structural work, and thence conclusions, about the molecular structures of these species was presented. Here we report a re-examination of this reaction, from which we confirm the empirical formulation of the bright orange-red $B_{18}H_{20}Py_2$ species **2** and now show that it is of rare *arachno* ten-vertex : *nido* ten-vertex two-atoms-in-common macropolyhedral constitution. We also determine the identity of the yellow crystalline material as $B_{16}H_{18}Py_2$ **3a**, also of unprecedented constitution, now ten-vertex *nido* : eight-vertex *arachno*, with an unexpectedly very low solubility in common solvents. We also identify an additional minor product as $B_{18}H_{20}-8'-Py$ **4**, previously unreported, but of established ten-vertex *nido* : ten-vertex *nido* eighteen-boron architecture that has precedent in *anti*- $B_{18}H_{22}$ itself, and that is closely related to the ligand derivative $B_{18}H_{20}\{(MeNH)C_3N_2HMe_2\}$ that has an unusual N-heterocyclic carbene (NHC) ligand.¹⁶ Some preliminary

summary general aspects have been previously mentioned at a conference.¹⁷

Results and discussion

Synthesis and Structural Characterisation. The reaction of *anti*- $B_{18}H_{22}$ **1** with an excess of pyridine (Py) in refluxing benzene or chloroform results in the formation of $B_{16}H_{18}Py_2$ **3a** as a pale yellow solid precipitate (ca. 53 % yield), together with an amber solution that contains brick-red $B_{18}H_{20}Py_2$ **2** (ca. 15 %) and a trace quantity of yellow $B_{18}H_{20}-8'-Py$ **4** ($\leq$ ca. 1 %).[‡] Known $BH_3 \cdot Py$ and the $[anti-B_{18}H_{21}]^-$ anion are also present in the reaction product mixture. Compounds **2** and **4** can be separated and purified by column and thin layer chromatography on silica-gel. Pale yellow **3a** is remarkably insoluble in common solvents such as chloroform, benzene and dichloromethane, but dissolves in dimethylformamide from which pure crystals may be obtained by vapour diffusion of diethyl ether or dichloromethane. Pure crystals of **2** and **4** were obtained from concentrated solutions in dichloromethane by overlaying with hexane. All three compounds were characterised by all-atom molecular structures as determined by single-crystal X-ray diffraction analysis, and by ^{11}B and 1H single- and multiple-resonance NMR spectroscopy which in each case confirmed the identity of the selected single crystals with the bulk samples.

Figure 1 - The crystallographically determined molecular structure of $B_{18}H_{20}Py_2$ **2**. The majority of the B-B interatomic distances fall within a usual borane cluster range of 1.74 Å – 1.88 Å with the following main exceptions: B5-B9' = 1.94 Å; B6-B6' = 1.90 Å within the *arachno* subcluster, and with B5-B10 = 2.01 Å and B7-B8 = 1.92 Å in the *nido* subcluster, typical of longer *nido*-decaboranyl 'gunwale' connectivities. No anomalies for the C-C, C-N and B-N distances were apparent. Other dimensions may be found in the supplementary information (SI 1). Displacement ellipsoids are shown at the 50% probability level in these Figures.

A representation of the molecular structure of brick-red $B_{18}H_{20}Py_2$ **2** is in Figure 1. It is seen to consist of a *nido* ten-vertex subcluster and an *arachno* ten-vertex subcluster, respectively modelled by the single-cluster species *nido*- $B_{10}H_{14}$ and 6,9- Py_2 -*arachno*- $B_{10}H_{12}$ **5**, fused with two boron atoms held in common (schematic connectivity diagrams I and II). The fusion of these two classic *nido* and *arachno* ten-vertex all-boron cluster types, although often speculated upon, has hitherto been elusive, although an analogous macropolyhedral thiaborane, the $[SB_{17}H_{19}]^-$ anion, fusing *nido* ten-vertex borane and *arachno*

ten-vertex thiaborane units (schematic **III**), has been isolated and characterised.¹⁸

The dimetallaborane [(PMe₂Ph)₃Pt₂B₁₆H₁₈(PMe₂Ph)], fusing *nido* ten-vertex {PtB₉} and *arachno* ten-vertex {Pt₂B₈} units (schematic **IV**), is also related, but somewhat more distantly.¹⁹ Here it may be noted that macropolyhedral thiaboranes and transition-element metallaboranes have proved to be more flexible than corresponding binary boranes in their reaction chemistry and structural variants, a versatility probably facilitated by the flexible valency states of sulphur and of transition-element centres.^{20,21} It also may be noted in this context that attempts to make the purely binary boron hydride analogue of **2**, viz. the [B₁₈H₂₂]²⁻ dianion, by reduction of *anti*-B₁₈H₂₂ **1**, surprisingly led instead in the isolation of the macropolyhedral [OB₁₈H₂₁]⁻ oxaborane monoanion.²²

Measured ¹H and ¹¹B NMR data for B₁₈H₂₀Py₂ **2** are in Table 1. Assignments were made by the established procedure^{23,24} and by combining results from ¹¹B and ¹H single- and multiple-resonance spectroscopies.^{25,26} Stick representations of the chemical shifts and relative intensities are shown in Figure 2, together with those of *nido*-B₁₀H₁₄, *anti*-B₁₈H₂₂ **1**, and 6,9-Py₂-*arachno*-B₁₀H₁₂ **5** for comparison. There is a significant change when B₁₀H₁₄ and *anti*-B₁₈H₂₂ **1** are compared,²⁶ although the general *nido* pattern, with ¹¹B(2,4) to high field, ¹¹B(5,7,8 and 10) at intermediate field, and ¹¹B(1 and 3), together with ¹¹B(6 and 9), tending towards lower field, is traceable. This pattern follows through to the *nido* subcluster of B₁₈H₂₀Py₂ **2** but the overall differences from *nido*-B₁₀H₁₄ itself are now more marked. Compared to *nido*-B₁₀H₁₄, therefore, the *nido* subcluster of compound **2** shows quite a considerable change. By contrast, comparison of the shieldings of the single-cluster *arachno* model **5** with the *arachno* subcluster of **2** shows much less perturbation.²⁷ Since magnetic nuclear shieldings depend intimately and directly upon molecular-orbital structure, similarities in shielding patterns imply similarities in molecular-orbital structure. On this criterion, the *arachno* subcluster of **2**

is electronically much more similar to that of 6,9-Py₂-*arachno*-B₁₀H₁₂ **5** than the *nido* subcluster is to that of *nido*-B₁₀H₁₄. For an expansion on this discussion and a rationalisation of the electronic characteristics of the two constituent subclusters of compound **2**, refer to Supporting Information, **SI 2** (schematic structures **V** to **IX**).

One overall inference is that the physicochemical characteristics of the *arachno* single-cluster model 6,9-Py₂-*arachno*-B₁₀H₁₂ **5** should be much better mimicked in B₁₈H₂₀Py₂ **2** than those of the *nido*-B₁₀H₁₄ single-cluster model **1**. As far as the *arachno* subcluster is concerned, the eight-boron non-common {B₈H₁₁} element of the *nido* subcluster of **2** is effectively behaving as a substituent that bridges the B(5,10) 'gunwale' positions on the *arachno* unit **5**, and does not significantly affect the overall electronic structure of that unit.

Table 1. Selected measured ¹¹B and ¹H NMR parameters for B₁₈H₂₀Py₂ (compound **2**), together with tentative assignments; (CD₃)₂CO solution at ca. 293 K.^a

Assignment	δ(¹¹ B)/ppm	δ(¹ H)/ppm
BH(3)	+13.6	+1.49
BH(10)	+10.9	+1.52
B(6)	+1.7	<i>conjuncto</i> site
BH(9)	-4.8	+2.87
BH(8)	ca. -6.1	+2.13 or +2.49
BH(2')	ca. -6.8	+2.49 or +2.13
BH(1) and BH(2')	ca. -9.0	+2.83 and +2.26
BH(9')	-10.8	+0.64 (<i>endo</i> site)
B(5)	ca. -12.6	<i>conjuncto</i> site
BH(6')	ca. -12.6	+1.00 (<i>endo</i> site)
BH(2)	ca. -19.3	+1.82
BH(8')	ca. -19.7	+1.54
BH(7')	-23.6	+1.45
BH(7)	-31.4	+1.25
BH(3')	-34.5	+1.02
BH(1')	-35.8	-0.53
BH(4)	-41.1	+0.10
μH(9,10)	-	+1.26
μH(6,7)	-	-0.76
μH(8,9)	-	-2.82
μH(7',8')	-	-4.03
Py	-	+7.64 (2H, doub of trips) +8.08 (1H, doub of trips), +8.75 (2H, multiplet)

Notes: ^a For the bridging hydrogen atoms, hydrogen/deuterium exchange noted to occur in the (CD₃)₂CO solvent; this type of prototropic phenomenon is common in macropolyhedral boron-containing compounds. For compound **2**, the μH(6,7) positions are exchanged within ca. 10 minutes, and μH(8,9) in ca 2 hours.

One remarkable feature of compound **2** is its interaction with light. It has an intense brick-red colour, and it is noticeably red-orange fluorescent under UV irradiation. At room temperature, solutions of **2** in dichloromethane emit fluorescence at 690 nm. In the solid-state this emission is shifted to 620 nm and intensifies due to restriction of the rotation of the pyridine ligands. In addition, there is a thermochromicity to the

fluorescence of $B_{18}H_{20}Py_2$ – cooling to 8 K engenders a further shift in the emission wavelength to 585 nm in the yellow region and a two-fold increase in intensity. A detailed investigation of these phenomena is presented elsewhere.²⁸

Figure 2 - Stick representations of the chemical shifts and relative intensities in the ^{11}B spectra of (from top to bottom) *nido*- $B_{10}H_{14}$, *anti*- $B_{18}H_{22}$ **1**, $B_{18}H_{20}Py_2$ **2**, and $B_{10}H_{12}Py_2$ **5**. Lines join equivalent positions; hatched lines are for the boron positions held in common.²⁷

The main product from the reaction of pyridine with *anti*- $B_{18}H_{22}$ is pale yellow $B_{16}H_{18}Py_2$ **3a**. A representation of the molecular structure of **3a** is in Figure 3. It is seen to consist of a *nido* ten-vertex subcluster and an *arachno*-type eight-vertex subcluster, fused with two boron atoms held in common (schematic connectivity diagrams **X** and **XI**). Interestingly, the bridging hydrogen-atom dispositions suggest that an effective proton transfer has occurred from the *nido*-decaboranyl subcluster to the *arachno* octaboranyl subcluster and the constituent subclusters would therefore be formally modelled by an anionic *nido* $[B_{10}H_{13}]^-$ single-cluster species and a cationic *arachno*- $[B_8H_{11}Py_2]^+$ single-cluster species (schematics **XII** and **XIII**) rather than neutral *nido*- $B_{10}H_{14}$ and a neutral *arachno*- $B_8H_{10}Py_2$ species. The X-ray diffraction analysis of **3a** indicated some cluster disorder, and so we prepared the picoline (NC_5H_4-4-Me) analogue **3b** in the same way as for **3a** in the hope that it might not exhibit such disorder. This similarly has very low solubility in common solvents such as chloroform, dichloromethane, acetonitrile and benzene, and exhibits a molecular structure that is very similar to **3a**, although the two crystal structures are not isomorphous. Unfortunately, there was also a disorder of the type associated with the structure of **3a**; however, in both

cases the disorder was largely resolved in the crystallographic analysis.

Figure 3 - The crystallographically determined molecular structure of $B_{16}H_{18}Py_2$ **3a** (major disorder component only). The majority of the B-B interatomic distances fall within a usual borane cluster range of 1.74 Å – 1.88 Å with the following exceptions: B5-B10 and B7'-B8' both long at 1.89-1.90 Å; and B6-B7, the site in the formally anionic *nido*-decaboranyl subcluster, short at 1.66 Å. No anomalies for the C-C, C-N and B-N distances were apparent. Other dimensions may be found in the supplementary information (**SI 3**). Although this and the picoline congener $B_{16}H_{18}(NC_5H_4Me)_2$ **3b** have very similar molecular structures and the crystal structures have the same space group, they are not isomorphous, having quite different packing arrangements (see Supporting Information **SI 4** for molecular structure of **3b**).

Measured ^1H and ^{11}B NMR data for $\text{B}_{16}\text{H}_{18}\text{Py}_2$ **3a** are in Table 2. Values for the picoline analogue **3b** and the 4-iso-propylpyridine analogue **3c** are given in the Support Information (SI 5). As with compound **2** above, assignments were made by the established procedure²³⁻²⁶ of combining results from ^{11}B and ^1H single and multiple resonance spectroscopies. Stick representations of the chemical shifts and relative intensities for **3a** are shown in Figure 4, together with those of the anionic subcluster of the $[\text{anti-B}_{18}\text{H}_{21}]^-$ anion²⁶ and $[\text{3-(NH}_2\text{Et)-arachno/hypho-B}_8\text{H}_{11}(\text{NH}_2\text{Et})]$ **6** (schematic connectivity diagram **XIV**)²⁹ for comparison. As far as we are aware, no *arachno*-octaboranes with two two-electron ligands are known, although the amido-amino *hypho/arachno*-type cage species such as $[(\text{NH}_2\text{Et})\text{B}_8\text{H}_{11}(\text{NH}_2\text{Et})]$ **6** are somewhat related, as are monoligand species exemplified by *arachno*- $[\text{B}_8\text{H}_{12}(\text{PMe}_2\text{Ph})]$ **7** (schematic **XV**).²⁹⁻³¹ The ^{11}B NMR spectrum of the unsubstituted ‘parent’ *arachno*-octaborane B_8H_{14} has a simple 2:4:2 relative intensity pattern and the molecule is therefore generally taken to have a symmetrical structure **XVI**, although it cannot be discounted that it has a very low-energy fluxionality that involves both bridging and *endo*-terminal hydrogen atoms of the type exhibited in **3a** and **6**.³²

Table 2

Selected measured ^{11}B and ^1H NMR parameters for $\text{B}_{16}\text{H}_{18}\text{Py}_2$ (compound **3a**) at ca. 293 K together with their tentative assignments.

Assignment	CD_2Cl_2 $\delta(^{11}\text{B})/\text{ppm}$	CD_2Cl_2 $\delta(^1\text{H})/\text{ppm}$	$(\text{CD}_3)_2\text{CO}$ $\delta(^{11}\text{B})/\text{ppm}$	DMF-d_6 $\delta(^1\text{H})/\text{ppm}$
B(6)	+21.4	<i>conjuncto</i> site	+21.8	<i>conjuncto</i> site
BH(3)	+4.2	+2.83	+4.3	+2.93
BH(10)	+1.1	+3.10	+1.1	+3.13
BH(2')	-0.2	+3.27	+0.4	+3.27
B (5)	-6.5	<i>conjuncto</i> site	-6.7	<i>conjuncto</i> site
BH(1)(8) and (9)	-7.9	+2.60	ca. -8.3	+2.56
	-8.2	+2.07	ca. -8.3	+2.00
	-8.6	+2.51	ca. -8.3	+2.56
BH(7)	-10.5	+2.33	-10.1	+2.49
BH(8')	-15.0	+2.84	-15.2	+2.34
BH(3')	-17.8	+2.03	-18.2	+1.98
BH(7)	-22.5	+2.05	-23.3	+2.00
BH(4')	-25.7	+1.67	-27.7	+1.63
BH(2)	-28.2	-0.72	-27.7	-0.62
BH(4)	-43.0	+0.09	-43.1	+0.18
BH(1')	-46.3	-1.26	-46.0	-1.26
mH(6,7')	-	-1.73	-	-1.71
mH(9,10)	-	-1.73	-	-1.71
mH(8,9)	-	-2.88	-	-2.86
mH(5,4')	-	+0.86	-	+0.82
Py	-	+7.7 to +8.8	-

Figure 4 - Stick representations of the chemical shifts in the ^{11}B spectra of (from top to bottom) the anionic subcluster of the $[\text{anti-B}_{18}\text{H}_{21}]^-$ anion, $\text{B}_{16}\text{H}_{18}\text{Py}_2$ **3a** and $[\text{3-(NH}_2\text{Et)-arachno/hypho-B}_8\text{H}_{11}(\text{NH}_2\text{Et})]$ **6**. Lines join equivalent positions; hatched lines are for the boron positions held in common.²⁷

The shielding pattern of *nido*- $\text{B}_{10}\text{H}_{14}$ does not map so well onto that of the *nido* ten-vertex subcluster of **3a**, as may be expected from the effective $[\text{nido-B}_{10}\text{H}_{13}]^-$ anionic character of the latter, although the basic *nido*-decaboranyl characteristics [with $^{11}\text{B}(2$ and $4)$ to high field, $^{11}\text{B}(5,7,8$ and $10)$ at intermediate field, and $^{11}\text{B}(1$ and $3)$, together with $^{11}\text{B}(6$ and $9)$ tending towards lower field, as mentioned above] can still be traced through. More pertinently, however, it can be seen from Figure 4 that the shielding pattern of the *nido* ten-vertex subcluster of **3a** is mimicked very closely indeed by the monoanionic *nido* ten-vertex subcluster of the $[\text{anti-B}_{18}\text{H}_{21}]^-$ anion,²⁶ in accord with the effective factorisation of **3a** into anionic ten-vertex *nido* and cationic eight-vertex *arachno*-type subclusters **XII** and **XIII** as discussed above. The close correlation suggests that the electronic structure of the quasi-anionic ten-vertex subcluster of **3a** mimics very closely the electronic structure of the anionic subcluster of the $[\text{anti-B}_{18}\text{H}_{21}]^-$ anion, supporting a polar zwitterionic constitution as suggested by the **XII** / **XIII** factorisation.

Comparison NMR data for the eight-vertex subcluster are very limited. Because of the symmetry, whether absolute or time-averaged,³² of the parent model *arachno*- B_8H_{14} , a comparison with its ^{11}B nuclear magnetic shielding pattern is not very informative. As discussed above, the *arachno*-octaborane subcluster of **3a** is formally cationic. The hydrogen-atom disposition of its hypothetical cationic single-cluster model *arachno*- $[\text{B}_8\text{H}_{11}\text{Py}_2]^+$ (schematic **XIII**) matches that proposed for $[\text{3-(PMe}_2\text{Ph)-arachno-B}_8\text{H}_{12}]$ **7** (schematic **XV**).²⁹ However, the ^{11}B magnetic shielding patterns of **7** and the eight-vertex subcluster of **3a** do not match well. Interestingly, of available comparators, the shielding pattern for the *arachno/hypho* species $[\text{3-(NH}_2\text{Et)-B}_8\text{H}_{11}(\text{NH}_2\text{Et})]$ **6** gives the best match for the eight-vertex subcluster of **3a** (Figure 4). The ordering and general shielding pattern from six of the eight positions

correlate well, with a general lower shielding for the macropolyhedral compound. The exceptions are the B3' site, which in **3a** has a ligand substituent at that position that is lacking in **6**, and the B6' site, the site of intercluster conjunction that combines with the more highly shielded B(6) centre of the formally anionic *nido* ten-vertex subcluster,²⁷ adjacent to the short B6-B7 linkage of 1.65 Å, formally the anionic site.

Figure 5 - The crystallographically determined molecular structure of anti-B₁₈H₂₀-8'-Py **4**. The B8'-N81 distance is 1.549 Å, and the common boron-boron edge B5-B6 1.807 Å. Three *nido*-decaboranyl 'gunwale' distances are long, with B5-B10 1.969 Å, B7-B8 1.950 Å, and B5'-B10' 2.037 Å, but the B6-B9' distance at 1.831 Å adjacent to the ligand site is significantly shorter than these. Other dimensions may be found in the supplementary information (SI 6). The basic {B₁₈} residue resembles that in [5'-{(MeNH)C₃N₂HMe₂}-anti-B₁₈H₂₀]⁶ and in [5'-{(terBuNHCH){terBuNHC(CN)}CH₂}-anti-B₁₈H₂₀], and, indeed, that in the [anti-B₁₈H₂₁]⁻ anion.^{26,33}

A representation of the crystallographically determined molecular structure of the third isolated reaction product, yellow B₁₈H₂₀-8'-Py **4**, is in Figure 5 (see also schematic connectivity projection **XVII**). It is seen to consist of two *nido* ten-vertex subclusters fused with two boron atoms held in common, as with the starting compound *anti*-B₁₈H₂₂ **1**. In terms of empirical formulations, notional deprotonation of compound **1** would give the [anti-B₁₈H₂₁]⁻ anion, and thence formal replacement of one two-electron anionic hydride {H}⁻ unit by the two-electron Py ligand formally results in the formulation of neutral compound **4** with no change in cluster-electron count and therefore with the *nido* decaboranyl character of the two subclusters remaining intact. Interestingly, however, the pyridine ligand is in the 8'-position, in contrast to previously established compounds of this general B₁₈H₂₀L compound type, *e.g.* [5'-{(MeNH)C₃N₂HMe₂}-anti-B₁₈H₂₀]¹⁶ and [5'-{(terBuNHCH){terBuNHC(CN)}CH₂}-anti-B₁₈H₂₀] (schematic connectivity projection **XVIII A**),³³ and thus constitutes a new configurational type. Note that, for self-consistency within this present report, we use a cluster numbering here that differs from that used in references 16 and 33; the science is unaffected. Both numberings are within IUPAC-recommended conventions.

Figure 6 shows stick representations of the chemical shifts and relative intensities for the substituted subclusters in the ¹¹B spectra of the [anti-B₁₈H₂₁]⁻ anion,²⁶ [8'-Py-anti-B₁₈H₂₀] **4**, and [5'-{(MeNH)C₃N₂HMe₂}-anti-B₁₈H₂₀].¹⁶ For clarity, the data for the unsubstituted subclusters are omitted because the shieldings for equivalent positions in these unsubstituted subclusters in all three compounds are very similar indeed; this similarity indicates that for these three species the electronic structures within the unsubstituted subclusters are not affected significantly by changes in the second, substituted, subclusters. Full listings of the measured ¹¹B and ¹H NMR data for compound **4**, together with [anti-B₁₈H₂₁]⁻ anion and [5'-{(MeNH)C₃N₂HMe₂}-anti-B₁₈H₂₀] for comparison, is in the supplementary data (SI 7 and SI 8 respectively).

Figure 6 - Stick representations of the chemical shifts and relative intensities in the ¹¹B spectra of the anionic subcluster of the *nido:nido* [anti-B₁₈H₂₁]⁻ anion (centre diagram), and the equivalent subclusters of [8'-Py-anti-B₁₈H₂₀] **4** (top diagram) and [5'-{(MeNH)C₃N₂HMe₂}-anti-B₁₈H₂₀] (bottom diagram).¹⁶ Lines join equivalent positions. Unusually for a two-cluster macropolyhedral species of this molecular size,^{16,26} there was insufficient definitive connectivity data from multiple resonance NMR experiments to enable complete unambiguous assignment; nevertheless, it can be seen that the cluster shielding patterns for the anion and the {(MeNH)C₃N₂HMe₂} species are very similar indeed, whereas that for compound **4** deviates more significantly.

In accord with the general structural and electronic parallels just mentioned, it can be seen from Figure 6 that the cluster ¹¹B magnetic shielding pattern of the substituted subcluster of the {(MeNH)C₃N₂HMe₂} species maps directly onto that for the anionic subcluster of the [anti-B₁₈H₂₁]⁻ anion, and is in fact very similar indeed. In contrast, however, that for the substituted

subcluster of pyridine species **4** does not correspond so well. Even though there was insufficient COSY correlation data for a complete specific assignment for this subcluster of compound **4**, it can nevertheless be seen that the extreme similarities between the ^{11}B and ^1H NMR shielding patterns [5'-{(MeNH)C₃N₂HMe₂}-*anti*-B₁₈H₂₀] and the [*anti*-B₁₈H₂₁][−] anion are not well replicated.

The origins of this difference are twofold. First, the substituent effect of the {(MeNH)C₃N₂HMe₂} unit is very similar to that of the hydride anion that it notionally replaces in an electronic and structural comparison, whereas the substituent effect of the pyridine moiety is quite different: for example, in the single-cluster species B₁₀H₁₂Py₂ the ^{11}B nuclei of the pyridine-substituted vertices resonate at some 15 ppm to lower field than those in the equivalent positions in the [B₁₀H₁₄]^{2−} anion. Second, the positioning of the {(MeNH)C₃N₂HMe₂} unit on the B5' position of [5'-{(MeNH)C₃N₂HMe₂}-*anti*-B₁₈H₂₀] dictates that it is the adjacent B5-B5' site that lacks a bridging hydrogen atom (schematic connectivity diagram XVIII A), just as it does in the anionic subcluster of the [B₁₈H₂₁][−] anion (schematic connectivity diagram XVIII B). The overall electronic structure of the {(MeNH)C₃N₂HMe₂} compound will therefore mimic that of the [B₁₈H₂₁][−] anion much more closely than of compound **4**, in which the ligand in the B8' site dictates that it is the adjacent B8'-B9' site that lacks the bridging hydrogen atom (schematic connectivity diagram XVII), rather than the B5-B5' site as exhibited by the [B₁₈H₂₁][−] anion and the {(MeNH)C₃N₂HMe₂} species.

Mechanism of product formation. The mechanism of the formation of these species is problematical. B₁₈H₂₀Py (compound **4**) would formally derive from a monoanionic [B₁₈H₂₁][−] unit. [PyH]⁺[B₁₈H₂₁][−] would be an obvious initial product from B₁₈H₂₂ **1**, which is of very high Brønsted acidity.^{34,35} A formal replacement of negative hydride by neutral pyridine would thence generate **4**. Monitoring the reaction by NMR spectroscopy confirms the initial presence of the [B₁₈H₂₁][−] anion on the dissolution of **1** in pyridine. Overall, however, this formal hydride replacement would be an oxidative process, and it is not clear what the oxidizing agent might be in this system, although it may be noted that in the well-known reaction of *nido*-B₁₀H₁₄ with ligands L to give L₂B₁₀H₁₂, there is formally just simple dihydrogen loss. In the case of macropolyhedral species, however, it is noted that the formation of its *syn*-B₁₈H₂₀(SMe₂) congener from SMe₂ and *syn*-B₁₈H₂₂ requires elemental iodine as an oxidizing agent,³⁶ and in the formation of the *anti*-B₁₈H₂₀-5'-{(MeNH)C₃N₂HMe₂} congener from MeNC and *anti*-B₁₈H₂₂, mentioned in the introduction, the cluster oxidation is redox-complementary to the reductive trimerisation of three MeNC units.¹⁶ In these processes the basic *nido-nido* conjunction is retained with no ostensible rearrangement.

By contrast, the formation of B₁₈H₂₀Py₂ (compound **2**) clearly involves a cluster rearrangement. One simplistic interpretation involves a 'vertex-flip' of a boron centre (schematics XIX and XX) as the *nido* subcluster develops into *arachno*. A similar cluster rearrangement has been shown to occur in reactions of two-electron ligands with single-cluster *nido*-decaboranyl models,³⁷ which give bis(ligand) *arachno*-decaboranyl species, reactions which have long been known to occur quickly and quantitatively. Here the relative low yield of B₁₈H₂₀Py₂ **2**, in what should ostensibly be an analogous process, may result from an inhibition of this reaction because a rearrangement is discouraged by the rigid constraints of the two-atoms-in-common inter-cage fusion linkage. This inhibition may thence favour the dominance of the alternative reaction pathway to give B₁₆H₁₈Py₂ **3a**, which is the predominant product. What the mechanism may be for this latter preferred cluster-dismantling process to give **3a** is far from clear. Reaction conditions for the yields that are obtained are relatively critical; attempts to force the reaction by using a larger excess of pyridine are not successful. The loss of boron vertices is obviously a key part of the process to give **3a**. Clues for the mechanism may derive from the reaction of [(PPh₃)₂(CO)OsB₅H₉] with phosphines L, which quantitatively and reversibly afford [(PPh₃)₂(CO)OsB₄H₇(BH₂L)] in solution^{38,39} – here, in the formation of the cluster-bound exopolyhedral {BH₂L} moiety, the two-electron ligand L has clearly engendered an extrusion of a boron vertex. In macropolyhedral systems, reaction of PMe₂Ph with S₂B₁₇H₁₇ results in loss of a boron vertex to give [S₂B₁₆H₁₄(PMe₂Ph)₂] and [S₂B₁₆H₁₆(PMe₂Ph)]; of these, the latter has some structural similarities to compound **3a**. Relevant here is that [S₂B₁₆H₁₆{BH(PMe₂Ph)₂}] is also isolatable from the reaction, the still-attached exopolyhedral {BH(PMe₂Ph)₂} moiety clearly modelling a step in the vertex-extrusion process.⁴⁰ Here it may be noted that excited-state CASSCF calculations for compound **2** (reported in reference 28) have molecular geometries with a partially extruded {B(6)Py} vertex, suggesting a potential for cluster dismantling at this vertex. Also it is clear from schematics XIX and XX that attack by pyridine is associated with a labile boron vertex. Overall it is tempting to postulate a sequence of reaction B₁₈H₂₂ → B₁₈H₂₀Py → B₁₈H₂₀Py₂

→ $B_{16}H_{18}Py_2$, but at present there is no direct experimental evidence realistically to support this.

Further Considerations. Two interesting phenomena that merit further elucidation arise out of the initial preparative and characterisation work on the two bi(pyridine) species **2** and **3**: (a) for $B_{16}H_{18}Py_2$ **3a** and **3b** the exceptionally low solubility in common polar solvents, and (b) for $B_{18}H_{20}Py_2$ **2** the brick-red fluorescence. Factors limiting the solubility of $B_{16}H_{18}Py_2$ **3a** and its picoline congener **3b**, of which both have such limited solubility, and of which both have very similar molecular structures, are conveniently dealt with in this present paper. The fluorescence of **2** merits more detailed specialist photophysical investigation, particularly in the light of the ongoing revelation of the fluorescence of *anti*- $B_{18}H_{22}$,¹⁵ the fine tuning and precise tailoring of the fluorescence properties of $B_{18}H_{22}$ by substituent chemistry,⁴¹ and, cumulatively, by the milestone utilisation of the fluorescence properties for *anti*- $B_{18}H_{22}$ to devise the first borane laser.⁵ The interesting specific fluorescence properties of $B_{18}H_{20}Py_2$ **2** are dealt with in detail in a contemporaneous submission.²⁸ Here, however, we provide a comparative treatment of the photophysical properties of the other two reaction products, **3a** and **4**.

Examination of Solid-State Structures of Compounds 3a and 3b. The low solubility of these sixteen-boron species must arise from an exceptional stability of the solid-state structures of crystalline $B_{16}H_{18}Py_2$ **3a** and $B_{16}H_{18}Pic_2$ **3b**, such that solvation effects of the common solvents, such as C_6H_6 , $CHCl_3$, CH_2Cl_2 and CH_3CN , cannot compete. For the solid state, inspection of the overall crystal structures show that the molecules pack together in centrosymmetric head-to-tail diads, as illustrated by the yellow pair at the top left-hand corner of projection **XXI** (as viewed perpendicular to the (201) crystal plane). This projection is for the Py species **3a**, which we use as the exemplar in this discussion. The picoline compound **3b** also forms centrosymmetric head-to-tail diads, although the pairs of molecules have a different relative orientation and the diads are not aligned approximately perpendicular to their neighbours (see Supporting Information **SI 9** for equivalent diagram). These diads in turn pack together to form layers in both crystal structures. Within the pairs that can be seen in **XXI**, space-filling representations (structures **XXII A** and **XXII B**) show very intimate complementary-surface Van-der-Waals packing, with nearest intermolecular inter-hydrogen distances from pyridine {CH} to borane {BH} at 2.347 Å; a typical Van-der-Waals inter-hydrogen radius sum being ca. 2.40 Å.

XXI

XXII A

XXII B

As a complementary measure to such considerations, we calculated the electrostatic potential (ESP) of **3a** in order to assess whether any strong polarity factors were significant. As discussed above (schematics **XII** and **XIII**) the compound is of zwitterionic nature. Representations **XXIII B** and **XXIII C** show the result of the calculations of ESP associated with a molecule of $B_{16}H_{18}Py_2$ **3a** (schematic **XXIII A**) in which positive to negative is scaled from red to blue. It can be seen that there is a considerable polarity; the dipole is calculated at 25.88 D for compound **3a** (and 28.10 D for **3b**). It can thence be seen from calculations based on the crystallographic coordinates of the resulting diad (representations **XXIV A** and **XXIV B**) that the Van-der-Waals intra-pair complementarity shown in **XXIV A** and **XXIV B** above is considerably augmented by these polar effects in what is effectively a synergic process.

XXIII A

XXIII B

XXIII C

XXIV A

XXIV B

In a simplistic application of a Kitaigorodskii type of Aufbau approach^{42,43} to the construction of the matrix based on these polarity considerations, it can be seen how two diads will pair to give a tetrad unit, as in representations **XXV A**, which takes as the example one of the diad pairs apparent from the alignments in projection **XXIII** above; the calculated overall ESP distribution for the resulting tetrad is represented in **XXV B**.

XXV A

XXV B

It can thence be seen (very schematic representations **XXVI A** to **XXVI C**) how the overall polarity of the tetrad **XXVI A** maps into an octad **XXVI B** and thence into the infinite layer **XXVI C** shown in the crystallographic representation **XXI** above.

XXVI A

XXVI B

XXVI C

XXVII

XXVIII

A significant component of the interaction that generates the tetrad assembly **XXV B** is a head-to-tail 'biting' interaction. At first sight the shape and polarity of the molecule suggest that this may occur in linear manner as in **XXVII** and thence play a significant role in the overall stability of the lattice. Such an interaction does indeed occur, but rather takes the form of a 'sideways bite' as in **XXVIII**. Overall this results in the stabilisation of a zig-zag interconnecting chain motif along the *b*

direction of the lattice, as can be followed by tracing the path of the red molecules in representation **XXI** above. The distances from the aromatic ring centroid to the nearest {BH} hydrogen atoms are 3.486 and 3.728 Å. There is also an aromatic ring-alignment parallelism between layers of type **XXI**, as in **XXIX**, which will be assisted by the opposing inherent directional polarities of the pyridine residues. The distance between the pyridine ring centroids is 4.517 Å, with a mean inter-plane distance of 14.50 Å. This 'ring-stacking' is probably much less significant than the intimate polar and Van-der-Waals attractions within the **XXI** plane.

XXIX

In this particular case, therefore, we conclude that the unexpected, and remarkably very low, solubility of these B₁₆H₁₈Py species **3** arises from a particularly advantageous combination of Van-der-Waals intimate complementarity and a particularly strong complementarity of dipolar and electrostatic interactions.

Photophysical Considerations. There is a strongly developing theme of useful fluorescence from the macropolyhedral borane compound *anti*-B₁₈H₂₂ **1**^{5,15} and its derivatives,⁴¹ including B₁₈H₂₀Py₂ (compound **2**)²⁸ of which preparative and NMR spectroscopic aspects are now also dealt with in this present paper. Consequently, we are interested in a rationalisation of the weak luminescence that we have found for compound **3a** during the course of this present work, and the contrasting non-fluorescence of B₁₈H₂₀-8'-Py (compound **4**), as part of an overall and fuller understanding of the photochemistry of macropolyhedral boranes.

Figure 7 - Absorption spectrum for B₁₈H₂₀-8'-Py (compound **4**; measured in solution in CH₂Cl₂). The absorption maximum is at 320 nm.

It is convenient to consider the mono-ligand B₁₈H₂₀Py compound **4** first. Figure 7 shows the absorption spectrum for **4**, recorded from a crystalline sample dissolved in freshly distilled dichloromethane. No measurable luminescence was observed whilst exciting **4** between 250-400 nm. Following from this experimental observation, a CASPT2 theoretical analysis of the photophysical and photochemical properties of **4** was employed. CASPT2 – Complete-Active-Space Second-Order Perturbation Theory – is a multireference electron-correlation method for computational investigation of electronic states in a molecular system.⁴⁴ Table 4 compiles the computed energies of the five lowest-lying electronic states (the S₀ ground state, followed by the first four excited states, S₁ – S₄) at the most relevant points of the potential energy hypersurfaces (PEH) of **4**, namely its ground-state minimum (S₀)_{min}, the first singlet excited-state minimum (S₁)_{min}, and the crossing point between the S₀ and the S₁ surfaces; *viz.* the conical intersection point (S₀/S₁)_{CI}. Additionally, the oscillator strengths associated with the S₀ → S₁₋₄ absorptions at the (S₀)_{min} geometry are included in parentheses as a measure of the relative probability of each respective transition.

Table 4 - CASPT2 energies (in eV) of the five lowest-lying electronic states at the most relevant points for the elucidation of the photophysics of B₁₈H₂₀-8'-Py (compound **4**), relative to the ground-state energy at the CASSCF equilibrium structure, (S₀)_{min}. Oscillator strengths *f* are within parenthesis.

State / Geometry	Nature of the main electronic transition at the (S ₀) _{min} structure	(S ₀) _{min}	(S ₁) _{min}	(S ₀ /S ₁) _{CI}
S ₀	-	0.00	0.98	2.50
S ₁	B ₁ → π ₁ [*]	3.69 (0.0082), 3.27 (0.0073) ^a	2.76	2.66
S ₂	B ₂ → π ₁ [*]	4.54 (0.2265), 3.95 (0.1972) ^a	4.43	5.33
S ₃		4.64 (0.0077), 4.01 (0.0066) ^a	4.72	5.71
S ₄		4.83 (0.0325), 4.26 (0.0287) ^a	5.55	7.43

^a Data computed with the CASPT2 method with an IPEA shift of 0.00 a.u.

Upon irradiation of **4** with light from 250 nm to 400 nm, the most intense and, therefore, the most probable electronic transition, is computed at 273 nm (4.54 eV). This transition (S₀ → S₂) has a charge-transfer in→out character with promotion from the B₂ orbital, which is mainly located on the pyridine-bound subcluster of the eighteen-boron cage, to the π₁^{*} orbital situated solely on the pyridine ligand (see Figure 8, and Supporting Information SI 10). A S₀ → S₁ transition, calculated at 336 nm (3.69 eV), involves promotion from the B₁ orbital that is almost entirely located on the boron cluster to the same π₁^{*} orbital involved in the S₀ → S₂ transition (also see Figure 8).

Figure 8 - Most relevant CASSCF natural orbitals that compose the CAS active space of compound **4**.

All things considered (see Supporting Information SI 11 for full rationale), it is reasonable to assign the S₀→S₂ electronic transition to the experimentally measured absorption band maximum at 320 nm (see Figure 7) and the S₀→S₁ transition to the broad curve of the same band appearing at lower energies. Furthermore, it is reasonable that the transitions related to S₃ and S₄ are responsible for the absorbance in the 250-300 nm range. Taking into account the experimental observation of no luminescence in the 250-400 nm range of wavelengths used for

excitation, Kasha's rule⁴⁵ can be assumed to apply to compound **4**. This implies that excitation to states S_2 - S_4 will be followed by rapid decay to the lowest-lying excited state S_1 *via* internal conversions. Hence, in the present work we have only focused on the photochemical path of the system after excitation to the S_1 state in order to rationalize the non-emissive properties of **4**. Alternative decay paths, although possible, may be considered minor pathways of little or no relevance as evidenced by the absence of any experimentally recorded emission of light. The decay path of **4** upon excitation to S_1 is depicted in Figure 9. In it may be seen that the excited molecule rapidly evolves along an essentially flat minimum energy path (MEP), *via* its $(S_1)_{\min}$ structure, towards a conical intersection (CI) point, namely the $(S_0/S_1)_{\text{CI}}$ structure, that funnels the system to the ground state in a non-radiative manner. A negligible barrier of 0.07 eV between the $(S_1)_{\min}$ and the $(S_0/S_1)_{\text{CI}}$ structures of this system is estimated (as an upper boundary) using the linear interpolation of internal coordinates (LIIC) procedure. Taking also into account that the CI point is significantly lower in energy (~ 1 eV) than the S_1 state at the Franck Condon (FC) region (PEH coordinate 1 in Figure 9), it is apparent that there is sufficient energy on excitation to carry the system through to its $(S_0/S_1)_{\text{CI}}$ structure and, consequently, relaxation to its ground-state without luminescence.

Figure 9 - CASPT2 potential energy hypersurfaces of the two lowest-lying electronic states S_0 and S_1 of $B_{18}H_{20}-8'-Py$ **4**, computed along the relaxation path on the S_1 state. The PEH coordinates 1, 9, and 13 correspond to the $(S_0)_{\min}$, $(S_1)_{\min}$, and $(S_0/S_1)_{\text{CI}}$ structures, respectively.

As compound **4** progresses along its S_1 PEH, there is a change in its molecular structure that is concentrated about the B8'-Py cluster boron vertex. The B6-B8' and B8'-B9' cluster connectivities elongate from 1.87 to 2.26 Å in the case of the former, and from 1.66 to 1.95 Å in the case of the latter (see Figure 10). Indeed, a length of 2.26 Å for the B6-B8' connectivity at the CI can be considered non-bonding; the B8'-Py vertex almost extruded from the cluster. This excited-state structural behaviour is very similar to that of the bis-ligand derivative compound **2**,²⁸ which also has a CI structure in which one of its two ligated boron vertices is almost extruded from the cluster. The key structural difference between compounds **2** and **4** in relation to their photophysics therefore appears to be the difference in the geometry of the ligated subclusters, which is *arachno* in the case of **2** and *nido* in the case of **4**.

Figure 10 - Relevant molecular parameters of the (from left to right) S_0 minimum, excited-state S_1 minimum, and the S_0/S_1 conical-intersection-point (PEH coordinate point 1, 9 and 13 respectively in Figure 9) structures of $B_{18}H_{20}-8'-Py$ (compound **4**). Interatomic distances are in Å, whereas pyramidalisation angles between the ring plane and the B-N bond are in degrees.

The bis(pyridine) sixteen-boron *arachno-nido* compound $B_{16}H_{18}Py_2$ **3a** is of particular interest because its photophysical behaviour contrasts markedly with the bis(pyridine) eighteen-boron *arachno-nido* compound $B_{18}H_{20}Py_2$ **2**, which exhibits very obvious brick-red fluorescence.²⁸ However, the highly insoluble nature of **3a** (discussed above) which causes precipitation directly from the reaction mixture, limited our experimental study of its photophysics to its solid state. On excitation at wavelengths between 300-400 nm, a solid sample emits a weak but measurable emission (quantum yield ~ 0.01) recorded with a maximum at 590 nm (see Figure 11). The lifetime of this luminescence is in the order of several microseconds, which suggests that the luminescence may in fact be a phosphorescence from a low-lying triplet excited state.

Figure 11 - Emission spectrum from a solid sample of $B_{16}H_{18}Py_2$ (compound **3a**) under excitation at 400 nm. Emission maximum recorded at 590 nm.

The CASPT2 study of **3a** computes two low-lying and intense electronic transitions: a $S_0 \rightarrow S_1$ transition at 385 nm, and a $S_0 \rightarrow S_2$ transition at 289 nm (Table 5 summarises a fuller list of the CASPT2 energies of the five lowest-lying electronic states). The relevant CASSCF natural orbitals involved in the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions are shown in Figure 12 (see Supporting Information SI 12 for full listing of orbitals). Once again, as is seemingly becoming the rule for borane-pyridine systems, albeit in the limited number of studies so far reported,^{28,46} there are charge-transfer transitions of in $\rightarrow$ out character, with promotion from the B_1 orbital, which is mainly located on the boron cluster, to the π_1^* orbital (in the case of $S_0 \rightarrow S_2$) or to the π_2^* orbital (in the case of $S_0 \rightarrow S_1$), both of which are delocalized solely over the pyridine ligand (see Figure 12). Both S_1 and S_2

states are thus of the same nature, with the π_2^* and the π_1^* orbitals being the symmetric and anti-symmetric combination, respectively, of the π^* orbitals of the aromatic rings.

Table 5 - CASPT2 energies (in eV) of the five lowest-lying electronic states at the most relevant points for the photophysics of $B_{16}H_{18}Py_2$, compound **3a**, relative to the ground-state energy at the CASSCF equilibrium structure, $(S_0)_{min}$. Oscillator strengths f are within parenthesis.

State / Geometry	Nature of the main electronic transition at the $(S_0)_{min}$ structure	$(S_0)_{min}$	$(S_1)_{min}$	$(S_0/S_1)_{CI}$
S_0	-	0.00	0.68	2.36
S_1	$B_1 \rightarrow \pi_2^*$	3.22 (0.1673)	2.58	2.45
S_2	$B_1 \rightarrow \pi_1^*$	4.29 (0.2081)	3.37	4.54
S_3		4.41 (0.0419)	3.95	4.78
S_4		4.64 (0.0020)	4.16	5.24

Figure 12 - Most relevant CASSCF natural orbitals that compose the CAS-active space of compound **3a**.

Excitation at 300-400 nm would thus lead to population of the S_2 and S_1 excited states with almost equal probability. From this upper level, energy is funneled rapidly *via* internal conversion into the S_1 state, from where the molecule evolves steadily to the (S_0/S_1) conical-intersection point, with no energy barrier to hinder its progress (see figure 13). This would lead to very efficient non-radiative relaxation once the system reaches the S_1 state. However, experiments measure a weak and long-lived luminescence, which, according to the barrierless decay path obtained for the singlet manifold, can only be ascribed to an inter-system crossing (ISC) into a low-lying triplet state leading to phosphorescence. Accordingly, the lowest-lying triplet state (T_1) has also been computed along the MEP on the S_1 state. T_1 is placed at ~ 4 eV at the FC region and becomes degenerated with the S_1 along the flat PEH between the $(S_1)_{min}$ and $(S_0/S_1)_{CI}$ points (see Figure 13), enabling the population transfer to the triplet state. It is therefore reasonable to expect that some molecules can be trapped in the triplet manifold, relaxing to the ground state through long-lived phosphorescence emission

from the T_1 state. The plausibility of such singlet to triplet population transfer is confirmed by the computation of spin-orbit couplings (SOCs) between the S_1 and the T_1 states which determine the inter-system crossing (ISC) efficiency. Indeed, the obtained values are around 1.5 cm^{-1} along the S_1 decay curve ($1.36, 1.42, 1.47, 1.53, 1.42, 1.52, 1.51$ and 1.46 cm^{-1} for PEH coordinates 1, 2, 3, 4, 5, 6, 7 and 8 of Figure 13, respectively), which implies low but non-negligible ISC probability. The experimentally recorded quantum yield of phosphorescence being 0.01 supports the dominance of non-radiative decay from the S_1 state as opposed to ISC and relaxation via luminescence from a T_1 state.

Figure 13 - CASPT2 potential energy hypersurfaces of the two lowest-lying singlet electronic states S_0 and S_1 and the first triplet state T_1 of $B_{16}H_{18}Py_2$ (compound **3a**) computed along the relaxation path on the S_1 state. The PEH coordinates 1, 2, and 10 correspond to the $(S_0)_{min}$, $(S_1)_{min}$, and $(S_0/S_1)_{CI}$ structures, respectively.

Relevant molecular parameters along the excited-state decay of compound **3a** are shown in Figure 14. The excitation energy appears to be concentrated in the vibrational modes linked to the B8'-Py vertex of the boron hydride cluster. Consequently, evolution along the S_1 surface sees a subtle elongation in the B8'-B7' connectivity, and a marked protraction of the B8'-B3' connectivity from $1.89 \text{ \AA}$ in the S_0 minimum to a non-bonding $2.42 \text{ \AA}$ in the S_0/S_1 conical-intersection-point structure. Accompanying this separation between ligated boron vertices, is a flap of the B8'-pyridine ring that results in a decrease of almost 40° in the pyramidalisation angle between the pyridine ring plane and the B8'-N bond.

Figure 14 - Relevant molecular parameters of the (from left to right) S_0 minimum, excited-state S_1 minimum, and the S_0/S_1 conical-intersection-point (PEH coordinate point 1, 2 and 10 respectively in Figure 13) structures of $B_{16}H_{18}Py$ (compound **3a**). Interatomic distances are in $\text{\AA}$, whereas pyramidalisation angles between the ring plane and the B-N bond are in degrees.

Conclusions

Three new compounds $B_{18}H_{20}Py_2$ **2** (ca. 15 %), $B_{16}H_{18}Py_2$ **3a** (the major product, ca. 53 %) and small quantities of $B_{18}H_{20}-8'-Py$ **4** as a minor product, are formed by means of a one-step derivatisation with pyridine of highly-fluorescent *anti*- $B_{18}H_{22}$ (compound **1**). In the cases of compounds **2** and **3a**, our elucidation of their molecular structures reveal macropolyhedral *arachno-nido* boron hydride architectures without precedence in the current literature. Compound **4** exhibits a ligand position previously unseen on the {*anti*- $B_{18}H_{20}$ } matrix. The surprisingly low solubilities of compound **3a** and its bis(picoline) analogue **3b** are rationalisable in terms of the results of molecular electrostatic potential (ESP), polarity, and Van-der-Waals complementarities, which together inculcate strong intermolecular contact intimacy. The photophysical properties of **2**, **3a** and **4** relate well to the results of ground- and excited-state structural and molecular-orbital calculational work: the excited states populated after irradiation of **2**, **3a** and **4** are of charge-transfer nature, involving electronic transitions from the boron cluster to the organic pyridine substituents. It is noteworthy that this direction runs opposite to that commonly found in luminescent carborane-based molecular systems, for which charge-transfer generally occurs from organic ligand to the carborane cluster.^{12,47} Furthermore, and similarly to carborane-derivatized luminophors,⁴⁷ intramolecular charge transfer from borane cluster to pyridine ligand in the case of compounds **2**, **3a**, and **4** proceed with significant conformational changes as shown in Figures 10 and 14 and reference 28. In the case of **2**, fluorescent emission is observable from its twisted-intramolecular charge transfer (TICT) state.²⁸ This emission is potentially valuable because the molecular contortions involved in the TICT-state, and hence the emission wavelength and intensity, are greatly affected by environmental factors such as solvent polarity, ambient temperature, and viscosity (solution, solid-state, polymer-dissolved). This relationship between luminescent emission and environmental factors gives potential for sensing changes in these conditions; a principle currently being developed with other luminophors elsewhere.⁴⁷⁻⁵⁰ The non-emissive properties of **3a** and **4** have been rationalized by means of accessible conical intersection areas between the S_1 excited and the S_0 ground states, which mediate the deactivation of the excited state by means of vibrational relaxation. In the case of **3a**, a small fraction of molecules can populate the lowest-lying triplet state T_1 and give rise to experimentally detectable phosphorescence. The far more photoactive nature of compound **2** appears to be reasonably associated with its disubstituted 10-vertex {*arachno*- $B_{10}Py_2$ }-subcluster: A structural aspect that might prove important in the targeted development of other new luminescent macropolyhedral boranes. Overall, these results provide further evidence of the potential of macropolyhedral borane systems as sources of both structural novelty and, in these cases, as useful alternative molecular components in the fabrication of luminescent devices.

Experimental

Preparation and isolation. A sample of *anti*- $B_{18}H_{22}$ 350 mg (1.6 mmol) was dissolved in anhydrous $CHCl_3$ (30 ml). To this, a solution of pyridine (5.2 mmol, 41 mg, 0.4 ml) in $CHCl_3$ (10 ml) was added, sending the solution an immediate yellow colour on the ready and complete formation of [*anti*- $B_{18}H_{21}$] $[PyH]^+$ (confirmed by ^{11}B NMR of an aliquot of reaction mixture.). This solution was then heated to reflux under dry N_2 and stirred, under reflux, for 24 hours, during which time a pale yellow precipitate developed. This precipitate was filtered and kept aside (see below). The $CHCl_3$ filtrate was evaporated *in vacuo* at room temperature, and the residue was extracted with benzene (2 x10 ml). The combined benzene extracts were evaporated and subjected to column chromatography on silica gel (2 cm x 30 cm) with benzene as eluting liquid, yielding the following fractions (a) R_F 0.42 (analytical TLC; silica on foil; CH_2Cl_2 : hexane 2:1 as eluting liquid) colourless BH_3-Py identified by NMR spectroscopy, (b) R_F 0.38, a yellow solid after evaporation, identified by NMR spectroscopy and single-crystal X-ray analysis as $B_{18}H_{20}-8'-Py$ (compound **4**, 4.7 mg; 0.016 mmol, ~ 1%, MP = 252-253°C), (c) R_F 0.26, an orange solid after evaporation, identified by NMR spectroscopy and single-crystal X-ray analysis as $B_{18}H_{20}Py_2$ (compound **2**, 91.5 mg; 0.245 mmol, ~ 15 %, MP = 238-239°C), (d) R_F 0.05, yellow known [*anti*- $B_{18}H_{21}$] $[PyH]^+$ (124 mg; 0.42 mmol, ~ 26 %) identified by NMR spectroscopy.¹⁶ Recrystallisation of **2** was effected in a ca. 10 mm test tube by overlayering hexane onto a concentrated solution of **2** in CH_2Cl_2 , and then allowing diffusion to occur slowly, giving orange-red crystals. The pale-yellow solid residue remaining after the initial extraction with benzene was further extracted with CH_2Cl_2 (2 x 20 ml) to clean it, giving reasonably pure $B_{16}H_{18}Py_2$ (compound **3a**) as a pale-yellow powder. This was dissolved in anhydrous dimethylformamide (DMF; 10 ml); vapour-phase diffusion of diethyl ether thence gave large pale-yellow crystals of **3a**, which were filtered off and dried *in vacuo* (299 mg; 0.86 mmol; 53%. MP = 222-223°C).

Subsequent general procedures targeting compounds **2** and **3a** for further examination were typically as follows. A sample of *anti*- $B_{18}H_{22}$ (0.25 g) was dissolved in anhydrous $CHCl_3$ (30 ml) and to which was added pyridine (2 ml). The mixture was heated at reflux with stirring for ca. 12 hours under an inert atmosphere. Subsequent manipulations were carried out in air. After the reaction the mixture was cooled and filtered. The red filtrate was evaporated and the viscous residue was subjected to column chromatography on silica-gel (2.5x30cm) with hexane: CH_2Cl_2 (1:4) as eluting medium. A fraction with analytical R_F 0.70 [hexane: CH_2Cl_2 (1:4)] was identified as the $B_{18}H_{20}-8'-Py_2$ **2** and purified as above. The crude solid product after filtration was washed with diethyl ether and dry acetone to clean it, and dried *in vacuo*. This product is quite pure $B_{16}H_{20}Py_2$ **3a**, which was purified further by crystallisation *via* vapour diffusion of diethylether or dichloromethane into a concentrated solutions in *N,N*-dimethylformamide, giving light-yellow crystals that had remarkably low solubility in all other available organic solvents. Typical yields of **3a** under these conditions were in the range 55-65%, and of $B_{18}H_{20}Py_2$ **2** 10-20

%. The procedure to obtain the bis(picoline) analogue (4-MeC₆H₄)₂B₁₆H₂₀ **3b** was essentially the same, with a similar yield range.

NMR spectroscopy. NMR spectroscopy was carried out using commercially available instrumentation. In each case use of straightforward ¹¹B, ¹¹B-{¹H (broadband)} and ¹H-{¹¹B (broadband)} procedures²³⁻²⁶ clearly showed the number of boron atoms and the number of cluster hydrogen atoms. ¹H - {¹¹B(selective)} spectroscopy⁵¹ thence related the hydrogen resonances to the boron sites to which the hydrogen atoms are directly bound and the results of [¹¹B -¹¹B]-{¹H(broadband)}^{25,52} and [¹H -¹H]-{¹¹B(broadband)}⁵³ experiments thence provided sufficient correlations for unambiguous NMR assignment. All results were consistent with the molecular structures obtained from the X-ray work, showing that the crystals were representative of the bulk samples.

Mass spectrometry. LC Mass Spectrometry was performed using a ThermoScientific LCQ Fleet Ion Trap. The mass spectrum recorded for samples of B₁₈H₂₀(NC₅H₅)₂ (compound **2**) gave an envelope of mass values typical for boron species with a cut-off m/z of 375, which correlates precisely with the theoretical mass of [¹¹B₁₈¹H₁₉(¹⁴N¹²C₅¹H₅)₂]⁻. For samples of B₁₈H₂₀(NC₅H₅) (compound **4**) the mass spectrum recorded gave an envelope of mass values typical for boron species with a cut-off m/z of 296, which correlates precisely with the theoretical mass of [¹¹B₁₈¹H₁₉(¹⁴N¹²C₅¹H₅)]⁻. The loss of a hydrogen unit in the mass spectrometer is a regularly occurring and expected event. High insolubility precluded the collection of any good mass spectrometry data for compound **3a**.

X-ray crystallography. Crystals of B₁₈H₂₀Py₂ (compound **2**), B₁₆H₁₈Py₂ (compound **3a**), B₁₆H₁₈Pic₂ (compound **3b**) and B₁₈H₂₀Py (compound **4**) were examined on single-crystal diffractometers (Stoe STADI4 four-circle for **2** and **3a**, Bruker SMART 1K for **3b**, Bruker-Nonius Kappa-APEXII for **4**) at reduced temperatures. Standard diffractometer control software was used, complemented by locally written programs.⁵⁴ Selected crystallographic data are given in Table 6.

Table 6 Crystallographic data

Compound reference	2	3a	3b	4
Chemical formula	C ₁₀ H ₃₀ B ₁₈ N ₂	C ₁₀ H ₂₈ B ₁₆ N ₂	C ₁₂ H ₃₂ B ₁₆ N ₂	C ₅ H ₂₅ B ₁₈ N
Formula Mass	372.94	349.30	377.35	293.84
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
<i>a</i> /Å	9.5876(8)	9.0781(6)	10.3215(2)	9.7834(4)
<i>b</i> /Å	10.6882(8)	16.8243(10)	18.2213(6)	15.4854(7)
<i>c</i> /Å	11.4414(10)	13.8309(9)	12.2492(4)	12.5752(4)
<i>α</i> /°	73.923(5)	90	90	90
<i>β</i> /°	77.187(5)	95.355(6)	100.762(3)	106.589(2)
<i>γ</i> /°	88.805(4)	90	90	90
Unit cell volume/Å ³	1097.51(16)	2103.2(2)	2263.20(12)	1825.84(13)
Temperature/K	160(2)	120(2)	150(2)	150(2)
Space group	<i>P</i> 1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
No. of formula units	2	4	4	4
per unit cell, <i>Z</i>				
Radiation type	CuKα	MoKα	Synchrotron	MoKα
No. of reflections measured	3672	3362	15715	11002
No. of independent reflections	3604	3362	6239	3584
<i>R</i> _{int}	0.0658	0.0000	0.0507	0.0348
Final <i>R</i> _i values (<i>I</i> > 2σ(<i>I</i>))	0.0397	0.0623	0.0866	0.0454
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2σ(<i>I</i>))	0.1059	0.1450	0.1837	0.1116
Final <i>R</i> _i values (all data)	0.0433	0.0640	0.0975	0.0658
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.1085	0.1459	0.1884	0.1233
Goodness of fit on <i>F</i> ²	1.040	1.211	1.335	0.986
Difference map extremes /e Å ⁻³	0.27, -0.13	0.19, -0.19	0.38, -0.23	0.25, -0.18
CCDC reference	1441507	1441506	1441504	1441505

The structures were solved with programs of the SHELX family, and final refinements were carried out with SHELXL-2014.⁵⁵ Twofold disorder of one part of the fused boron cage was found in **2** and **3b**, and was partially resolved and refined in each case (all B and most H atoms for **2**, two B and some H atoms for **3b**). Most hydrogen atoms of the boron cages were located in difference maps and refined freely with individual isotropic displacement parameters, while ligand H atoms were included with a riding model.

Computational details. The multiconfigurational CASPT2//CASSCF protocol has been used to rationalize the photochemical features of compounds **4** and **3b**. This implies that geometries have been computed with the CASSCF method^{56,57} and at the optimized structures, energies have been obtained with the CASPT2 method.^{44,56,58} For **4**, the CAS active space used for the characterisation of the PEHs have comprised 10 electrons distributed into 8 molecular orbitals [10in8], namely the most relevant three π and the three π* of the pyridine ligand and the two occupied orbitals localised in the boron cluster (see SI 10). Meanwhile, the CAS active space of **3b** has been composed by the most relevant six π and the six π* of the pyridine ligand and the two occupied orbitals localised in the boron cluster, constituting a total of 14 electrons distributed into 13 molecular orbitals [14in13] (see SI 12). The double-ξ atomic natural orbital S-type (ANO-S-VDZP) basis set has been used for all the calculations as an acceptable

compromise between accuracy and computational cost.⁵⁹ Geometry optimisations of the S_0 ground and the S_1 excited state have been carried out demanding one and two roots in the CASSCF and state-average (SA)-CASSCF procedures, respectively. In the case of the smaller compound **4**, the calculation of the minimum energy path (MEP) from the FC region to the S_1 minimum has been affordable, whereas in the case of **3b** only a standard optimisation of S_1 has been possible due to computational cost reasons.

On top of the CASSCF geometries, the energies of the states of interest have been corrected by using the SA-CASSCF/CASPT2 method within an error of ~ 0.2 eV. Five roots have been demanded in the SA-CASSCF procedure in order to compute the lowest-lying singlet and triplet electronic states. Similarly, to our previous study,²⁸ an ionisation-potential electron-affinity (IPEA)⁶⁰ parameter of 0.25 a.u. has been used for the computations. For the absorption properties of compound **4**, the IPEA parameter with a value of 0.00 a.u. has been also considered. On the other hand, a level shift parameter of 0.2 au has been used in all cases in order to minimize the presence of weakly interacting intruder states.

The CI searches have been performed at the CASSCF level imposing energy degeneracy between the S_0 and the S_1 states by means of the Lagrange multipliers. CASPT2 calculations have subsequently been performed on top of the obtained set of geometries in order to estimate the corresponding minimum energy crossing points at the CASPT2 level (this approach is described elsewhere).⁶¹ The linear interpolation of internal coordinates (LIIC) procedure has been used to estimate possible barriers between the CI and the S_1 structures.

Oscillator strengths (f) have been computed according to the formula $f = \frac{2}{3} E_{VA} TDM^2$, where TDM stands for the CASSCF transition dipole moment between the initial φ_1 and final φ_2 electronic states, and $TDM = \langle \varphi_1 | \vec{d} | \varphi_2 \rangle$, where $\vec{d}$ is the dipole moment operator. The SOCs have been computed with the restricted active space state-interaction method using the atomic mean field approximation, and the following formula:

$$SOC_{lk} = \sqrt{\sum_u |\langle T_{l,u} | \hat{H}_{SO} | S_k \rangle|^2} \quad u = x, y, z$$

where $\hat{H}_{SO}$ is the spin-orbit Hamiltonian and T and S refer to the triplet and singlet states, respectively.

All the electronic structure calculations have been performed with the MOLCAS 8 suite of programs.⁶²

Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ Compound **2** is formally (IUPAC nomenclature recommendations) 6',9'-bis(pyridine)-*arachno*-decaborano-[10',5':5,6]-*nido*-decaborane, compound **3a** is formally 3',8'-bis(pyridine)-*arachno*-octaborano-[5',6':5,6]-*nido*-decaborane, and compound **4** is formally 8'-(pyridine)-*nido*-decaborano-[6',7':5,6]-*nido*-decaborane. Each is formed as a racemate, with both enantiomers present in the crystal structure, the other enantiomers being formally 6',9'-bis(pyridine)-*arachno*-decaborano-[10',5':6,7]-*nido*-decaborane, 3',8'-bis(pyridine)-*arachno*-octaborano-[5',6':6,7]-decaborane, and 10'-pyridine-*nido*-decaborano-[5',6':6,7]-*nido*-decaborane, respectively.

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