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A Stacking Interaction between a Bridging Hydrogen Atom and Aromatic π Density in the n-$B_{18}H_{22}$–Benzene System

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Abstract: The structures of n-$B_{18}H_{22}$ and of n-$B_{18}H_{22}\cdot C_6H_6$ were determined by single-crystal X-ray analysis at −60 °C. The geometry of the boron cluster itself does not seem to be appreciably affected by solvation. There does, however, appear to be an unusual interaction of a polyborane bridging hydrogen atom with the benzene π system, giving rise to an extended stacked structure. The $^1H\{^{11}B\}$ spectrum of n-$B_{18}H_{22}$ in [D$_6$]benzene differs from that in [D$_{12}$]cyclohexane most noticeably in the bridging proton region. Upon moving from the aliphatic to the aromatic solvent, the greatest increase in shielding was for the signal corresponding to the bridge hydrogen atom that interacts with the π system of benzene; the signal was shifted upfield by 0.49 ppm. Density functional theory calculations were performed on 1:1 and 2:1 complexes of the n-$B_{18}H_{22}$ unit with benzene.

Keywords: boranes • cluster compounds • density functional calculations • NMR spectroscopy • pi interactions • X-ray diffraction

Introduction

Nonclassical interactions of aromatic π electrons with cations, neutral molecules, and within biomolecules such as DNA have been known for some time, and continue to be the subject of considerable research interest.[1–7] Models based on electrostatic and van der Waals interactions have been proposed to explain many of the typically observed behaviors in these systems.[2] These types of interactions have been widely promoted as having potential applications in fields including supramolecular chemistry, crystal engineering, and molecular recognition.[8–10]

A variety of structural and theoretical studies have been performed on systems based on conventional hydroaromatic molecules as well as on perfluoroaromatics.[9–12] The interest in these systems arose following the discovery in 1960 that benzene and perfluorobenzene form a solid phase with a melting point of 24 °C, higher than that of either pure component.[12]

This was consistent with a structure showing an offset packing arrangement that maximized interactions between the electron-poor π system of perfluorobenzene and its relatively electron-rich counterpart in benzene. Recent estimates of the strength of the interaction between the two components in this system range from 3.7–4.3 kcal mol^{-1}.[13,14]

Bridging hydrogen atoms in polyhedral boranes are known to be acidic in character, and bear partial positive charges in neutral molecules, in contrast to the hydridic nature of terminally bonded hydrogen atoms on boron.[15,16] In general, the degree of acidity of the bridging hydrogen atoms increases with increasing size of the cluster.[17]

An in-depth study of the ^{11}B and ^1H NMR properties of n-$B_{18}H_{22}$ (as well as the n-$[B_{18}H_{21}]^-$ and n-$[B_{18}H_{20}]^{2-}$ ions) has previously been performed by Kennedy and co-workers.[18] Analysis of two-dimensional spectra afforded complete assignments for all resonances in the proton spectrum of n-$B_{18}H_{22}$. Of particular note were differences in the spec-

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trum observed on going from aliphatic (CD_2Cl_2) to aromatic ([D_6]benzene) solvents. In the latter case, particularly evident shielding of protons in the bridging region was observed, suggestive of a π interaction between the cluster and solvent molecules.

The estimated pK_a value for n-$B_{18}H_{22}$ has been reported as 2.68, only marginally smaller than that of $B_{10}H_{14}$ (2.70), suggesting that these two species have similar Brønsted acidities.[16] Additionally, Gibb and Kennedy[19] also used data obtained from detailed variable-temperature NMR experiments to obtain values for thermodynamic parameters for the solution of decaborane(14) in [D_8]toluene, suggesting that the bridging hydrogen atoms in decaborane(14) ($B_{10}H_{14}$) might also be capable of forming a weak interaction with the π-electron system of aromatic compounds, such as benzene or toluene, analogous to that described above for n-$B_{18}H_{22}$. In an effort to structurally characterize this type of arrangement, we have examined the interactions of $B_{10}H_{14}$ and n-$B_{18}H_{22}$ with aromatic molecules. The results presented here describe the X-ray structural characterization of a π-stacking arrangement in the n-$B_{18}H_{22}$–benzene system.

Results and Discussion

The X-ray crystal structure of n-$B_{18}H_{22}\cdot C_6H_6$ (**1**) and a redetermination of the structure of (nonsolvated) n-$B_{18}H_{22}$ (**2**) have been carried out. Structure **2**, originally determined in 1963,[20] was redetermined for purposes of direct comparison with **1**. The structures of **1** and **2** are shown in Figures 1 and 2, respectively, and crystal data are presented in Table 1.

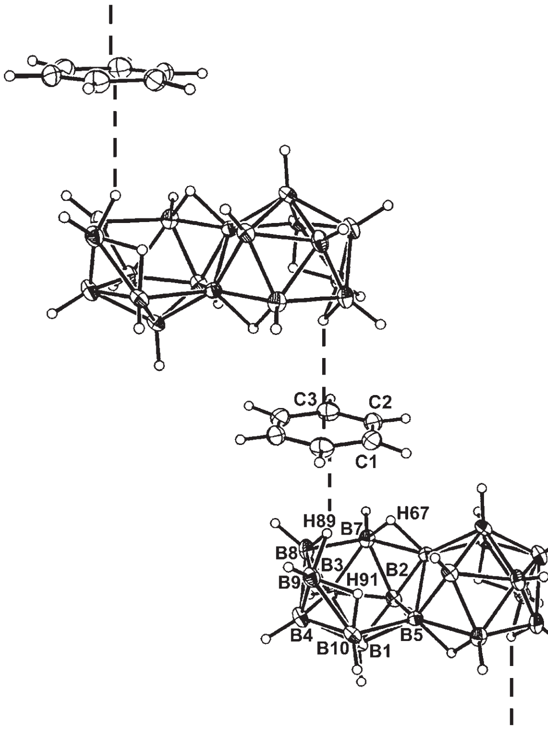

Figure 1. Plot showing stacking arrangement in n-$B_{18}H_{22}\cdot C_6H_6$ (**1**; 25% probability ellipsoids for boron and carbon).

Selected distances and angles for **1** are provided in Table 2, and selected bond lengths for **2** are given in Table 3.

The molecular structure of n-$B_{18}H_{22}$ in the n-$B_{18}H_{22}\cdot C_6H_6$ crystal is not greatly affected by its interaction with the benzene molecule. B–B distances in n-$B_{18}H_{22}$ (**2**) are longer than corresponding distances in n-$B_{18}H_{22}\cdot C_6H_6$ (**1**). In agreement with this, principal mean-square atomic displacements (given in the Supporting Information) for corresponding B atoms in **2** are smaller than those in **1**. Distances between H89 and B8 and B9 within the borane in structure **1** are 1.26(3) and 1.31(3) Å, respectively. These values are not significantly different from the corresponding distances in structure **2**, which are 1.27(2) and 1.33(1) Å, respectively.

All close intermolecular contacts for **2** are normal with H-to-H distances ranging from 2.55 to 2.83 Å. In **1** H-to-H distances between boron cages vary from 2.53 to 2.82 Å. Normal intermolecular H-to-H contacts, 2.47 to 2.83 Å, are present between $B_{18}H_{22}$ and C_6H_6, but there appears to be

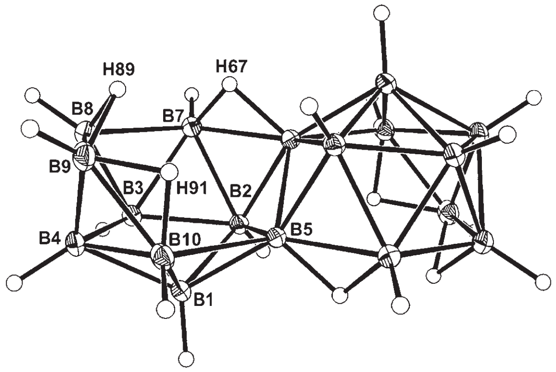

Figure 2. Plot of n-$B_{18}H_{22}$ (**2**; 25% probability ellipsoids for boron).

Table 1. Crystal data and structure refinement for n-$B_{18}H_{22}\cdot C_6H_6$ (**1**) and n-$B_{18}H_{22}$ (**2**).

	1	**2**
formula	$H_{28}B_{18}C_6$	$H_{22}B_{18}$
M_r	294.86	216.76
crystal system	monoclinic	orthorhombic
space group	$P2_1/n$	$Pccn$
a [Å]	6.800(2)	10.810(2)
b [Å]	14.078(3)	12.058(3)
c [Å]	10.226(2)	10.762(2)
β [°]	105.04(3)	
V [$Å^3$]	945.5(2)	1402.9(2)
Z	2	4
ρ_{calcd} [$g\,cm^{-3}$]	1.036	1.026
μ [mm^{-1}]	0.043	0.038
2θ limits [°]	4–50	4–50
reflns measd/unique	3601/1663	4735/1231
variables	165	127
R_1[a] [$I>2\sigma(I)$]	0.0687	0.0452
wR_2[b] (all data)	0.1453	0.1205
GOF[c]	1.001	1.112
max/min $\Delta\rho$ [$e\,Å^{-3}$]	0.163/−0.247	0.209/−0.258

[a] $R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. [b] $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] $GOF=S=\{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$.

Table 2. Selected bond lengths [Å] and angles [°] for $n\text{-}B_{18}H_{22}\cdot C_6H_6$ (**1**).

B1–B10	1.740(5)	B7–B8	1.946(5)
B1–B5	1.746(5)	B7–H7	1.13(3)
B1–B3	1.778(5)	B7–H67	1.29(3)
B1–B2	1.786(5)	B8–B9	1.795(5)
B1–B4	1.786(5)	B8–H8	1.09(3)
B1–H1	1.06(3)	B8–H89	1.26(3)
B2–B3	1.746(5)	B9–B10	1.783(6)
B2–B5#1[a]	1.765(4)	B9–H9	1.06(3)
B2–B7	1.774(5)	B9–H89	1.31(3)
B2–B5	1.802(4)	B9–H91	1.28(3)
B2–H2	1.02(2)	B10–H10	1.12(3)
B3–B8	1.723(6)	B10–H91	1.19(3)
B3–B7	1.746(5)	C1–C2	1.371(5)
B3–B4	1.774(5)	C1–C3#2[a]	1.379(5)
B3–H3	1.05(3)	C1–H1A	0.98(3)
B4–B9	1.702(5)	C2–C3	1.366(5)
B4–B10	1.775(5)	C2–H2A	0.98(4)
B4–B8	1.789(5)	C3–H3A	0.92(3)
B4–H4	1.06(3)	H89–X1A[b]	2.816
B5–B5#1	1.805(6)	H89–C1	3.050
B5–B7#1	1.815(5)	H89–C2	3.094
B5–B10	1.968(5)	H89–C3	3.081
B7–B5#1	1.815(5)		

B3-B7-H67	128(1)	B10-B9-H91	42(2)
B2-B7-H67	103(1)	B8-B9-H91	118(1)
B5#1-B7-H67	47(1)	H9-B9-H91	108(2)
B8-B7-H67	90(1)	H89-B9-H91	98(2)
H7-B7-H67	111(2)	B1-B10-H91	128(2)
B3-B8-H89	129(1)	B4-B10-H91	101(2)
B4-B8-H89	101(1)	B9-B10-H91	46(2)
B9-B8-H89	47(1)	B5-B10-H91	90 (2)
B7-B8-H89	93(1)	H10-B10-H91	107(2)
H8-B8-H89	104(2)	C2-C1-C3#2	119.6(3)
B4-B9-H9	134(1)	C2-C1-H1A	118(2)
B10-B9-H9	127(1)	C3#2-C1-H1A	122(2)
B8-B9-H9	127(1)	C3-C2-C1	120.2(4)
B4-B9-H89	103(1)	C3-C2-H2A	119(2)
B10-B9-H89	118(1)	C1-C2-H2A	121(2)
B8-B9-H89	44(1)	C2-C3-C1#2	120.2(3)
H9-B9-H89	108(2)	C2-C3-H3A	120(2)
B4-B9-H91	101(2)	C1#2-C3-H3A	120(2)

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x$, $-y$, $-z$; #2: $-x$, $-y$, $-z-1$. [b] X1A is the centroid of benzene molecule.

Table 3. Selected bond lengths [Å] for $n\text{-}B_{18}H_{22}$ (**2**).

B1–B10	1.755(2)	B4–H4	1.07(2)
B1–B5	1.755(2)	B7–B5#1	1.820(2)
B1–B2	1.791(2)	B7–B8	1.970(2)
B1–B4	1.792(2)	B7–H7	1.06(1)
B1–B3	1.795(2)	B7–H67	1.24(1)
B1–H1	1.07(2)	B8–B9	1.802(2)
B2–B3	1.761(2)	B8–H8	1.09(2)
B2–B5#1[a]	1.770(2)	B8–H89	1.27(2)
B2–B7	1.794(2)	B9–B10	1.783(2)
B2–B5	1.810(2)	B9–H9	1.05(2)
B2–H2	1.04(2)	B9–H89	1.33(1)
B3–B8	1.753(2)	B9–H91	1.30(1)
B3–B7	1.762(2)	B10–B5	1.984(2)
B3–B4	1.783(2)	B10–H10	1.08(1)
B3–H3	1.07(2)	B10–H91	1.26(1)
B4–B9	1.720(2)	B5–B5#1	1.805(2)
B4–B10	1.779(2)		
B4–B8	1.806(2)		

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x+1$, $-y+1$, $-z$.

an unusual interaction of a bridging hydrogen atom (H89) on the polyborane cluster with the benzene π system as shown in Figure 1, with a separation between the benzene ring centroid and the bridging H89 atom of 2.816 Å. The van der Waals radii for carbon and hydrogen are 1.7 and 1.2 Å, respectively.[21] No other short contacts are apparent.

The observed weak interaction between H89 and the benzene π-system is consistent with the increased shielding observed for the bridging hydrogen atoms, most noticeably H89, in the $^{1}H\{^{11}B\}$ NMR spectrum of $n\text{-}B_{18}H_{22}$ in aromatic solvents. Details of this aromatic-solvent-induced shift (ASIS) effect,[19,28] in the $n\text{-}B_{18}H_{22}$ system are described in detail below.

The existence of weak hydrogen bonds,[5] in particular C–H⋯π hydrogen bonds,[6,7] is well established. As evidence for the presence of such a bond in a crystal, the normalized distance[23] between H and the center of a phenyl ring should be less than 2.8 Å and the angle C–H⋯π close to 180°. Thus there are two complications in evaluating the significance of the 2.82 Å distance in the present structure. First, the bridging hydrogen atom is nearly equidistant between two boron atoms and a customary correction of 0.1 Å in the distance measured by X-ray diffraction is not applicable. Instead, a comparison of X-ray and neutron data[24] indicate that a correction of 0.06 Å along the H⋯π direction would be appropriate, thereby reducing the normalized distance to 2.76 Å. Second, since the hydrogen atom is attached to two boron atoms, the B–H⋯π angles are not close to 180°. However, the angle between H⋯π and the plane of the benzene ring is 88°, close to an ideal value of 90° for a hydrogen bond to a π face.

Density functional theory[25] calculations were also performed on 1:1 and 2:1 complexes of the $n\text{-}B_{18}H_{22}$ unit with benzene. For each case, the geometry was fully optimized at the B3LYP/6-31+G** level,[26] and thereby provided the energies and geometries for further analysis. The optimized geometries for these two model complexes are shown in Figure 3 left and right, respectively.

The binding energy for complexation in the 1:1 complex is $-1.0\,\text{kcal}\,\text{mol}^{-1}$, and the effect is almost additive as the 2:1 complex has a $-1.8\,\text{kcal}\,\text{mol}^{-1}$ binding energy.

The calculated distance between the nearest bridging hydrogen atom in the $n\text{-}B_{18}H_{22}$ unit and the center of the benzene ring is 3.647 and 3.567 Å in the 1:1 and 2:1 complexes, respectively, indicative of a favorable interaction between the hydrogen atom and the electron-rich aromatic ring. The geometric and structural information is provided in the Supporting Information.

Although the potential existence of borane–aromatic π interactions was suggested by Kennedy two decades ago,[18,19] there has, to our knowledge, been no specific mention in the literature of such an interaction being observed in the solid state. However, a survey of the Cambridge Structural Database (CSD) revealed ten contacts of the type considered here, involving a boron-bridged hydrogen atom with B–H⋯π distances of less than 3.0 Å.[27] Table 4 lists all of the relevant contacts identified from the CSD survey.

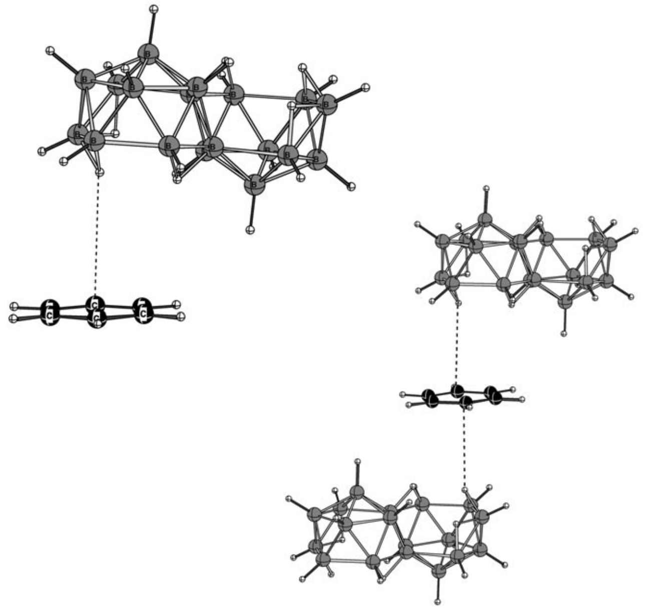

Figure 3. B3LYP/6-31+G** optimized geometries of the 1:1 complex of n-$B_{18}H_{22}$ with benzene (left) and the 2:1 complex of n-$B_{18}H_{22}$ with benzene (right).

None of the reports of the studies that featured these relatively short contacts made any specific mention of these interactions. However, certain of these interactions are particularly illustrative, and are shown in Figures 4–6 below.

Table 4. Identified short contacts of boron-bridged hydrogen atoms with aromatic ring centroids.

Source	Ref.	d [Å][a]	Angle [°][b]	Molecularity
1-($SnClPh_2$)-B_5H_8	[27a]	2.74	176	inter
[(PPh_3)($PhCOS)_2Ni(B_{10}H_{10}$)]·0.5 C_6H_{14}	[27b]	2.81	140	intra
n-$B_{18}H_{22}$·C_6H_6	this work	2.82	149	inter
1-($SnClPh_2$)-B_5H_8	[27a]	2.83	169	inter
[{(PPh_3)PdS_2(B_6H_8)}$_2$]·C_7H_8	[27c]	2.83	142	intra
Be(B_5H_{10})$_2$·C_8H_{10}	[27d]	2.88	159	inter
[(PMe_2Ph)$_3$HRe(B_9H_{13})]	[27e]	2.93	148	intra
[(CO)$_2$(PMe_2Ph)$_2$Mo(B_9H_{12}Cl)]	[27f]	2.94	150	intra
[(PMe_2Ph)$_3H_2$Re(B_8H_{11})]·0.5 CH_2Cl_2	[27g]	2.98	158	intra
[(Ph_3P)$_3$Au][B_9H_{12}S]	[27h]	2.98	133	inter
[(Ph_3P)$_2$N][B_3H_7NCBH$_3$]	[27i]	3.00	159	inter

[a] Distance from the bridging hydrogen atom to the ring centroid. [b] Angle defined by center of bridged B–B connectivity, the bridging hydrogen atom, and aromatic ring centroid.

Figure 4 shows the shortest of these interactions (2.74 Å), in the 1-($SnClPh_2$)-B_5H_8 system.[27a]

This particular system is unique among these examples, in that it possesses two bridging H···π interactions per pair of molecules. The two interactions within each molecular pair are identical due to a crystallographically imposed plane of symmetry. Another essentially identical, but crystallographically independent, pair of molecules in this structure exhibits analogous behavior, albeit with a slightly longer H···π distance (2.83 Å).

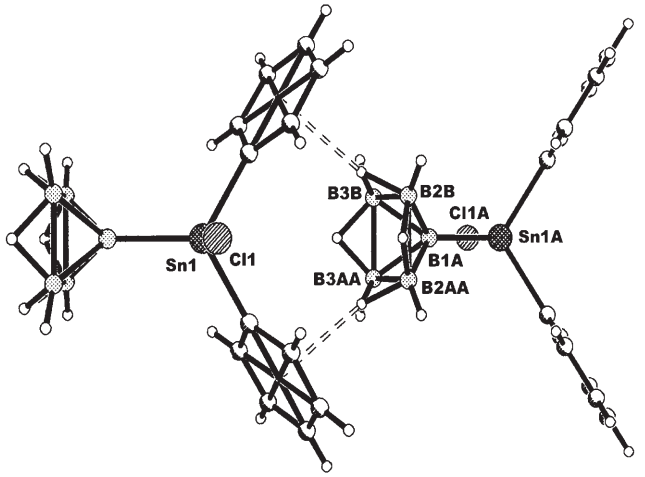

Figure 4. The intermolecular interactions in the 1-($SnClPh_2$)-B_5H_8 system. (Figure derived from data in reference [27a]).

Figure 5 shows two very similar structures that feature intramolecular interactions between B–H–B bridges and the π system of a phenyl ring from a PPh_3 moiety in a *nido*- 10 vertex metallaborane.[27e,f]

Note should be made in these cases that the PPh_3 unit involved in the interaction is oriented in such a way as to maximize interaction with the available bridging hydrogen atom. This is supportive of a significant stabilizing effect of the interaction in question. Simple rotation about the metal–phosphorus bond (as well as about the P–C bond) could easily be effected to minimize the interaction were it unfavorable.

A similar interaction with a PPh_3 group is observed in the 11-vertex *nido*-nickelaborane system shown in Figure 6.[27b]

Again, the conformation of the interacting phenyl ring is such that maximal overlap with the bridging hydrogen atom is maintained in the solid state.

The overall evidence supports the presence of a (rare) weak hydrogen bond in our structure. Figure 7 shows the scope of hydrogen-bonding interactions in various systems.[6]

The type of interaction discussed here undoubtedly lies to the weaker end of the scale, or to the lower right of the diagram, as indicated by the theoretical results presented above. Further observations of this structural type are needed.

The bridging proton H89 in the n-$B_{18}H_{22}$·C_6H_6 structure was found to have the shortest contacts with the benzene system, as described above.

Consistent with this is the observation that the $^1H\{^{11}B\}$ NMR spectrum of n-$B_{18}H_{22}$ in [D_6]benzene differs noticea-

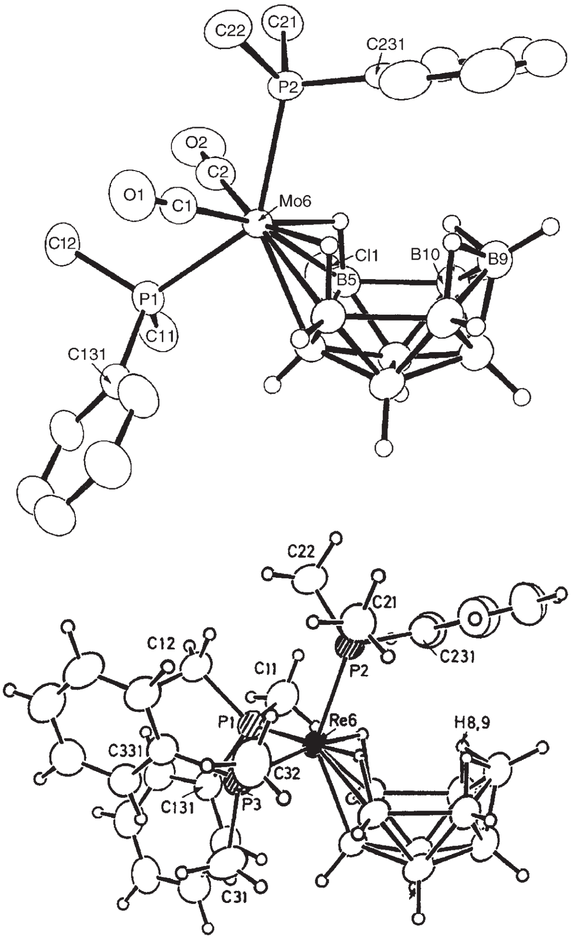

Figure 5. Top: Plot of $(PMe_2Ph)_3HReB_9H_{13}$, from reference [27e]. Reproduced by permission of the Royal Society of Chemistry. Bottom: Plot of $(CO)_2(PMe_2Ph)_2MoB_9H_{12}Cl$, from reference [27f]. Reproduced by permission of Wiley-VCH publishers.

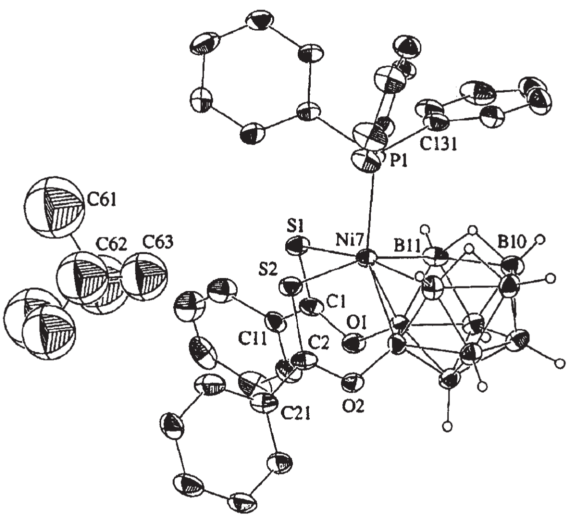

Figure 6. Plot of $(PPh_3)(PhCOS)_2NiB_{10}H_{10}\cdot 0.5\ C_6H_{14}$, from reference [27b]. Reproduced by permission of the International Union of Crystallography.

bly from that in $[D_{12}]$cyclohexane in the bridging proton region. Specifically, upon moving from the aliphatic to the aromatic solvent, the greatest increase in shielding was for the signal corresponding to H89, which was shifted upfield by 0.49 ppm. Similarly, in $[D_8]$toluene, an upfield shift of 0.45 ppm was observed for the interacting bridge resonance. Even in a 1:1 C_6D_{12}/C_6D_6 solvent mixture, this peak was shifted upfield by 0.42 ppm from its position in C_6D_{12} alone. This type of aromatic-solvent-induced shift (ASIS) has been discussed previously for polyboranes, with correlation to calculated atomic charge, and molecular dipole.[19,28] n-$B_{18}H_{22}$ has no net dipole due to the inversion center midway along the shared B–B vertex, but each decaboranyl fragment has a local dipole with the more positive end pointing to the open face of the subcluster. Hydrogen atoms associated with the open face of the cluster generally display an ASIS effect moving their chemical shifts to lower frequency (i.e., additional shielding). In the case of n-$B_{18}H_{22}$, all of the hydrogen atoms associated with the nonfacial atoms are shifted in the opposite sense, with the exception of the H2 signal.

$^1H\{^{11}B\}$ and ^1H NMR data for n-$B_{18}H_{22}$ in various solvents are presented in Table 5.

Indeed, to further support this conclusion, we have also studied the behavior of n-$B_{18}H_{22}$ with other aromatic species, such as toluene and hexamethylbenzene. Attempts were made to obtain crystals of n-$B_{18}H_{22}$ showing solvation by toluene, but this did not prove successful. n-$B_{18}H_{22}$ does appear to possess greater solubility in toluene than in benzene, which might be suggestive of slightly stronger intermolecular attraction, consistent with the electron-donating capability of the methyl substituent on toluene. Efforts were also directed towards creating a molecular complex between n-$B_{18}H_{22}$ and hexamethylbenzene, but the only crystals obtained were of the individual components, with no indication of the desired interaction. While these methyl-bearing aromatics may provide more electron-rich π systems with which the borane could interact, they also possess greater steric requirements than benzene, which may be ultimately responsible for non-observation of molecular complexes in these cases.

Since the structure of n-$B_{18}H_{22}$ is derived from two edge-sharing *nido*-B_{10} units, it might also be a reasonable expectation that decaborane(14) might indulge in a similar interaction with aromatic hydrocarbons, such as benzene or toluene. This is in accord with earlier NMR observations showing the influence of aromatic solvents on bridging-hydrogen-atom shifts in $B_{10}H_{14}$.[19,28] Previous work in this laboratory showing a charge-transfer complex between $B_{10}H_{14}$ and I^- is also consistent with this idea, illustrating the ability of the bridging hydrogen atoms in the borane to form interactions with sources of available electron density.[29] Crystals were grown by concentration and cooling of solutions of $B_{10}H_{14}$ in benzene and toluene, as well as from solutions containing stoichiometric equivalents of $B_{10}H_{14}$ and hexamethylbenzene in an analogous manner to that used to prepare crystals of **1**. Unit cell data indicated that no solid-state molecular complexes were produced in these particular systems.

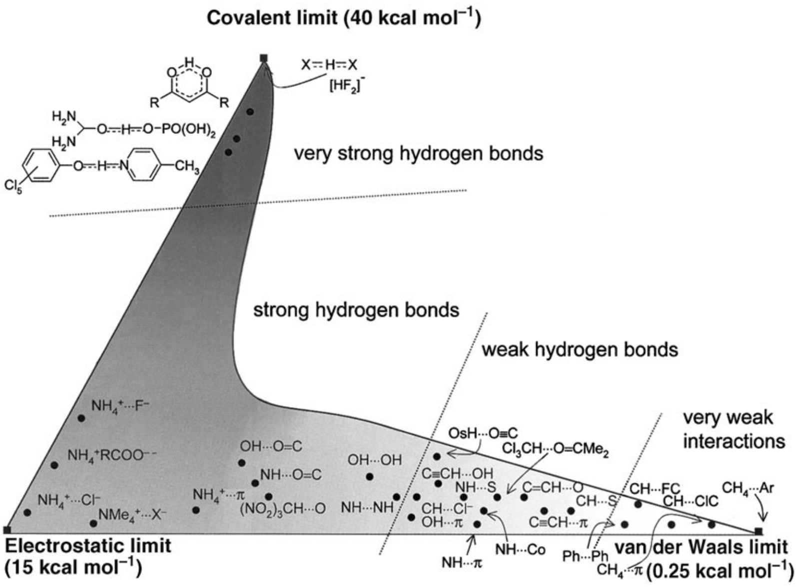

Figure 7. The hydrogen bridge. Reprinted with permission from reference [6]: *Acc. Chem. Res.* **2002**, *35*, 565–573. Copyright 2002 American Chemical Society.

Table 5. NMR data for n-$B_{18}H_{22}$ in various solvents.

	$^1H\{^{11}B\}$ δ [ppm]			
	C_6D_{12}	C_6D_6	C_7D_8	C_6D_{12}/C_6D_6 (1:1)
H10	4.16	4.08	4.10	4.00
H3	4.00	4.18	4.16	4.00
H9	3.39	3.04	3.07	3.08
H1	3.14	3.19	3.21	3.08
H7,H8	3.05	2.91	2.91	2.85
H4	0.59	0.82	0.78	0.61
H2	−0.04	−0.29	−0.25	−0.25
H9,10	0.36	−0.77	−0.74	−0.73
H6,7	−0.95	−1.34	−1.30	−1.29
H8,9	−3.03	−3.52	−3.48	−3.45
	^{11}B δ [ppm] (J_{BH} [Hz])			
	C_6D_{12}	C_6D_6	C_7D_8	C_6D_{12}/C_6D_6 (1:1)
B3	17.88 (152)	17.58 (150)	17.60 (148)	17.66 (151)
B10	12.49 (161)	12.12 (157)	12.14 (156)	12.22 (160)
B5	8.58 (s)	8.14 (s)	8.15 (s)	8.26 (s)
B9	6.22 (155)	6.31 (149)	6.29 (143)	6.24 (161)
B1	3.95 (150)	3.76 (148)	3.80 (149)	3.80 (153)
B8	−1.02 (154)	−1.11 (155)	−1.13 (153)	−1.09 (153)
B7	−8.86 (155)	−8.75 (161)	−8.76 (156)	−8.74 (153)
B2	−28.45 (159)	−29.00 (160)	−28.94 (159)	−28.83 (157)
B4	−36.67 (162)	−36.69 (157)	−36.71 (157)	−36.73 (159)

While the type of interaction described above is unusual for polyboranes, similar structural motifs are known in a variety of other systems.

Supramolecular architectures have been reported in which Pd_6Cl_{12} clusters cocrystallize and stack in an essentially parallel fashion with polycyclic aromatic hydrocarbons, the closest intermolecular contacts in these cases being on the order of 3.3 Å between bridging Cl atoms of the cluster and carbon atoms of the polyaromatic species.[30]

The interaction between 1,2-$C_2B_{10}H_{12}$ (o-carborane) and the concave-shaped cyclotriveratrylene (CTV) molecule can be regarded as the first example of a genuine host–guest complex of a main group cluster (other than C_{60}).[22] The structure is shown in Figure 8. The stability of this complex can presumably be attributed to the nonclassical interactions between the somewhat acidic hydrogen atoms attached to carbon atom on the carborane and two of the three aromatic moieties in the CTV. The third aromatic ring is forced to adopt a less favorable interaction with a (terminal) B−H of the cluster. The π stacking between the CTV molecules themselves also contributes to the overall crystal packing in the structure, which contains an overall 1:2 ratio of o-carborane to CTV.

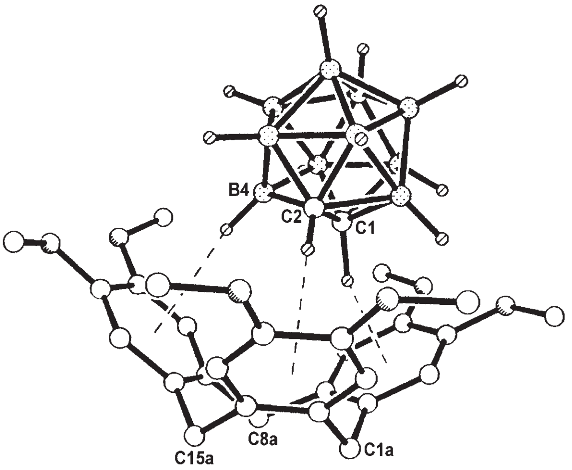

Figure 8. Plot of the complex between o-carborane and cyclotriveratrylene, from reference [22]. Reproduced by permission of Wiley-VCH publishers.

Distances from the centroids of the aromatic rings to the H atoms on C1, C2, and B4 are 2.184, 2.556, and 2.765 Å, respectively. A theoretical study was performed to model the strength of the interaction between o-carborane and benzene, yielding information on the stabilizing effect associated with such carborane C−H⋯π interactions. This showed each such interaction to confer a stability of 2.72 kcal mol^{-1}. This study also predicted a C−H⋯benzene centroid separation of 2.694 Å.

This result is also consistent with the results presented earlier for the n-$B_{18}H_{22}\cdot C_6H_6$ sytem, in which the calculated distances between the bridging hydrogen atom and the ring centroid were consistently longer than that observed in the X-ray study.

As part of a larger ab initio study of the interaction between the benzene system and 2nd period non-metal hydrides, it was found that the highest binding energy was for the BH_3–C_6H_6 system, with an approximate value of 6.2 kcal mol^{-1}. This interaction is, however, fundamentally different from that expected for polyborane clusters (or other 2nd row hydrides) with aromatics, since it does not involve a π–H interaction, but rather an interaction between the π system and the empty $2p_z$ orbital on boron.[31,32] Clearly for larger boranes, clustering already alleviates this electron deficiency.

Experimental Section

X-ray structure determinations of *n*-$B_{18}H_{22}$·C_6H_6 (1) and *n*-$B_{18}H_{22}$ (2): For both structures, single-crystal X-ray diffraction data were collected at −60 °C on an Enraf-Nonius KappaCCD diffraction system, employing graphite-monochromated $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å. Unit cell parameters were obtained by indexing the peaks in the first ten frames and refined by using the whole data set. All frames were integrated and corrected for Lorentz and polarization effects by using DENZO.[33] The structures were solved by direct methods and refined by using SHELXTL (difference electron density calculations, full-matrix least-squares refinement).[34]

n-$B_{18}H_{22}$·C_6H_6 (1): Diffraction-quality crystals of **1** were grown by cooling of a concentrated solution of *n*-$B_{18}H_{22}$ in benzene. A blocklike crystal of dimensions 0.40 × 0.40 × 0.40 mm was mounted in a glass capillary to prevent solvent loss. Diffraction data were collected at −60 °C, and the structure was solved and refined in the monoclinic space group $P2_1/n$.

n-$B_{18}H_{22}$ (2): Diffraction-quality crystals of **2** were grown by vacuum sublimation onto a water-cooled cold finger. A crystal of dimension 1.00 × 0.52 × 0.26 mm was mounted on a glass fiber. Diffraction data were collected at −60 °C, and the structure was solved and refined in the orthorhombic space group *Pccn*.

Additionally, a number of other attempts were made to produce molecular complexes between polyboranes and aromatic molecules. The following combinations were tested, producing only crystals of one or other of the pure components:

1) Cooling of a solution of *n*-$B_{18}H_{22}$ in toluene.
2) Cooling of a solution of an equimolar mixture of *n*-$B_{18}H_{22}$ and hexamethylbenzene in CH_2Cl_2.
3) Slow evaporation of a solution of an equimolar mixture of *n*-$B_{18}H_{22}$ and hexamethylbenzene in CH_2Cl_2.
4) Cooling of a solution of $B_{10}H_{14}$ in benzene.
5) Cooling of a solution of $B_{10}H_{14}$ in toluene.
6) Cooling of a solution of an equimolar mixture of $B_{10}H_{14}$ and hexamethylbenzene in CH_2Cl_2.
7) Slow evaporation of a solution of an equimolar mixture of $B_{10}H_{14}$ and hexamethylbenzene in CH_2Cl_2.

Further details of the crystal structure determinations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository numbers CSD-391 324 and CSD-391 325.

NMR spectroscopy: $^1H\{^{11}B\}$ and ^{11}B NMR spectra were recorded in C_6D_{12}, C_6D_6, C_7D_8, and a 1:1 C_6D_{12}/C_6D_6 mixture at 500.020 MHz and 160.422 MHz by using a Bruker AM-500 instrument, referenced against $SiMe_4$ (^1H) $\delta = 0.00$ ppm and BF_3OEt_2 (^{11}B) $\delta = 0.00$ ppm. Assignments were made by reference to the previous work by Kennedy and co-workers.[18] NMR data are presented in Table 5.

Theoretical studies: All theoretical calculations on 1:1 and 2:1 model complexes of the *n*-$B_{18}H_{22}$ unit with benzene were performed by using GAUSSIAN 03.[35] Density functional theory[25] calculations were performed using geometries that were fully optimized at the B3LYP/6-31+G** level.[26]

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