Bonding in Clusters. Part 5.[1] The Electronic, Molecular, and Crystal Structure of 1,10-$B_{10}H_8(N_2)_2$: † A Combined Theoretical, Photoelectron, and *X*-Ray Crystallographic Study

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The structure and bonding of the title compound have been studied using He(I) and He(II) photoelectron spectroscopy, *X*-ray crystallography, and molecular-orbital calculations. The molecular structure is based on the *closo* B_{10}-bicapped square antiprism cage. Assignment of the photoelectron spectra is made with the aid of calculations on the title compound and on *closo*-$B_{10}H_{10}^{2-}$. Analysis of the calculations shows that both these *closo* B_{10} cages have very similar electronic structures and the BN_2 unit is formally analogous to the BH^- unit.

The study of the electronic structure of *closo*-borane compounds is severely limited in the techniques available. The anions $B_nH_n^{2-}$ (n = 6—12) are prepared as white crystalline materials with no experimentally accessible ultraviolet absorptions and are involatile, prohibiting the use of photoelectron spectroscopy. Theoretical studies provide an obvious approach for investigating these compounds and have been applied by many researchers at various levels of sophistication, however, such studies are considerably strengthened if they can be combined with some experimental work. Correspondence between theoretical minimum-energy geometry and experimental molecular geometry provides one such check, and photoelectron spectroscopy can be used if the compounds can be substituted in some way to neutralise the negative charge and produce volatile species.

To date, substitution of BH^- by CH or some metallo-group has been used to give uncharged carboranes or metalloboranes. However, in both these cases, and particularly with metallo-groups, one is starting with a significant perturbation of the *closo* framework which is a major feature of interest. The compound 1,10-$B_{10}H_8(N_2)_2$ is one of a number of compounds derived from $B_{10}H_{10}^{2-}$ which avoids perturbation of the *closo* skeleton by having the charge-compensating substituent *exo* to the borane cage.

In this paper we are concerned with the electronic structure of 1,10-$B_{10}H_8(N_2)_2$ and related compounds studied through the MNDO semi-empirical calculation of Dewar and McKee.[2] The tactics of this paper are to establish the validity of the calculational method by comparing the theoretically determined geometry and molecular-orbital energies with the crystallographically determined molecular structure and the gas-phase photoelectron spectrum respectively. These properties, testing as they do quite separate aspects of the molecule, can be taken together as stringent tests of the calculation's validity. The results of the calculation are then used to discuss various aspects of the electronic structure, *e.g.* the cluster bonding of the B_{10} cage and the comparison between BN_2 and BH^- cluster bonding units.

Experimental

The compound 1,10-$B_{10}H_8(N_2)_2$ was prepared by the literature method,[3] and was characterised by its melting point, i.r. spectrum, and mass spectrometry. The mass spectrum was recorded on an AEI-Kratos MS 30DB double-focusing spectrometer operating with 70 eV ionisation voltage, 4 kV accelerating potential, 300 μA trap current, and 80—100 °C source temperature. The spectrum showed parent molecular ions at m/z 174—164 and successive loss of N_2 molecules (ions centred at m/z 144 and 115). Fragmentation by H_2 loss from these ions, which is typical of borane derivatives, was a notable feature.

Photoelectron spectra were obtained on a spectrometer previously described.[4] The sample was introduced into the ionisation region as a solid and its vapour pressure at room temperature was sufficient for the spectra to be obtained. Typical He(I) count rates were $>3\,000$ counts s^{-1}.

The MNDO program was used as supplied by Quantum Chemistry Program Exchange without alteration. All MNDO calculations were run with complete free variation of all geometry parameters (≈ 70 parameters). Overlap populations were obtained from the self-consistent charge calculation of Hoffmann and co-workers[5] using the MNDO output geometry. The necessity and validity of mixing the results from these two calculations has been discussed previously.[1]

Crystal-structure Determination.—Crystals for *X*-ray crystallography were grown by sublimation onto a water-cooled probe with the sample held at 40 °C in a 10^{-2} mmHg vacuum for several days. The *X*-ray structure was determined using a Syntex diffractometer with Mo-K_α radiation, graphite monochromatised, λ = 71.069 pm.

Crystal data. $B_{10}H_8N_4$, M = 172.2, a = 1.1411 (2), b = 0.6658(2), c = 1.3058 (3) nm, β = 90.76(2)°, U = 0.9920(4) nm^3, Z = 4, D_c = 1.153 Mg m^{-3}, $F(000)$ = 344, μ(Mo-K_α) = 0.566 cm^{-1}, space group $I2/a$.

Structure analysis. Cell dimensions were determined by least-squares treatment of the setting angles for 15 reflections with $30 < 2\theta < 40°$. Intensities of all independent reflections with $2\theta < 45°$ were measured in the ω—2θ scan mode. The structure analysis used the 564 reflections having $I > 3\sigma(I)$; 90 reflections below this threshold were rejected as 'unobserved'. The structure was solved using MULTAN 80[6] and refined by full-matrix least squares. With allowance for anisotropic vibrations for B and N and with isotropic thermal

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† 1,10-Bis(diazo)-*closo*-decaborane(10).

Supplementary data available (No. SUP 23428, 6 pp.): thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. units employed: eV ≈ 1.60×10^{-19} J; mmHg ≈ 134 Pa.

Table 1. Atomic co-ordinates with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
B(1)	0.132 64(16)	0.231 87(29)	0.084 56(14)
B(2)	0.171 71(16)	0.046 46(31)	0.006 12(14)
B(3)	0.269 37(16)	0.154 32(30)	0.108 63(13)
B(4)	0.228 88(17)	0.416 55(29)	0.066 37(14)
B(5)	0.131 33(16)	0.307 29(31)	−0.037 00(14)
N(1)	0.032 75(13)	0.236 42(21)	0.157 90(11)
N(2)	−0.039 56(15)	0.243 33(26)	0.211 57(12)
H(2)	0.125 8(12)	−0.091 4(27)	0.005 6(11)
H(3)	0.291 7(12)	0.094 3(26)	0.184 6(11)
H(4)	0.223 7(14)	0.555 9(27)	0.108 8(12)
H(5)	0.052 3(15)	0.363 0(27)	−0.070 6(12)

Table 2. Experimental and calculated i.e.s of m.o.s of $B_{10}H_8(N_2)_2$ with their symmetries and assignments

I.e.[a]/eV			
Experimental	Calculated	Symmetry	Orbital character assignment
9.40	10.09	$3e_1$	Cluster
10.44	10.89	$3e_2$	Cluster
11.53	11.77	$3e_3$	Cluster
12.25	12.54	$2e_2$	BH
13.76	13.71	$6a_1$	Cluster
	13.91	$5b_2$	BH
15.86	17.29	$2e_3$	$(N_2)_2$ π
	17.45	$5a_1$	BH
	17.52	$1e_2$	BH
ca. 16.6 (sh)	18.38	$2e_1$	$(N_2)_2$ π
	18.45	$4b_2$	$(N_2)_2$ σ
	19.16	$4a_1$	$(N_2)_2$ σ
	19.47	$1e_3$	BH
ca. 21.2	23.65	$3b_2$	BN σ
	25.09	$1e_1$	Cluster
ca. 22.9 (sh)	27.57	$3a_1$	BN σ, $(N_2)_2$ σ
	29.57	$2b_2$	Cluster
ca. 25[b]	37.44	$2a_1$	Cluster
	44.12	$1a_1 + 1b_2$	$(N_2)_2$ σ

[a] sh = Shoulder. [b] See text for comments.

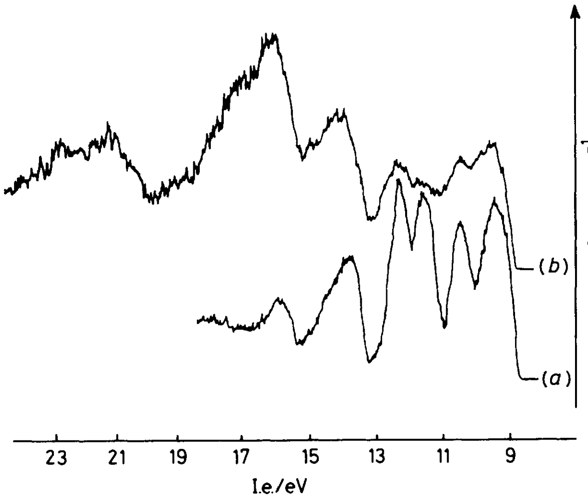

Figure 1. He(I) (*a*) and He(II) (*b*) photoelectron spectra of 1,10-$B_{10}H_8(N_2)_2$

factors for H the refinement converged at $R = 0.043$, $R' = 0.058$. Atomic scattering factors were calculated from the analytical approximation and coefficients given in ref. 7, those for hydrogen being the ' bonded-atom ' values.[8] Least-squares weights were calculated from the modified variances $\sigma^2(I) = \sigma_c{}^2(I) + (0.03I)^2$, where $\sigma_c{}^2$ is the variance from counting statistics. The atomic co-ordinates and their estimated standard deviation are in Table 1.

Results and Discussion

(*a*) *Photoelectron Spectroscopy.*—The He(I) and He(II) spectra are shown in Figure 1 and the measured ionisation energies (i.e.s) are reported in Table 2 together with results of the calculations. In the He(I) spectrum six bands are observed, and the first five of these have a similar appearance in the He(II) spectrum, although there are some small relative intensity changes. However, the sixth band, at 15.9 eV, shows a substantial intensity increase and the shape changes dramatically on changing to the He(II) excitation. The simplest interpretation of the change in shape is that a very broad component centred at 16.6 eV is too weak to be detected in the rising background of scattered electrons in the He(I) spectrum, but increases in the He(II) spectrum by a factor of at least three compared to the component at 15.9 eV. A seventh very broad band is detected between 20 and 23 eV which shows a clear maximum at 21.2 eV and a shoulder at 22.9 eV. There is also an indication of an eighth band on the high-i.e. side of the line due to atomic He from the light source. Beyond 26 eV the He(II) spectrum is obscured by the spectra excited by the He(I) β (23.09 eV) and α(23.74 eV) lines.

The first four bands are almost symmetrical and have similar intensities, and since a large number of doubly degenerate ionisations are expected in the spectrum of this symmetrical molecule it seems probable that each of these bands represents ionisation from a doubly degenerate orbital. A slight shoulder on the first band may be ascribed to a weak Jahn–Teller effect. The fifth, sixth, and seventh bands are highly asymmetric and much broader, and are probably due to overlapping ionisations. Ionisations from the N_2 groups are expected beyond 15 eV by analogy with molecular dinitrogen.[9] The substantial changes in the sixth band in the He(II) spectrum can be assigned most readily to differential cross-section changes between ionisations of N- and (B,H)-centred orbitals. The corresponding changes between O- and (C,H)-centred orbital ionisation cross-sections in organometallic molecules containing CO groups lead to domination of the He(I) spectra by C- and (C,H)-centred orbitals, while the He(II) spectra emphasise the CO ionisations.[10] The shape change, according to the interpretation above, suggests that the component at 15.9 eV contains both (B,H)- and N-centred orbital ionisations since this is much more intense in the He(I) spectrum than the component at 16.6 eV. In support of this contention there is an apparent reduction by about 0.2 eV of the i.e. for the component at 15.9 eV in the He(II) spectrum, which suggests that an N-centred component has a slightly lower i.e. than the B,H-centred component. By analogy with other boron hydrides,[11] particularly $B_{10}H_{14}$, the seventh and eighth bands probably correspond to orbitals with substantial B 2*s* character.

A more detailed analysis of the probable orbital sequence can be made using the approach of Stone,[12] in which the $B_{10}H_{10}{}^{2-}$ cluster is treated as approximately spherical. The cluster bonding molecular orbitals (m.o.s) are then labelled by their spherical *l* quantum number and by their B–H unit orbital compositions, either the axial (σ) orbitals directed at the centre of the cluster, or perpendicular (π) orbitals, tan-

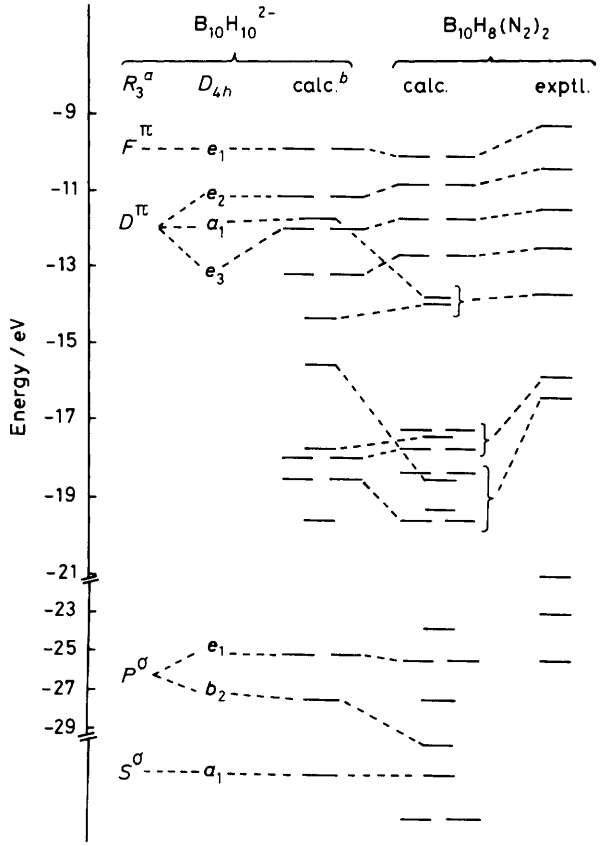

Figure 2. Correlation diagram for $B_{10}H_{10}^{2-}$ and $B_{10}H_8(N_2)_2$ molecules. [a] Spherical symmetry label (ref. 12). [b] 9 eV added to all m.o. energies to allow for comparison of the anion and neutral compound

gential to the surface of the sphere. Using the results and notation of Stone's paper, the cluster-orbital sequence in spherical symmetry is predicted to be grouped in two sets. First a lower-lying S^σ orbital, with a triply degenerate P^σ lying slightly above. Then, at much higher energy, because of the B 2*s*—B 2*p* separation, there will be five occupied degenerate D^π levels and the F^π levels, two of which are occupied by four electrons. The B–H bonding levels can be expected to be between the σ and π cluster sets because of their orbital character. It has been shown by Beltram and Fehlner [13] that the photoelectron spectra of several boron hydrides and carboranes are consistent with an approximate separation of orbitals into σ *endo*-, σ *exo*-(B–H), and π *endo* or ' surface ', in order of increasing energy.

In D_{4d} symmetry there will be a splitting of the P^σ set into $b_2 + e_1$ orbitals, and of the D^π set into $a_1 + e_2 + e_3$. The only occupied F^π orbitals can be determined to be of e_1 symmetry from consideration of the form of the spherical harmonics. The likely energy sequence of the e_2 and e_3 D^π orbital levels can be determined as $e_2 > e_3$ from a comparison with the i.e. of related orbitals in other units containing B_4 rings. The e_2 orbitals are essentially combinations of the highest occupied orbital due to the B_4 unit in 1,6-$B_6C_2H_4$, which ionises at 9.9 eV,[13] while the e_3 orbitals are related to the second highest level in this compound (i.e. 11.8 eV, containing some C 2*p* character) and to the 3*e* level in B_5H_9 (i.e. 10.5 eV).[11] Substitution of the terminal H atoms of $B_{10}H_{10}^{2-}$ by N_2 groups can only affect the a_1 and b_2 symmetry orbitals and is unlikely to change this orbital sequence, although a_1 (D^π) may be stabilised. Thus the likely assignment for the first three bands in the photoelectron spectrum is e_1 (F^π) followed by e_2 (D^π) and e_3 (D^π). The fourth band is too intense to be due to a_1 (D^π) so this is almost certainly ionisation of the highest of the doubly degenerate B–H bonding orbitals, and a_1 (D^π) is probably one component of the asymmetric fifth band. At the other end of the spectrum, the seventh band probably contains the P^σ ionisations. The i.e. of about 21 eV is substantially greater than that of the corresponding 1*e* orbitals in B_5H_9 at 18.4 eV.[11] This analysis suggests that most of the B–H orbitals ionise as a group in the sixth band, which also contains a number of N_2 ionisations. By analogy with metal carbonyls,[4,10] and with CO on metal surfaces,[14] the orbitals which correlate with $1\pi_u$ and $2\sigma_g$ of N_2 are likely to have similar ionisation energies in the cluster compound, so both types of ionisation probably contribute to the sixth band. In carbonyls the orbitals corresponding to 4σ of CO give rise to a well defined band at an i.e. similar to that in the free ligand, but there is no sign of any related ionisation from N_2 $1\sigma_u$ orbitals in Figure 1. It seems probable that substantial mixing of the N_2 σ levels occurs on bonding to the cluster, destroying the ' lone-pair ' character of these orbitals. Similar comments can be made about the only other dinitrogen compound for which ultraviolet photoelectron spectra are available, diazocyclopentadiene.[15]

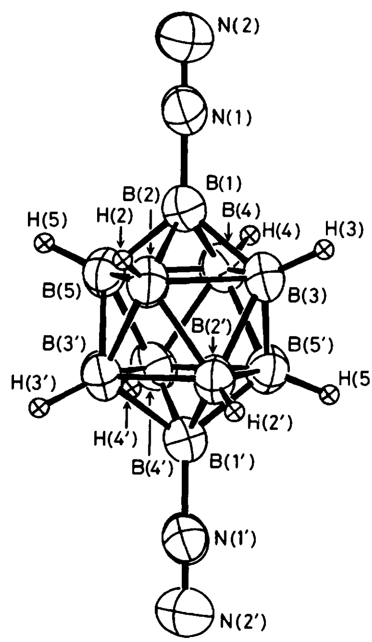

Figure 3. ORTEP drawing showing the molecular structure and atom numbering for 1,10-$B_{10}H_8(N_2)_2$. A crystallographic two-fold axis passes through the midpoints of the B(2)–B(2′) and B(4)–B(4′) bonds

The results of the calculations provide substantial confirmation of these qualitative ideas on the orbital sequence. Figure 2 summarises the correlation between the classification of Stone, calculations on $B_{10}H_{10}^{2-}$ and on $B_{10}H_8(N_2)_2$, and the experimental i.e.s. The higher i.e.s are overestimated by an amount which increases with i.e., but this is common with good quality *ab initio* calculations; for example, the 1*e* level of B_5H_9 ionises at 18.4 eV but in a double-zeta-basis calculation it has an eigenvalue of −22.0 eV.[11] In agreement with the experimental deductions the N_2 $1\pi_u$ orbitals and orbitals of N_2 σ character ionise in the same region as the main group of BH orbitals. The comparison is discussed further in section (*c*).

(*b*) *Crystal and Molecular Structure*.—The molecular structure and atom numbering are shown in Figure 3, and the bond

Table 3. Experimental (with estimated standard deviations in parentheses) and calculated bond lengths (pm) *

	Exptl.	Calc.		Exptl.	Calc.
B(1)–B(2)	166.9(3)	171.8	B(2)–B(3′)	180.0(3)	180.9
B(1)–B(3)	166.9(3)	172.1	B(3)–B(5′)	179.6(3)	179.6
B(1)–B(4)	166.8(3)	171.6	B(4)–B(5′)	179.9(3)	180.0
B(1)–B(5)	166.5(3)	171.7	B(4)–B(4′)	180.5(3)	179.8
B(2)–B(3)	187.3(3)	197.1	N(1)–N(2)	109.1(2)	110.8
B(3)–B(4)	188.7(3)	197.1	B(1)–N(1)	149.9(2)	147.1
B(4)–B(5)	188.4(3)	197.3	B(2)–H(2)	106(2)	116.2
B(5)–B(2)	188.1(3)	197.3	B(3)–H(3)	110(2)	116.2
B(2)–B(2′)	179.6(3)	179.1	B(4)–H(4)	108(2)	116.2
			B(5)–H(5)	106(2)	116.2

* The primed atoms are related to the unprimed atoms by the molecular two-fold axis.

lengths with their estimated standard deviations are in Table 3. The molecule has crystallographic symmetry C_2, but shows only slight deviations from D_{4d}. In fact the only significant deviations from this higher symmetry are shown in the four N(1)–B(1)–B bond angles which are 125.7(1)—128.2(1)°, and the N(2)–N(1)–B(1) angle of 178.7(1)°, which departs significantly from 180°. But the four bonds of the type B(1)–B(2) do not differ significantly from their mean of 166.8 pm, the four of type B(2)–B(3) do not differ significantly from their mean of 188.1 pm, and the five independent bonds of type B(2)—B(2′) do not differ significantly from their mean of 179.9 pm. The four angles of type B(1)–B(2)–H(2) range from 119.2 (8)° to 121.2 (9)°, mean 120.2°.

(*c*) *Calculations.*—The MNDO calculation converges on a geometry of almost exactly D_{4d} symmetry, and the calculated bond lengths are compared with the experimental values in Table 3. The calculation tends to slightly overestimate the boron–boron bond lengths between the two B_4 squares and also the B–H bond lengths, but all other bond lengths agree within 5 pm. The slight asymmetry is not significant and is typical of the results of MNDO. The excellent agreement between the calculated and experimental bond lengths in the BN_2 units where the bonding is complicated is noteworthy. Overall the agreement between the calculated and experimental data is excellent.

The calculated m.o. energies, their symmetries, and assignments are given in Table 2 and compared with the experimental energies. The first three orbitals are degenerate cluster-bonding orbitals corresponding to Stone's F^{π} (e_1), D^{π}(e_2, e_3) orbitals; the fourth is a degenerate (e_2) B–H bonding orbital. The fifth orbital is the D^{π} (a_1) cluster-bonding orbital which is localised on the apical boron atoms and hence is stabilised compared to D^{π} (e_2, e_3) by the presence of the nitrogen groups, and has a slight admixture of a non-bonding nitrogen component. The sixth orbital is a non-degenerate (b_2) B–H bonding orbital. The fifth and sixth orbitals give rise to the fifth band of the photoelectron spectrum (13.76 eV). The correspondence between theory and experiment for the energies and order of these five bands is excellent.

For lower-energy orbitals the calculation consistently overestimates the binding energies of the electrons. However, this is a fault of almost all calculational methods, and correspondence between theory and experiment is seldom pursued to the low-iying orbitals. Further, the low-lying orbitals tend to ' bunch ' together and the photoelectron bands cover numerous ionisation events. The calculation places 11 orbitals between −17.2 and −19.3 eV, five (a_1, e_2, e_3) are B–H bonding, four (e_3, e_1) N_2 π bonding, and two (b_2, a_1)N_2 σ bonding. The orbital energies undoubtedly correspond to the photoelectron band between 15.9 and 16.6 eV with its unusual He(I), He(II) variations. Five orbitals are calculated to have energies −23.5 to −29.5 eV, two (b_2, a_1) are B–H bonding and three (e_1, b_2) correspond to Stone's P^{σ} orbitals. The S^{σ} is calculated at −37.4 eV, and the N_2 (2*s*, σ) at −44.1 eV. Hence a choice of assignment of the photoelectron bands at 21.2 and 22.9 eV exists, which would be resolved by an ESCA spectrum of the molecule.

Figure 4. Bond diagrams for BN_2 unit

The above correspondence is based on Koopmans' theorem. We calculated the ground state of the $[1,10\text{-}B_{10}H_8(N_2)_2]^+$ ion to obtain a ΔSCF value for the first ionisation potential. The calculation shows that a distortion to C_{2v} symmetry occurs on ionisation. The C_{2v} principal axis is perpendicular to the N_4 axis of the neutral molecule with long bond lengths between the B_4 squares occurring on one side of the cage. This is consistent with the ionisation of a cluster-bonding orbital. The ΔSCF ionisation energy is 9.36 eV, in near perfect agreement with experiment.

Comparison of BN_2 *and* BH^- *units*. The comparison of results from the MNDO calculation and the two experimental tests show that MNDO provides a very good description of the $1,10\text{-}B_{10}H_8(N_2)_2$ molecule. Comparing the m.o. energies calculated for $B_{10}H_{10}^{2-}$ and $B_{10}H_8(N_2)_2$, Figure 2, it is seen that only orbitals localised on the apical boron atoms show any significant change in energy, and the composition of the other orbitals is very similar in both molecules. The BH units of $1,10\text{-}B_{10}H_8(N_2)_2$ are calculated to be slightly negatively charged B(−0.05), H(0.02) and the B–N–N system has charges of −0.34, 0.27, and 0.14 respectively. The BH units of $B_{10}H_{10}^{2-}$ are calculated as carrying charges B(−0.12),H(−0.04) for equatorial units, B(−0.32), H(−0.02) for apical units. The apical boron atoms in both molecules are almost equally charged.

The observed and calculated bond lengths suggest a valence-bond description for the BN_2 group as shown in Figure 4. The N_2 bond length is typical of diazonium and diazo-compounds and is known to be fairly insensitive to partial reduction in bond order; [16] the B–N bond length is at least of single-bond order.

The π bonding of the BN_2 unit can only be located in e_1 or e_3 symmetry m.o.s and the σ bonding in a_1,b_2 m.o.s. The majority of the π bonding is by the $2e_3$ m.o. which has significant density on all three atoms; $3e_1$ also contributes some π bonding but is predominantly on the N_2 group. These m.o.s are only marginally localised on the apical groups, hence the total contribution to π bonding of the B–N bond is not large.

The σ-*exo* orbitals involved in B–N bonding are stabilised compared with those involved in B–H bonding. In fact three orbitals with energies similar to the P^{σ} cluster-bonding m.o.s contribute all the B–N σ bonding. They can best be described as the N_2 $2\sigma_u$ m.o.s (with 2*p*-orbital polarisation towards the boron atom on the central N atom) interacting with boron *p* (b_2 symmetry at −23.6 eV), *sp*-hybrid (a_1, −27.6 eV), and 2*s* (b_2, −29.6 eV) orbitals.

The overlap population for the B–N bond is 0.87 compared with 0.82 for the B–H bond of $B_{10}H_{10}^{2-}$, *i.e.* close to a single-bond density. The B–N bonding is 75% σ, 25% π, and is best described by Figure 4(*b*), which correlates with the positive charge calculated for both N atoms in the group. These positive charges also correlate with the rather high ionisation potentials assigned for the N ionisations in the photoelectron spectrum.

Certainly these results bear out the initial assumption that the BN_2 subrogation of BH^- is not perturbing to the B_{10} *closo* cage significantly.

The bonding in the B_{10} closo *skeleton*. The results presented above support the separation of *closo*-borane molecular orbitals into σ-*endo*, σ-*exo*, and π-*endo* groups as used by Beltram and Fehlner,[13] based on ideas promoted by Hoffmann and Lipscomb.[17] More significantly, the agreement with Stone's spherical description of borane clusters [12] is very supportive of this useful and simple approach. Certainly the separation of σ-*endo* and π-*endo* orbitals appears to be valid, but this could be due more to the large energy separation of the two types of cluster orbitals than to their different properties in the idealised spherical geometry. Also Stone's theory ignores the σ-*exo* orbitals (B–H bonding) and the mixing of these with cluster-bonding orbitals can be large enough to make clear assignment of an orbital as one or the other impossible in some *closo* systems. This has not been a problem in $B_{10}H_{10}^{2-}$ or $B_{10}H_8(N_2)_2$.

The overlap populations bonding the BN_2 and BH units into the $B_{10}H_8(N_2)_2$ cluster are 1.86 and 1.66 respectively. For BH(apical) and BH(equatorial) units in $B_{10}H_{10}^{2-}$ the values are 1.88 and 1.74. These show the similarity of the B_{10} cages in the two molecules considered and are very similar to all compounds we have previously discussed which include *closo*- and *nido*-boranes. The hybridisation of the cluster bonding of the apical BH unit is $(s^{0.51}\, p_z^{0.1})$, $p_x^{0.63}$, $p_y^{0.63}$ and for an equatorial BH unit on the *x* axis is $(s^{0.73}, p_x^{0.17})$, $p_y^{0.58}$, $p_z^{0.57}$. This provides another example of a feature of BH bonding we have discussed previously, namely that the hybrid cluster-bonding orbital of Wade's [18] description is essentially *s*-type and only slightly polarised by the *p* contribution.

The localisation of negative charge on the apical boron atoms of $B_{10}H_{10}^{2-}$ is similar to that in *nido*-B_5H_9 which of course has a similar structure to half the B_{10} cage. The apical BH is therefore more like a BH^- unit than the equatorial units, and this may be significant in the selection of the apical sites in the diazotisation reaction. However, the existence of a strongly localised charge is not necessary for BN_2 subrogation as $B_{12}H_{10}(CO)_2$ compounds are known and all BH units of $B_{12}H_{12}^{2-}$ are equally charged, and all considerably less charged than the apical atoms of $B_{10}H_{10}^{2-}$.

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