Calculation of the Electronic Structure of Boranes by the Self-consistent Molecular Orbital Method. Part II.[1] Highly Symmetrical Cage Anions

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The electronic structures of the cage borane anions $B_6H_6^{2-}$, $B_6Cl_6^{2-}$, $B_{10}H_{10}^{2-}$, $B_{12}H_{12}^{2-}$, and $B_{12}Cl_{12}^{2-}$ and the species $B_{20}H_{20}$ are studied by the self-consistent molecular orbital method. All valence electrons are included, as also are the terminal hydrogen atoms attached to the borons. The closed-shell ground state of the first five systems is confirmed but the symmetries of the highest bonding levels are not as previously calculated: the discrepancy stems from our inclusion of the terminal hydrogen atoms. Some of the eigenvalues are found to be displaced upwards in energy by the crystal field exerted by the anionic charge.

In $B_6H_6^{2-}$ and $B_{12}H_{12}^{2-}$ the excess of charge is distributed between boron and hydrogen with a preponderance towards the boron atom: this situation is changed by substitution of chlorine for hydrogen and in $B_6Cl_6^{2-}$ and $B_{12}Cl_{12}^{2-}$ the chlorine has the greater formal negative charge.

Electron-density contours, plotted across planes of symmetry in the hydrogen-substituted ions, show that, for $B_6H_6^{2-}$, the charge is concentrated both at the centre of the cage and in the centres of the trigonal faces. For each of the two larger boron cages the electron density forms a symmetrical spherical shell inside the cage, the density decreasing towards the centre.

The electronic structure of the $B_{20}H_{20}$ species predicts that the closed-shell configuration is that of a tetranegative ion. More extensive work, however, suggests that the closed-shell structure does not have the lowest energy and that there are several highly spin-degenerate excited states which are more stable.

A PREVIOUS paper[1] has dealt with some simple chloroboranes and the neutral open-cage species $B_{10}H_{14}$. There is great theoretical interest in the electronic structures of the highly symmetrical boranes and their anions because, *e.g.*, the $B_{12}H_{12}^{2-}$ anion belongs to the icosahedral point group which allows four- and five-fold degeneracy, a degree unknown in any other molecular system. Moreover, the borane $B_{20}H_{20}$ has not yet been prepared and it is therefore interesting to enquire into whether this structure would give a neutral borane or whether extra electrons would be required to complete a closed shell. The present paper, therefore, presents calculations on a series of closed-cage charged boranes together with some of their chloro-derivatives. Of these species, $B_{12}H_{12}^{2-}$, $B_6H_6^{2-}$, and $B_{10}H_{10}^{2-}$ have been examined previously[2-4] but the calculations performed were of an unsophisticated kind and did not explicitly include electronic interaction. Moreover, the terminal hydrogen atoms were removed from consideration although they may modify cage energies appreciably. The systems $B_6Cl_6^{2-}$ and $B_{12}Cl_{12}^{2-}$ have not been studied previously. Further, no examination of the distribution of *electron density*, as against *electron population*, has ever been made for any of these species. This is of interest because of the way in which the density may build up inside the cage: this factor has been shown to be important in the cases of the P_4 [5] and B_4Cl_4 [1] cages.

Accordingly, we now examine the doubly charged species $B_6H_6^{2-}$, $B_6Cl_6^{2-}$, $B_{12}Cl_{12}^{2-}$, and $B_{10}H_{10}^{2-}$. The highly symmetrical borane $B_{20}H_{20}$ was also studied in order to establish whether such a species would be neutral or whether it would need to be anionic in order to satisfy the requirement of a closed-shell ground state.

We find that, in general, the calculated electronic structures account satisfactorily for the properties of these systems. On direct calculation the charged species yield eigenvalues which are linearly shifted in energy by the extra electronic repulsion terms introduced by the overall charge. The first calculation of the ground-state structure of $B_{20}H_{20}$ indicated an anionic charge of four electrons: however, more extensive work showed that the closed-shell formulation is almost certainly not the most stable configuration. Electron-density maps, plotted for the $B_6H_6^{2-}$, $B_{10}H_{10}^{2-}$, and $B_{12}H_{12}^{2-}$ ions, reveal that the electron density builds up inside the cage, reaching a maximum at the centre and on the trigonal faces for the former ion and forming essentially a spherical shell in the latter two species.

METHODS, RESULTS, AND DISCUSSION

The calculations employed identical theoretical techniques to those described in the previous paper.[1] In all the species, all atoms were explicitly included and basis sets of 1*s*, 2*s*, and 2*p* orbitals selected for hydrogen and boron respectively. For chlorine 3*d* orbitals were not included, as it was shown[1] that they have little effect on the final electronic structure and, hence, on the conclusions. The $B_6H_6^{2-}$ and $B_6Cl_6^{2-}$ ions are regularly octahedral whilst the $B_{12}H_{12}^{2-}$ and $B_{12}Cl_{12}^{2-}$ ions form regular icosahedra [Figure 1(b)]. In $B_{10}H_{10}^{2-}$ the boron atoms lie at the corners of a bicapped square antiprism [Figure 1(a)] and, in this case, there are two inequivalent sets of boron atoms. Species of formula $B_{20}H_{20}^{n-}$ are, as yet, unknown but the most symmetrical structure here is that of a pentagonal dodecahedron [Figure 1(c)]. Geometrical data were abstracted from the review by Muetterties and Knoth:[6] all the B–Cl bond lengths were

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[1] D. R. Armstrong, P. G. Perkins, and J. J. P. Stewart, *J. Chem. Soc.* (*A*), 1971, 3674.

[2] R. Hoffmann and M. Gouterman, *J. Chem. Phys.*, 1962, **36**, 2189.

[3] S. F. A. Kettle and V. Tomlinson, *J. Chem. Soc.* (*A*), 1970, 2002.

[4] R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, 1962, **37**, 2872.

[5] R. M. Archibald and P. G. Perkins, *Chem. Comm.*, 1970, 569.

[6] E. L. Muetterties and W. H. Knoth, 'Polyhedral Boranes,' Marcel Dekker, New York, 1968, chap. 2.

set at 0·170 nm as in B_4Cl_4[6] whilst the B–B bond lengths in $B_6Cl_6{}^{2-}$, $B_{12}Cl_{12}{}^{2-}$, and $B_{20}H_{20}$ were set equal to that in $B_6H_6{}^{2-}$ in the first case and in $B_{12}H_{12}{}^{2-}$ for the last two. The interaction matrices for certain of the species were very large (*e.g.*, $B_{12}Cl_{12}{}^{2-}$ generates a basis set of 96 orbitals) but symmetry criteria applied as described[1] enabled these to be diagonalised: *e.g.*, for the above case the large overall matrices were reduced to a set of sub-matrices of dimension 18 × 18.

Symmetrical Species.—Energy levels. We first present (Tables 1 and 2) the computed data for the known $B_nX_n{}^{2-}$ series of anions; the electronic structure of the species $B_{20}H_{20}$ is discussed separately.

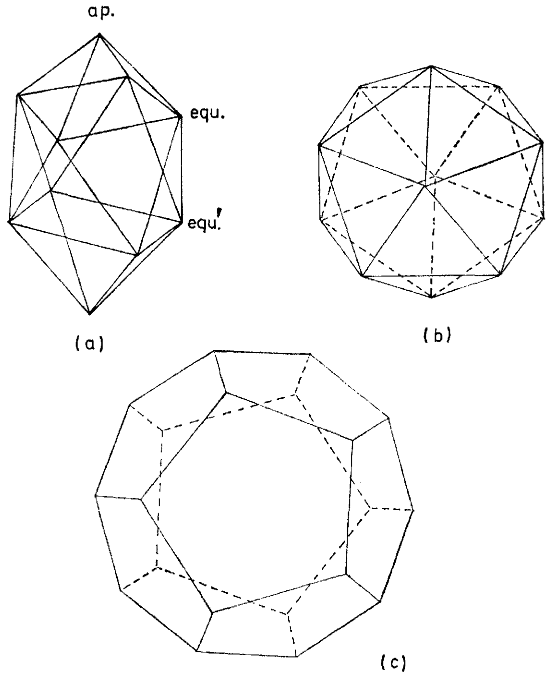

FIGURE 1 Geometries of the B_{10}, B_{12}, and B_{20} cages

The energy levels in $B_6H_6{}^{2-}$ have been calculated previously.[2-4] We cannot easily compare our orbital and energy sequence in detail with either that of Kettle and Tomlinson[3] or of Hoffmann and Gouterman,[2] but a better comparison can be drawn with the later work of Hoffmann and Lipscomb[4] who obtained absolute energy levels although they neglected both interelectronic repulsion and the B–H bond interactions. Our inclusion of interelectronic repulsions leads to many positive eigenvalues in our series. Broadly speaking, however, our energy levels for $B_6H_6{}^{2-}$, $B_{10}H_{10}{}^{2-}$, and $B_{12}H_{12}{}^{2-}$ fall in a similar order to theirs and, in all cases, the highest bonding and lowest virtual orbitals are degenerate though, because of the lower symmetry of the $B_{10}H_{10}{}^{2-}$ ion (D_{4d}), the maximum permitted degeneracy is two. Where the ordering differs in a significant way, the discrepancy can be ascribed to our inclusion in the calculation of the terminal hydrogen 1*s* orbitals; *e.g.*, the highest sets of bonding orbitals in $B_6H_6{}^{2-}$ are calculated by Lipscomb to be of symmetry t_{2g} and t_{1u} whilst those in $B_{12}H_{12}{}^{2-}$ belong to the g_u and h_g representations. From our work the symmetries of the corresponding orbitals are reversed, *i.e.*, t_{1u}, t_{2g} and h_g, g_u respectively. Now, the hydrogen 1*s* orbitals in these systems form bases for (among others) the representations t_{1u} and h_g of the octahedral and icosahedral point-groups. Hence these orbitals can mix with the cage levels and, indeed, both the t_{1u} and h_g cage orbitals under question contain strong B–H bonding components.

We further note that the bonding–antibonding energy gaps calculated by Hoffmann and Lipscomb are all near to 1 eV and are in very poor quantitative agreement with the present work where the energy gaps all lie above 10 eV. It is noteworthy that no complete electronic absorption bands have been observed[6] in the near-u.v. spectrum for any of these species.

The effect of substituting chlorine for hydrogen on the energy levels of $B_6H_6{}^{2-}$ and $B_{12}H_{12}{}^{2-}$ is clearly seen from the data in Table 1. In the former ion the two highest bonding levels become interchanged and the t_{1u} level in $B_6Cl_6{}^{2-}$ is 1·5 eV more stable than the t_{2g} orbitals. This happens because the t_{1u} orbitals are ' σ-bonding ' to the terminal chlorines and, hence, are strongly perturbed. For a similar reason, the highest h_g and g_u bonding levels in $B_{12}H_{12}{}^{2-}$ are reversed on passing to $B_{12}Cl_{12}{}^{2-}$. The h_g level becomes, in fact, negative in energy and hence is considerably stabilised with respect to the corresponding level in $B_{12}H_{12}{}^{2-}$. It is also noticeable that the bonding–antibonding energy gaps of the boranes are decreased by chlorine substitution and so a red shift in the absorption spectra should be expected.

Charge Distribution.—If the terminal hydrogen atoms were neglected in these systems, then each boron would carry a charge equal to $2/N$ electrons (where N is the number of cage atoms). Since no previous calculation has included these terminal hydrogens, then it is of interest to enquire to what extent the excess of charge is distributed over the boron–hydrogen bond. Table 2 gives the breakdown of the relevant data and shows, for the boranes, that both boron and hydrogen are negatively charged in the $B_6H_6{}^{2-}$ and the $B_{12}H_{12}{}^{2-}$ anions. The fact that terminal hydrogen atoms assume a much smaller charge than the cage borons in these ions explains why rationalisation of chemical reactivity based on a calculation of cage orbitals only has had some success. It is interesting that the formal charges on both types of atom in the former species is almost exactly twice that in the latter. In $B_{10}H_{10}{}^{2-}$ the situation is very different: here the boron atoms reflect strongly their differing environments (the apical sites being less nucleophilic) and the attached hydrogen atoms show charges of opposite sign. This ion illustrates well the effect of the terminal hydrogens, since these atoms are able to supply electrons to the equatorial boron atoms, thus making them more highly charged than the apical atoms. The effect of substituting chlorine is as might be expected: this atom takes on a high negative charge which is equal for the B_6- and B_{12}-based ions.

The B–B cage bond orders are built from a sum of all the components, as there is no criterion of σ–π separability in these systems. This parameter indicates a fairly constant bond strength in the cages. Of great interest is the apical–apical cross-cage bond order in $B_{10}H_{10}^{2-}$ which has the value 0·15 and is hence much higher than any other between non-adjacent atoms. This is consistent with many experimental observations whose rationalisation depends on invoking apical–apical conjugation.[6] An interesting and useful quantity to compare in these boranes is the ' valency ' of the boron atoms as defined by Armstrong, Perkins, and Stewart,[7] *i.e.*, equation (1), where V_A is the valency of atom A,

$$V_{\mathrm{A}} = \sum_{\text{all } \lambda \text{ on A}} 2p_{\lambda\lambda} - \sum_{\text{all } \lambda \text{ on A}} \sum_{\text{all } \sigma \text{ on A}} p_{\lambda\sigma}^{2} \qquad (1)$$

and the quantities $p_{\mu\nu}$, are elements of the orbital–orbital bond order matrix, *P*. The valencies of the boron atoms in this series of cages are markedly similar and are *ca.* 3·6—3·7. What is significant is that these valencies are considerably greater than the ' normal tervalency ' of boron and, moreover, they tend to the value 4 which boron will assume in a simple co-ordination compound like BH_4^-. These observations are consistent with the reasons usually advanced for the existence of the boranes, *i.e.*, the electron-acceptor property of the boron atoms is internally, at least partially, satisfied in these compounds.

TABLE 1

Energy levels of symmetric borane anions (eV)

$B_6H_6^{2-}$		$B_6Cl_6^{2-}$		$B_{10}H_{10}^{2-}$		$B_{12}H_{12}^{2-}$		$B_{12}Cl_{12}^{2-}$	
$1a_{1g}$	−43·1	$1a_{1g}$	−53·6	$1a_1$	−58·7	$1a_g$	−65·5	$1a_g$	−70·4
$1t_{1u}$	−18·9	$1t_{1u}$	−32·3	$1b_2$	−33·6	$1t_{1u}$	−35·5	$1t_{1u}$	−43·0
$1e_g$	−6·3	$1e_g$	−21·3	$1e_1$	−29·2	$1h_g$	−16·6	$1h_g$	−27·6
$2a_{1g}$	−5·4	$2a_{1g}$	−17·0	$2a_1$	−15·7	$2a_g$	−15·8	$2a_g$	−25·8
$1t_{2g}$	+1·7	$1t_{2g}$	−12·4	$1e_3$	−13·8	$2t_{1u}$	−5·5	$1t_{2u}$	−20·3
$2t_{1u}$	−2·7	$2t_{1u}$	−11·5	$3a_1$	−10·9	$1t_{2u}$	−2·5	$2t_{1u}$	−16·5
		$1t_{2u}$	−5·3	$1e_2$	−10·8	$1g_u$	+0·4	$2h_g$	−14·1
		$2e_g$	−4·2	$2b_2$	−5·4	$2h_g$	−1·3	$1g_g$	−12·7
$1t_{2u}$	17·0	$3t_{1u}$	−3·8	$3b_2$	−1·6			$3a_g$	−9·7
$1t_{1g}$	18·9	$1t_{1g}$	−3·6	$2e_1$	+0·2			$2t_{2u}$	−7·5
$3t_{1u}$	20·1	$3a_{1g}$	−0·9	$2e_2$	0·6	$1g_g$	14·7	$1g_u$	−7·2
$3a_{1g}$	20·5	$4t_{1u}$	+5·1	$2e_3$	1·5	$3t_{1u}$	16·3	$3h_g$	−7·0
$2e_g$	20·8	$2t_{2g}$	−6·6	$4a_1$	1·5	$1h_u$	16·4	$1h_u$	−6·3
$4t_{1u}$	21·0			$3e_1$	3·1	$1t_{1g}$	16·9	$3t_{1u}$	−6·1
$3e_g$	21·3					$3a_g$	17·9	$1t_{2g}$	−5·6
		$2t_{2u}$	16·1			$3h_g$	17·9	$4t_{1u}$	−5·1
		$2t_{1g}$	17·3	$3e_3$	14·7	$2t_{2u}$	18·2	$4h_g$	−1·7
		$5t_{1u}$	17·9	$3e_2$	16·3	$4t_{1u}$	18·6	$2g_u$	−0·3
		$4a_{1g}$	18·8	$1b_1$	16·4	$3t_{2u}$	18·7		
		$3e_g$	19·0	$4e_1$	17·2	$4h_g$	18·8		
		$6t_{1u}$	19·8	$1a_2$	17·4			$2g_g$	+10·1
		$4e_g$	19·8	$5e_1$	17·5			$5t_{1u}$	10·6
				$4e_3$	17·6			$4a_g$	11·0
				$4b_2$	17·6			$2h_u$	11·6
				$5a_1$	18·7			$2t_{2g}$	12·0
				$5e_3$	18·9			$3t_{2u}$	12·4
				$4e_2$	19·1			$5h_g$	12·5
				$5b_2$	19·3			$6h_g$	13·0
				$6a_1$	19·8			$6t_{1u}$	13·0
				$6e_1$	20·0			$4t_{2u}$	13·3
				$6e_3$	20·0				
				$5e_2$	20·1				
				$7b_2$	20·2				
				$7a_1$	20·2				

TABLE 2

Orbital populations, atomic charges, and cage bond orders in cage boranes

	$B_6H_6^{2-}$	$B_{12}H_{12}^{2-}$	$B_6Cl_6^{2-}$	$B_{12}Cl_{12}^{2-}$	$B_{10}H_{10}^{2-}$	
					Apical	Equatorial
B 2*s*	0·64	0·60	0·57	0·60	0·65	0·61
2*p*	2·59	2·52	2·52	2·32	2·60	2·54
Net charge on B	−0·23	−0·12	−0·09	+0·08	−0·25	−0·15
H 1*s*	1·10	1·05	—	—	1·05	1·03
Net charge on H	−0·10	−0·05	—	—	−0·05	−0·03
Cl 3*s*	—	—	1·54	1·71	—	—
3*p*	—	—	5·70	5·53	—	—
Net charge on Cl	—	—	−0·24	−0·24	—	—
B–B bond order	0·76	0·66	0·71	0·66		0·65 (apex–equator) 0·46 (equator–equator) 0·55 (equator–equator′)

Electron-density Contours for Cage Boranes.—Figures 2

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[7] D. R. Armstrong, P. G. Perkins, and J. J. P. Stewart, *J.C.S. Dalton*, 1973, in the press.

and **3** show total electron-density contours for the $B_6H_6^{2-}$ cage. Figure 2 shows that the electron density conforms to a pattern similar to that already described for B_4Cl_4. On the trigonal faces (Figure 3) again electron density is built up between the three boron atoms. Figure 4 shows how electron density changes along the cross cage H–B–B–H lines. (The right-hand edge of Figure 4 is the centre of the octahedron and the electron density is symmetric about this point.)

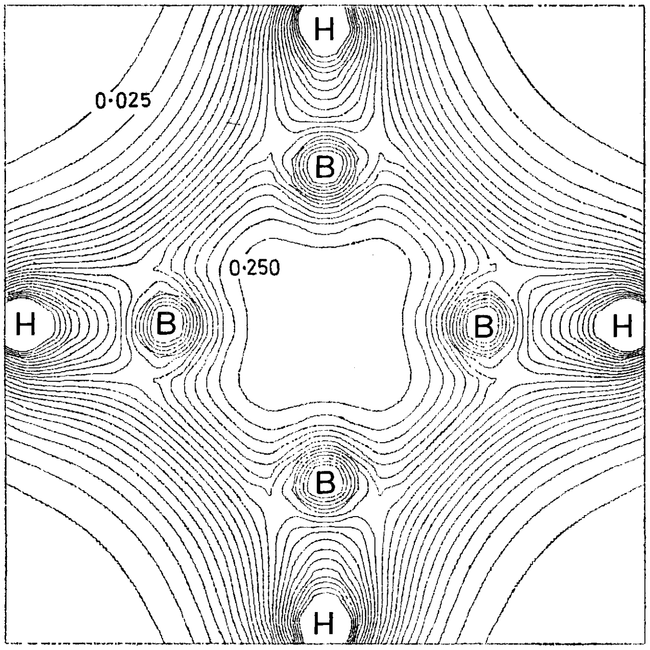


FIGURE 2 Electron density contours for $B_6H_6^{2-}$ section perpendicular to a C_4 axis

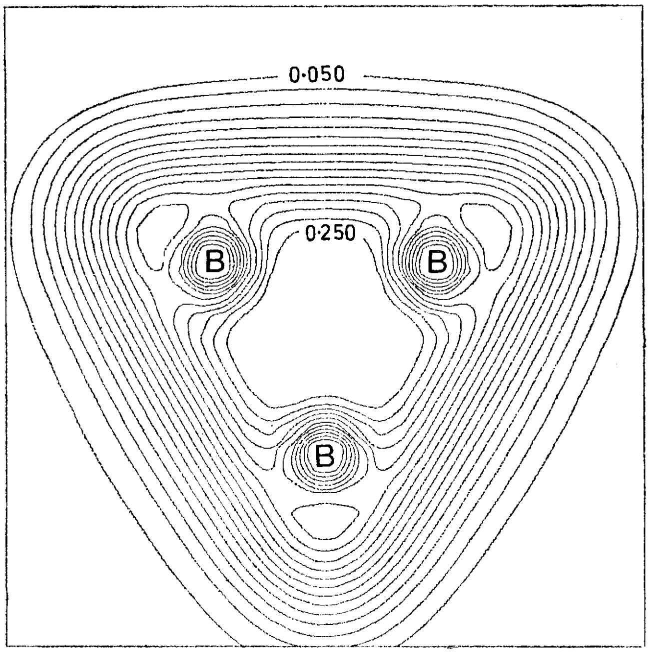


FIGURE 3 Electron density contours for $B_6H_6^{2-}$ section perpendicular to a C_3 axis

Electron-density contours such as these are a far better basis on which to study problems of chemical reactivity; *e.g.*, in Figure 2 the electron density between the B–H bonds builds up uniformly to the cage centre. This furnishes a weak point for electrophiles, since there is no positive centre to obstruct the attack.

In the centre of the trigonal faces (Figure 5) the electron density builds up to a similar value to that in the centre of the octahedron.

Figures 6 and 7 show contour analyses for the $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ ions. In both cases the electron density at the cage centre is substantial (although not a maximum) and hence, in these species, the electrons form a dense shell inside the cage, which is virtually spherical in the latter ion.

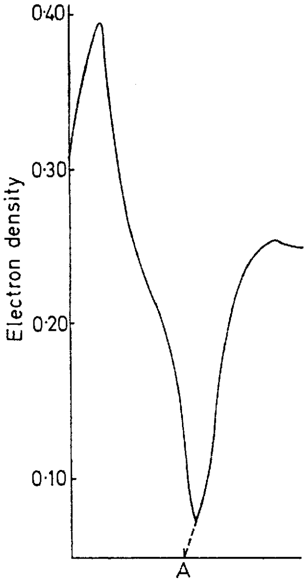


FIGURE 4 Electron density along a H–B–B–H line for $B_6H_6^{2-}$

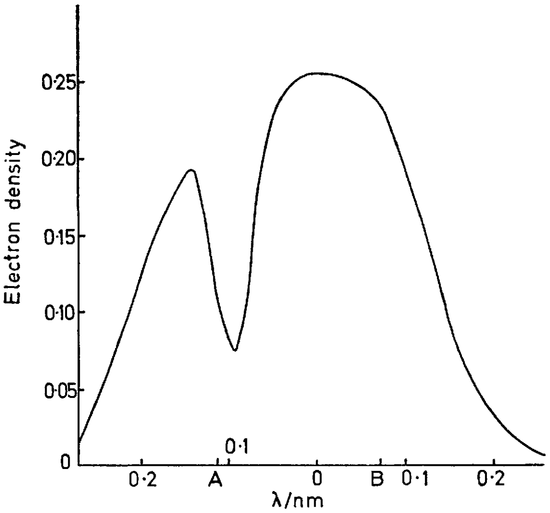


FIGURE 5 Electron density across a trigonal face of $B_6H_6^{2-}$

$B_{20}H_{20}$.—The theory of the bonding in this species

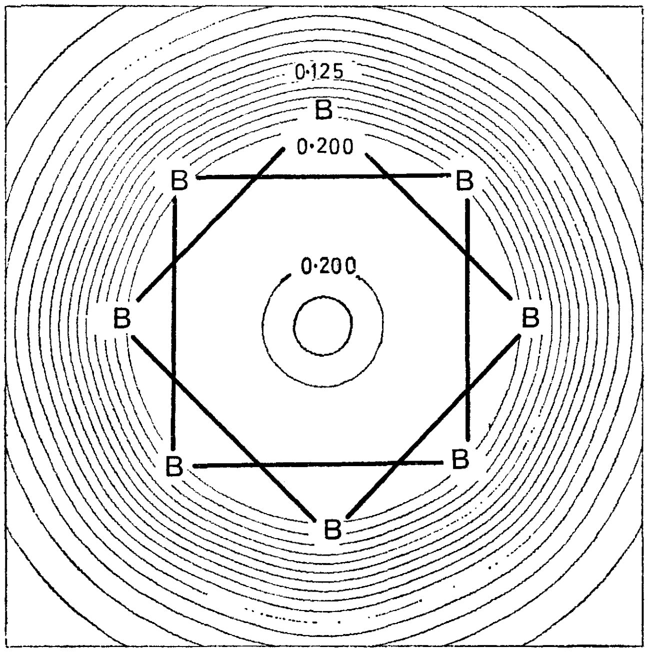


Figure 6 Electron density contours for $B_{10}H_{10}^{2-}$ section perpendicular to a C_4 axis

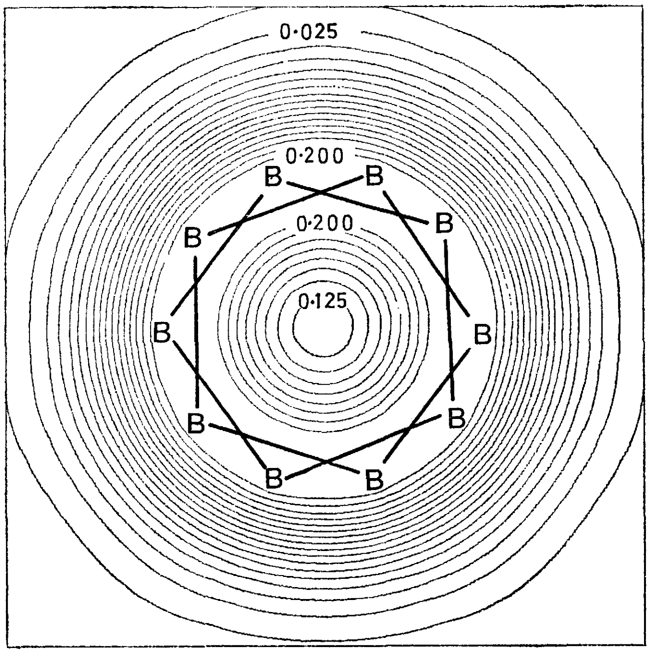


Figure 7 Electron density contours for $B_{12}H_{12}^{2-}$ section perpendicular to a C_5 axis

has not previously been discussed. The most symmetrical atomic arrangement is that of the pentagonal dodecahedron [Figure 1(c)]. The first point to ascertain is the definition of the ground-state closed-shell configuration: the establishment of this feature has always been one of the strong points of even simple types of molecular orbital calculation. In the method we used, it is not correct or sufficient simply to calculate an orbital sequence for a neutral $B_{20}H_{20}$ species and then to feed in electrons to form a closed shell. This is because the positions and order of the eigenvalues depend on interelectronic interaction. Hence, we performed separate calculations on the neutral, the dinegative, and the tetranegative species, in order to establish the proper orbital energy sequence. For brevity, only the results for the tetranegative ion are given here as, of the three, this is the only species which yields a closed shell. The results for the energies and charge distributions are given in Table 3. The highest bonding and lowest antibonding orbitals are, as expected, highly degenerate. The orbital energy sequence gives rise to features which must be given further consideration: first, the bonding–antibonding gap, 4·2 eV, is rather small compared with the energy differences calculated for the other ions. Secondly, the excited states generated by a single excitation from the bonding h_g to the antibonding g_g orbital set have a total degeneracy of 20, which is split by the icosahedral field, *i.e.*, $h_g \times g_g = t_{2g} + t_{1g} + g_g + 2h_g$. Thirdly, the decrease in electronic repulsion brought about by transition to any of these excited states could well offset the interorbital gap, *i.e.*, excited singlet and/or triplet states could have lower energy than the all-spin-paired ground state. We therefore calculated the energies of the set of singlet states generated by one-electron excitation from the h_g to the g_g levels. This exercise reveals (Table 3) that the singlet states arising have energies ranging from —0·260 eV to +0·605 eV, *i.e.*, most lie below that of the assumed ground state. Hence, the simple 4— ion is unlikely to exist if icosahedral symmetry is to be retained. Moreover, multiple excitations to the g_g orbitals would afford even more stable electronic states: the lowest energy of all would presumably be the state ${}^9H_g$ arising from the configuration $(h_g)^6(g_g)^4$.

Table 3

Calculated quantities for $B_{20}H_{20}^{4-}$

Eigenvalues/eV

Bonding

$1a_g$	$1t_{1u}$	$1h_g$	$2a_g$	$1g_u$	$1t_{2u}$
−43·9	−32·3	−20·1	−12·7	−8·2	−4·6
$2t_{1u}$	$1g_g$	$2h_g$	$2t_{2u}$	$1h_u$	$3h_g$
−2·9	+0·8	5·5	8·5	12·4	12·7

Antibonding

$2g_g$	$2g_u$	$3t_{1u}$	$1t_{2g}$	$3g_u$	$1t_{1g}$	$2h_u$	$4h_g$
16·9	17·2	21·9	22·8	24·4	24·4	24·5	24·7
$3g_g$	$3a_g$	$3t_{2u}$	$4t_{1u}$	$5h_g$	$4g_u$	$5t_{1u}$	$4g_g$
25·1	26·3	26·6	26·7	26·8	27·1	27·3	27·4

Charge distribution

B	2*s*	0·70	H	1*s*	0·96
B	2*p*	2·54	Net charge on H		+0·04
Net charge on B		−0·24	B–B bond order		0·74

Energies of single excited states relative to the ground state (eV)

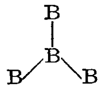
${}^1H_g$	−0·260	${}^1G_g$	−0·188
${}^1T_{1g}$	−0·213 *	${}^1H_g$	+0·605
${}^1T_{2g}$	−0·175 *		

* The eigenvectors of the configuration interaction matrix for these states are mixed and do not allow their unequivocal identification.

Stabilisation of the ions is possible in three ways: (*a*) by spontaneous Jahn–Teller distortion of the open-shell system. This would clearly have to be appreciable in order to create an energy gap sufficient to offset the increased electronic interaction; (*b*) by cation association. Since only four cations are required for neutralisation, then icosahedral symmetry could not be retained in a salt. Hence, cations exerting a large coulombic field would exert a powerful *differential* stabilising effect on the levels of the ion; and (*c*) by insertion of a cation into the cage. The cage radius for this species is 0·248 nm. This means that there should be room inside the cage to incorporate an ion of radius 0·12—0·15 nm, since the radial expectation value for the boron $2p$ orbital is 0·102 nm. A number of ions would therefore seem possible and of these, one having a stable $+4$ oxidation state would be most suitable so that the overall system would be electrically neutral. Energetically matching available d orbitals are also necessary to interact covalently with and stabilise the highest bonding h_g levels with respect to the g_g antibonding levels. Since the radial boron $2p$ orbitals form bases for the former irreducible representation, then the overlap with the d orbitals would be substantial.

The central ion is not required to supply any electrons and it seems that an early transition element would be the most suitable for the purpose. A lanthanide would be less appropriate, since the next highest antibonding orbitals, lying 0·3 eV above the g_g set, are of symmetry g_u and these could be stabilised by interaction with the $4f$ orbitals of the central ion. It is interesting that the g_g orbitals cannot interact with any central metal atom orbital at all, since they can only be generated at the origin from spherical harmonics of order 4.

An alternative and simple approach to the bonding in the B_{20} cage is illuminating. In an individual B_4 unit (I) the B–B–B angle is 108°. This is very close to the tetrahedral angle and, hence, we can consider the three B–B and the single B–H bonds in terms of sp^3 hybrids. Now, since each boron has only three electrons, we cannot set up four two-electron bonds. If we assign an electron to the B–H terminal bond, then only two can be put into the B–B bonding per atom. In the pentagonal dodecahedron, the pentagonal faces are too large to allow of strong bonding across them and, hence, the stability will depend a good deal on the edge B–B bonding. It is significant that in $B_{20}H_{20}^{4-}$, the next large gap in the eigenvalue spectrum, occurs at a position corresponding to a 20— ion. This is exactly the number of electrons required to produce a complete set of two-electron two-centre bonds.



(I)

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