Calculation of the Electronic Structure of Boranes by the Self-consistent Molecular Orbital Method. Part III.[1,2] Excited States of Cage Species

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The excited states of B_4Cl_4, $B_6H_6^{2-}$, $B_9H_9^{2-}$, $B_{10}H_{10}^{2-}$, $B_{12}H_{12}^{2-}$, and $B_{12}Cl_{12}^{2-}$ are calculated by a theoretical technique which includes extensive configuration interaction. The results confirm original assignments for the electronic spectrum of B_4Cl_4 and agree well with that of $B_9H_9^{2-}$. The remainder of the systems are calculated to possess no accessible states in the near-u.v. region.

We have discussed[1,2] the ground-state electronic structures of a number of cage boranes and their derivatives, and this has led to the suggestion that electron density is concentrated inside the cages of these species. There have, to our knowledge, been no calculations of the energies and structures of the excited states of the symmetrical anionic species. These are clearly of interest since, *e.g.*, the icosahedral species can give rise to 4- and 5-fold degenerate excited states which are not accessible by absorption of dipole radiation. Hence, the generally high symmetry in the polyhedral species should lead to particularly simple dipole spectra. Indeed, experimentally only B_4Cl_4 and $B_9H_9^{2-}$ show maxima in the readily accessible region.[3,4] Although it would be most desirable to pursue an *ab initio* study of the excited states, the size of the species involved precludes this at present. Accordingly, as a first attempt on the problem, we have calculated the excited states of some selected species by

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

[2] Part II, D. R. Armstrong, P. G. Perkins, and J. J. P. Stewart, *J.C.S. Dalton*, 1973, 627.

[3] A. G. Massey and D. S. Urch, *J. Chem. Soc.*, 1965, 6180.

[4] F. Klanberg and E. L. Muetterties, *Inorg. Chem.*, 1966, **5**, 1955.

an extensive configuration interaction method superimposed on a ground state calculated from a CNDO-based method. The systems studied include B_4Cl_4, $B_6H_6^{2-}$, $B_9H_9^{2-}$, $B_{10}H_{10}^{2-}$, $B_{12}H_{12}^{2-}$, and $B_{12}Cl_{12}^{2-}$. Our results confirm previous assignments of bands in the spectrum of B_4Cl_4 [3] and explain those of $B_9H_9^{2-}$. For the remainder of the anions, all the excited states are calculated to fall in the high-energy region of the spectrum, although salts of $B_{12}Cl_{12}^{2-}$ might well exhibit an absorption edge.

METHOD, RESULTS, AND DISCUSSION

For all species, the ground-state structure was calculated by the technique fully described previously.[1] Using the eigenvalues from these calculations, we calculated the energies and state vectors for the singlet and triplet states resulting from one-electron excitations. Configuration interaction (CI) to both first and second order is an essential feature of such calculations and was applied in all cases. Commonly, CI is carried out on all states arising from excitations from 3 to 7 occupied and virtual orbitals, giving rise to 9—49 excited states. Since, with increasing CI in this range, the behaviour of state energies is to some extent irregular, we examined the effect of extensively increasing the number of configurations. This necessitated the handling of a very large number of excited states but the problem was generally diminished by exploiting the high symmetry of the systems involved. By employing the projection operator technique to symmetry-factorise the matrices, 300 configurations were processed without difficulty. When the symmetry technique could not be applied, computational difficulties limited the study to 100 configurations.

It is emphasised that this extended CI treatment was carried through only to confirm that a limited inclusion of this feature is really necessary. By extended treatment of this kind one cannot, of course, hope to compensate completely for the fundamental deficiencies of the basic calculational method.

Tetraboron Tetrachloride.—The u.v. spectrum of B_4Cl_4, measured by Massey and Urch,[3] shows a broad peak at 245 nm (log ε *ca.* 4·25) which incorporates a shoulder at 285 nm (log ε 2·95). At higher energies the absorption increases sharply but no peak was identified. The peak at 245 nm was assigned to an allowed transition from a t_2 to an e orbital whilst the shoulder at 285 nm was ascribed to a forbidden transition. We are in substantial agreement with these conclusions.

The calculated states are shown in Table 1. The figures in parentheses were obtained from intermixing 242 states, rather than the 60 employed for the main calculation. The T_2 states only were chosen for the former calculation because transitions to them are allowed from the ground state. Table 1 shows that CI has only a limited effect on the lowest-lying $^1T_2$ state but the higher-energy T_2 states change significantly in energy. Because of configurational mixing it is not really rigorously possible to describe a state in terms of a particular orbital–orbital excitation. However, in the main, the first $^1T_2$ state results from the excitation of an electron from the $4t_2$ to the $2e$ orbitals (for the energies of these levels, see ref. 1): this involves charge transfer from the non-bonding chlorine p orbitals to the p orbitals on boron.

The agreement between the calculated and the observed spectrum is only tolerably good but, on the basis of all the available data, the interpretation is probably correct.

TABLE 1

Singlet excited states of B_4Cl_4

State symmetry	Energy */eV	Oscillator strengths *	Principal configuration
$^1T_1$	3·41		$4t_2 \longrightarrow 2e$
$^1T_2$	4·36(4·13)	0·157(0·115)	$4t_2 \longrightarrow 2e$
$^1T_1$	7·38		$4t_2 \longrightarrow 2t_1$
$^1A_2$	7·39		$4t_2 \longrightarrow 2t_1$
^1E	7·46		$4t_2 \longrightarrow 2t_1$
$^1T_2$	7·94(7·73)	0·001(0·000)	$4t_2 \longrightarrow 4a_1$
$^1T_1$	8·11		$4t_2 \longrightarrow 5t_2$
^1E	8·16		$4t_2 \longrightarrow 5t_2$
^1E	8·56		$3a_1 \longrightarrow 2e$
$^1T_2$	8·61(8·15)	0·026(0·020)	$4t_2 \longrightarrow 4a_1$
$^1A_1$	9·16		$4t_2 \longrightarrow 5t_2$

* Figures in parentheses result from mixing 242 states.

Although B_4Cl_4 is the most useful molecule in the series for 'calibration' purposes (since it has been studied experimentally) it is probable that the calculations are less accurate for this molecule than they are for the larger anions considered. This is because chlorine has four valency orbitals (apart from the $3d$ set) and the necessary atomic parametrisation must be less reliable than it is for hydrogen. Hence we expect that for the $B_6H_6^{2-}$, $B_{12}H_{12}^{2-}$, $B_{10}H_{10}^{2-}$, and $B_9H_9^{2-}$ ions the calculation should be quite reliable and the calculated states should lie within 0·5 eV of the experimental. We believe that the spectra red shift for $B_{12}Cl_{12}^{2-}$ is predicted correctly but the state energies are unlikely to be given to better than *ca.* ±0·8 eV.

$B_6H_6^{2-}$, $B_{10}H_{10}^{2-}$, $B_{12}H_{12}^{2-}$, *and* $B_{12}Cl_{12}^{2-}$.—Some of the calculated low-lying excited states of the above anions are listed in Table 2. In all cases, the lowest excited pure electronic state cannot be populated by absorption of dipole radiation and, indeed, it is remarkable for all the species that a number of excited states in the low-energy range are inactive towards dipole radiation. In all cases, a gap of *ca.* 2 eV exists between the lowest state and the first allowed state (falling at 9·49, 7·33, 9·56, and 6·96 eV for $B_6H_6^{2-}$, $B_{10}H_{10}^{2-}$, $B_{12}H_{12}^{2-}$, and $B_{12}Cl_{12}^{2-}$, respectively). Hence, for all species except $B_{12}Cl_{12}^{2-}$, salts of the ions are predicted not to absorb in the readily accessible u.v. region: this is indeed the experimental observation.[5] Unfortunately, this means that we cannot monitor the accuracy of our predictions but they are clearly qualitatively correct.

The relevant state energies of $B_{12}Cl_{12}^{2-}$ exhibit a strong shift to lower values relative to $B_{12}H_{12}^{2-}$. This

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[5] E. L. Muetterties and W. H. Knoth, 'Polyhedral Boranes,' Dekker, New York, 1968, ch. 2.

was predicted in the earlier work.[1] Hence, for $B_{12}Cl_{12}^{2-}$, tail-end absorption should be observed in the near-u.v. region, since the first allowed band should be very intense.

It is interesting to consider how the low-lying electronic states of these anions could become populated. Two obvious mechanisms are (*a*) distortion of the cage with resultant lowering of symmetry or (*b*) coupling of cage vibrations. In $B_6H_6^{2-}$ either of these would readily generate weakly allowed excited states, *e.g.*, coupled cage vibrations of T_{2u} or T_{1u} symmetry (of which there are 3) together with the first T_{1g} state would yield a T_{1u} vibronic state.

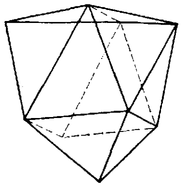
TABLE 2

Low-lying excited singlet states in borane anions

Anion	Symmetry	Energy/eV	Oscillator strength	Principal configuration
$B_6H_6^{2-}$	T_{1g}	7·38		$2t_{1u} \longrightarrow 1t_{2u}$
	T_{2g}	7·40		$2t_{1u} \longrightarrow 1t_{2u}$
	A_{2g}	7·53		$2t_{1u} \longrightarrow 1t_{2u}$
	A_{1u}	7·57		$1t_{2g} \longrightarrow 1t_{2u}$
	E_g	7·82		$1t_{2g} \longrightarrow 1t_{2u}$
	T_{2u}	8·11		$1t_{2g} \longrightarrow 1t_{2u}$
	E_g	8·40		$2t_{1u} \longrightarrow 1t_{2u}$
	T_{1u}	9·49	0·034	$2t_{1u} \longrightarrow 1t_{1g}$
$B_{10}H_{10}^{2-}$	B_1	5·25		$3e_1 \longrightarrow 3e_3$
	E_2	5·47		$3e_1 \longrightarrow 3e_3$
	A_2	6·62		$2e_3 \longrightarrow 3e_5$
	E_2	6·93		$2e_3 \longrightarrow 3e_2$
	E_3	6·95		$4a_1 \longrightarrow 3e_3$
	E_3	7·31		$3e_1 \longrightarrow 3e_2$
	E_1	7·33	0·012	$3e_1 \longrightarrow 3e_2$
$B_{12}H_{12}^{2-}$	T_{1g}	7·72		$2h_g \longrightarrow 1g_g$
	H_g	7·81		$2h_g \longrightarrow 1g_g$
	T_{2g}	7·98		$2h_g \longrightarrow 1g_g$
	G_g	8·03		$2h_g \longrightarrow 1g_g$
	A_u	8·18		$1g_u \longrightarrow 1g_g$
	H_u	8·35		$1g_u \longrightarrow 1g_g$
	H_g	8·59		$2h_g \longrightarrow 1g_g$
	G_u	8·59		$1g_u \longrightarrow 1g_g$
	T_{2u}	9·13		$1g_u \longrightarrow 1g_g$
	T_{1u}	9·56	0·002	$2h_g \longrightarrow 3t_{1u}$
$B_{12}Cl_{12}^{2-}$	A_u	5·02		$2g_u \longrightarrow 2g_g$
	H_u	5·15		$2g_u \longrightarrow 2g_g$
	G_u	5·38		$2g_u \longrightarrow 2g_g$
	T_{2u}	5·80		$2g_u \longrightarrow 2g_g$
	H_g	6·10		$2g_u \longrightarrow 5t_{1u}$
	G_g	6·13		$2g_u \longrightarrow 5t_{1u}$
	T_{2g}	6·35		$2g_u \longrightarrow 5t_{1u}$
	T_{2g}	6·78		$4h_g \longrightarrow 2g_g$
	T_{1g}	6·86		$4h_g \longrightarrow 2g_g$
	H_g	6·89		$4h_g \longrightarrow 2g_g$
	T_{1u}	6·96	0·456	$2g_u \longrightarrow 2g_g$

A more interesting case is that of the B_{12} cage. As in $B_6H_6^{2-}$, the only allowed excited state has T_{1u} symmetry. To activate the low-energy states in $B_{12}H_{12}^{2-}$, we need to couple the T_{1g} state with an A_u vibration or the H_g state with a T_{1u} vibration. For $B_{12}Cl_{12}^{2-}$ we need a T_{1g} vibration to activate the A_u state near 5 eV. In the B_{12} cages the genuine cage vibrations do not incorporate any of A_u symmetry and, moreover, the only T_{1g}-type vibration is non-genuine. This means that the T_{1g} electronic state of $B_{12}H_{12}^{2-}$ can only be activated by vibrations of T_{1u} or H_u symmetry (of which there is one each). The A_u state of $B_{12}Cl_{12}^{2-}$ cannot be activated at all, since the only other *g*-type cage vibrations are of H_g symmetry and the direct product of the two spans of unsplit H_u representation.

Of all the borane anions, only $B_9H_9^{2-}$ exhibits absorption in the near-u.v. region.[4] This occurs at 226 nm. The symmetry of the ideal structure is D_{3h} (Figure) but in the solid state, crystal packing or anion–cation forces distort the ion, reducing the symmetry to C_{2v}.[6] The states given in Table 3 have, therefore, been assigned under the latter symmetry. The lowest calculated singlet state has A_2 symmetry and transitions to it are forbidden. The next higher one has B_1 symmetry and is therefore allowed: it is calculated to occur at 5·58 eV and correlates very well with the observed electronic band at 5·52 eV. There are two more allowed bands lying below 6 eV which are experimentally accessible but they are predicted to be very weak. The lowest-energy intense band lies below 200 nm. All the low-energy transitions arise from *p*-to-*p* charge transfer on boron and hence bring about cage weakening in the excited states. The B–H bonds remain unaffected.



It is interesting to consider how certain of the electronic states could be reached *via* the non-linear terms in the multipole expansion of the electric field of the incident light with respect to the propagation vector. These terms arise because the radiation field is not constant over the area of the irradiated molecule. Hence, we have, *e.g.*, for the *x*-direction, equation (1). Now, in

TABLE 3

Singlet excited states of $B_9H_9^{2-}$

State symmetry	Energy/eV	Oscillator strength	Principal configuration
A_2	3·53	0	$5b_2 \longrightarrow 5b_1$
B_1	5·58	0·010	$5b_2 \longrightarrow 9a_1$
B_1	5·69	0·001	$8a_1 \longrightarrow 5b_1$
A_1	5·95	0·005	$5b_2 \longrightarrow 6b_2$
A_2	6·13	0	$5b_2 \longrightarrow 6b_1$
B_1	6·42	0·153	$5b_2 \longrightarrow 3a_2$
B_1	6·69	0·001	$5b_2 \longrightarrow 4a_2$
A_2	6·81	0	$4b_2 \longrightarrow 5b_1$
A_1	7·12	0·091	$3b_1 \longrightarrow 5b_1$
B_2	7·31	0·302	$2a_2 \longrightarrow 5b_1$
A_2	7·59	0	$2a_2 \longrightarrow 9a_1$
A_1	7·60	0·028	$8a_1 \longrightarrow 9a_1$
A_2	7·89	0	$8a_1 \longrightarrow 3a_2$
A_1	8·12	0·128	$3b_1 \longrightarrow 5b_1$
B_1	8·34	0·029	$8a_1 \longrightarrow 6b_1$
A_2	8·37	0	$4b_1 \longrightarrow 6b_2$
B_2	8·38	0·002	$2a_2 \longrightarrow 6b_1$
B_2	8·51	0·004	$4b_1 \longrightarrow 4a_2$

$$v = v_0 + x\left(\frac{\partial v}{\partial x}\right)_0 + \tfrac{1}{2}x^2\left(\frac{\partial^2 v}{\partial x^2}\right)_0 + \cdots \qquad (1)$$

[6] L. J. Guggenberger, *Inorg. Chem.*, 1968, **7**, 2260.

general, the fields arising from normal light sources are not sufficiently intense to allow exploitation of the second- and higher-order terms in the expansion: *e.g.*, the electric-field terms in the Einstein coefficient for spontaneous emission are [7] as in equation (2), where m

$$A_{m\rightarrow n} = \frac{32\pi^3\nu_{mn}^3}{3c^3\hbar}\left\{|\langle m|e\boldsymbol{r}|n\rangle|^2 + \frac{3}{10}\pi^3\frac{\nu_{mn}^2}{c^2}|\langle m|e\boldsymbol{rr}|n\rangle|^2\right\} + \ldots \quad (2)$$

and n are ground and excited states. Here the quadrupole term is *ca.* 10^{-7} times the dipole term.

However, laser sources provide light of every considerable intensity; in certain instances one can obtain optical fluxes of the order of mW cm^{-2} in focused beams. In the present context, this means that the states which are inaccessible by dipole radiation may be activated by the energy density of the laser light through the quadrupole effect. The quadrupole operator, $\boldsymbol{rr}$, transforms like the second-rank tensor components and hence obeys the same selection rules as for the Raman effect. In $B_{12}H_{12}^{2-}$ and $B_{12}Cl_{12}^{2-}$, this means that the H_g states could become populated and, in both cases, states of this symmetry are among those of lower energy. In $B_6H_6^{2-}$ the relevant state symmetries are T_{2g} and E_g and, again, one of the former lies second in the series at 7·40 eV (Table 2). The lowest-energy state in $B_9H_9^{2-}$ would also be attainable, as would the E_2 states in $B_{10}H_{10}^{2-}$.

A second possibility with laser sources is two-photon absorption. This has been observed in anthracene [8] crystal (by use of a ruby laser) and gives rise to blue fluorescence from the excited $^1B_{2u}$ state of the molecule. Moreover, intersystem crossing from this state to the $^3B_{2u}$ excitonic state has been postulated.[9] The two-photon absorption process follows different selection rules from those of simple one-photon absorption. Thus, the intensity of absorption is as in equation (3), where f is

$$I(2) \propto \left|\sum_n\left\{\frac{\langle f|\mathbf{r}|n\rangle\langle n|\mathbf{r}|0\rangle}{E_n + h\nu} + \frac{\langle f|\mathbf{r}|n\rangle\langle n|\mathbf{r}|0\rangle}{E_n - h\nu}\right\}\right|^2 \quad (3)$$

the final excited state, 0 the ground state, and n other excited states of the system. Since this expression does not contain the matrix element $\langle f|\mathbf{r}|0\rangle$, then the dipole selection rules will not operate for these systems in the ways discussed earlier. It is interesting that the two-photon energy of the ruby laser (28·8 kK) lies close to that of the first (non-allowed) singlet state of the $B_9H_9^{2-}$ anion. It would be interesting, therefore, to attempt a simple radiation experiment on this system where intersystem crossing to lower-lying triplets might also occur.

As well as intersystem crossing, one might also bring about internal conversion to higher vibrationally excited lower singlets. This process is governed by the same vibrational overlap rules as is intersystem crossing but is more likely, as there is no requirement for spin quantization to break down. However, states higher than the first excited singlet would have to be populated by the initial absorption.

We thank the S.R.C. for a maintenance grant (to J. J. P. S.).

[3/316 *Received*, 12*th February*, 1973]

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[7] H. Eyring, J. Walter, and G. E. Kimball, ' Quantum Chemstry,' Wiley, New York, 1944, p. 115.

[8] W. L. Peticolas, J. P. Goldsborough, and K. E. Rieckhoff, *Phys. Rev. Letters*, 1963, **10**, 43.

[9] S. Singh, W. J. Jones, W. Siebrand, B. P. Stoicheff, and W. G. Schneider, *J. Chem. Phys.*, 1965, **42**, 330.