1150. *The Ultraviolet Spectrum and Electronic Structure of Tetraboron Tetrachloride, B_4Cl_4* *

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The electronic structure of B_4Cl_4 is discussed in detail. By use of the high symmetry of the molecule it is possible to simplify the calculations considerably. Qualitative agreement is found between the theoretical model and the nature of the observed ultraviolet spectrum. It is suggested that both B_4F_4 and $B_4O_4^{4-}$ might be unstable, and a reason for the decomposition of B_4Cl_4 by 245 mμ radiation is proposed.

TETRABORON TETRACHLORIDE, a pale yellow solid, is readily decomposed by air and water. It is quite volatile and is thermally decomposed above 70°.[1,2] *X*-Ray analysis [3,4] shows that the four boron atoms lie at the apices of an almost regular tetrahedron (edge = 1·70 ±

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[1] A. K. Holliday and A. G. Massey, *Chem. Rev.*, 1962, **62**, 303.
[2] G. Urry, T. Wartik, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 1952, **74**, 5809.
[3] M. Atoji and W. N. Lipscomb, *Acta Cryst.*, 1953, **6**, 547.
[4] M. Atoji and W. N. Lipscomb, *J. Chem. Phys.*, 1953, **21**, 172.

0·01 Å) with one chlorine bound to each boron atom (B–Cl $= 1·70$ Å) so that the four boron-chlorine bonds point to the centre of the tetrahedron. The bonding has been briefly discussed by Longuet-Higgins [5] who showed that, if the six edges of the tetrahedron are assumed to be electron-pairs, then these localised bonds could be transformed, under the symmetry operations of the tetrahedral point group T_d, into six equivalent molecular orbitals of symmetry a_1, e, and t_2. Since each boron atom may be supposed to have only two electrons available to enter this bonding system, the B_4 tetrahedron is electron-deficient. The eight lone-pair $3p$-orbitals on the chlorine atoms are equivalent to eight molecular orbitals of symmetry e, t_1, and t_2. Electron donation may therefore take place from the chlorine atoms to the empty e molecular orbitals of the B_4 unit, so stabilising it. The purpose of this Paper is to discuss the bonding in B_4Cl_4 in greater detail and to attempt a correlation with the ultraviolet absorption spectrum.

Bonding in the B_4 *Tetrahedron.*—Let the p-orbitals on each boron be orientated so that one points to the centre of the tetrahedron. The valency orbitals of the four boron atoms may then be classified as in the Table.

	Operations					Irreducible
Orbitals	E	C_3	C_2	σ_d	S_4	representations
Four, boron $2s$	4	1	0	2	0	$A_1 + T_2$
Four, boron $2p$ (central)	4	1	0	2	0	$A_1 + T_2$
Eight, boron $2p$	8	−1	0	0	0	$E + T_1 + T_2$

Since the four centrally orientated p-orbitals and the four s-orbitals belong to the same irreducible representations, they will mix in all the bonds they form. The difference in ionisation potential between boron $2s$- and boron $2p$-orbitals is small (4·6 ev),[6] so the errors introduced by assuming simple sp-hybridisation will also be small, thus,

$$\phi_a = 1/\sqrt{2}(s + p), \text{ pointing to centre,}$$

$$\phi_b = 1/\sqrt{2}(s - p), \text{ pointing to chlorines.}$$

The four orbitals of type ϕ_b from each boron will be assumed to form four localised σ-bonds with the four chlorine atoms and will not be considered further. The four ϕ_a-orbitals will interact strongly with each other, forming molecular orbitals a_1 and t_2. Furthermore, these t_2-orbitals will interact with molecular orbitals of the same irreducible representation derived from the eight other boron p-orbitals. The interactions within and between various sets of orbitals will now be considered.

Mutual Interaction of the Eight, Non-central, Boron p-Orbitals.—These orbitals may be thought of as tangential to a sphere whose surface contains the four boron atoms. The x-, y-, and z-axes join mid-points of opposite edges of the boron tetrahedron. Figure 1 provides a view down the z-axis and shows diagrammatically the numbering and orientation of the orbitals; ϕ_1 to ϕ_4 lie in planes which contain the z-axis, and ϕ_5 to ϕ_8 lie in planes parallel to the xy-plane. There are many possible interactions between these p-orbitals. The resonance integrals of such interactions are listed below. $\int \phi_x H \phi_y$ is written x, y. The sign of each resonance integral has been assumed to be the same as that of the corresponding overlap integral.

$$\beta_0 = \quad 1,2 = \quad 3,4$$
$$\beta_1 = \quad 5,7 = \quad 6,7 = \quad 6,8 = \quad 8,5$$
$$\beta_2 = \quad 1,3 = \quad 1,4 = \quad 2,3 = \quad 2,4$$
$$\beta_3 = -5,6 = -7,8$$
$$\beta_4 = \quad 3,5 = \quad 4,6 = \quad 1,7 = \quad 2,8$$
$$\quad = -4,5 = -3,6 = -2,7 = -1,8$$

[5] H. C. Longuet-Higgins, *Quart. Rev.*, 1957, **11**, 121.
[6] H. H. Jaffe, *J. Chem. Educ.*, 1956, **33**, 25.

Whilst an approximate evaluation of these five resonance integrals is possible, it is much easier to utilise the symmetry of the molecule to reduce the number of unknown quantities. Molecular orbitals of the correct symmetry may be written down as follows:

$$e\begin{cases} \psi_1 = \tfrac{1}{2}(\phi_1 + \phi_2 + \phi_3 + \phi_4) \\ \psi_2 = \tfrac{1}{2}(\phi_5 + \phi_6 + \phi_7 + \phi_8) \end{cases}$$

$$t_2\begin{cases} \psi_3 = \tfrac{1}{2}(\phi_1 + \phi_2 - \phi_3 - \phi_4) \\ \psi_4 = \tfrac{1}{4}(-\phi_1 + \phi_2 - \phi_3 + \phi_4) + (\sqrt{3}/4)(-\phi_5 + \phi_6 - \phi_7 + \phi_8) \\ \psi_5 = \tfrac{1}{4}(+\phi_1 - \phi_2 - \phi_3 + \phi_4) + (\sqrt{3}/4)(-\phi_5 + \phi_6 + \phi_7 - \phi_8) \end{cases}$$

$$t_1\begin{cases} \psi_6 = \tfrac{1}{2}(\phi_5 + \phi_6 - \phi_7 - \phi_8) \\ \psi_7 = \tfrac{1}{4}(-\phi_5 + \phi_6 - \phi_7 + \phi_8) - (\sqrt{3}/4)(-\phi_1 + \phi_2 - \phi_3 + \phi_4) \\ \psi_8 = \tfrac{1}{4}(-\phi_5 + \phi_6 + \phi_7 - \phi_8) - (\sqrt{3}/4)(+\phi_1 - \phi_2 - \phi_3 + \phi_4) \end{cases}$$

From these expressions the energies of each molecular orbital may be determined $E_i = (\int\psi_i H\psi_i) \div (\int\psi_i\psi_i)$.
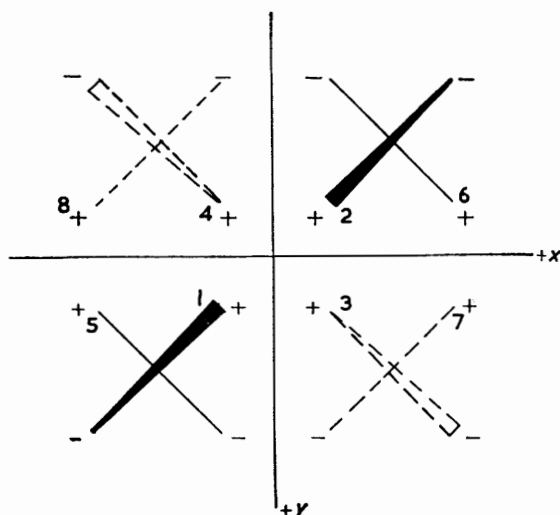

FIGURE 1. Orientation of the p-orbitals of boron. The axes meet at the centre of the tetrahedron of boron atoms. Broken-line orbitals lie below and full-line orbitals above the xy-plane. The view is from above, down the z-axis; the broad ends of orbitals 1—4 are nearest the viewer

If the Hückel approximations are used, then $\int\psi_i\psi_i = 1$ for each of the molecular orbitals ψ_1 to ψ_8 and the energies are (α_p = Coulomb integral for boron $2p$ atomic orbital)

$$E_1 = \alpha_p + \beta_0 + 2\beta_2$$
$$E_2 = \alpha_p + 2\beta_1 - \beta_3$$
$$E_3 = \alpha_p + \beta_0 - 2\beta_2$$
$$E_4 = E_5 = \alpha_p - \tfrac{1}{4}\beta_0 + \tfrac{3}{4}\beta_3 + \sqrt{3}\beta_4$$
$$E_6 = \alpha_p - 2\beta_1 - \beta_3$$
$$E_7 = E_8 = \alpha_p - \tfrac{3}{4}\beta_0 + \tfrac{1}{4}\beta_3 - \sqrt{3}\beta_4$$

Since the molecular orbitals fall into three degenerate groups it follows that:

$$E_1 = E_2 \therefore \beta_0 + 2\beta_2 = 2\beta_1 - \beta_3$$
$$E_3 = E_4 = E_5 \therefore \beta_0 - 2\beta_2 = -\tfrac{1}{4}\beta_0 + \tfrac{3}{4}\beta_3 + \sqrt{3}\beta_4$$
$$E_6 = E_7 = E_8 \therefore -2\beta_1 - \beta_3 = -\tfrac{3}{4}\beta_0 + \tfrac{1}{4}\beta_3 - \sqrt{3}\beta_4$$
$$\therefore \beta_0 = \beta_1 + \beta_2 + \beta_3 = 4\beta_2 + 3\beta_3, \text{ and } \beta_1 = 3\beta_2 + 2\beta_3$$

β_4 has been eliminated and the following inequalities established $\beta_0 > \beta_1 > 3\beta_2$ or $2\beta_3$. The e-orbitals are the most tightly bound. The t_2-orbitals are also bonding whereas the t_1-orbitals are strongly antibonding. The relative energy levels of these orbitals are shown qualitatively in Figure 2 (column " p ").
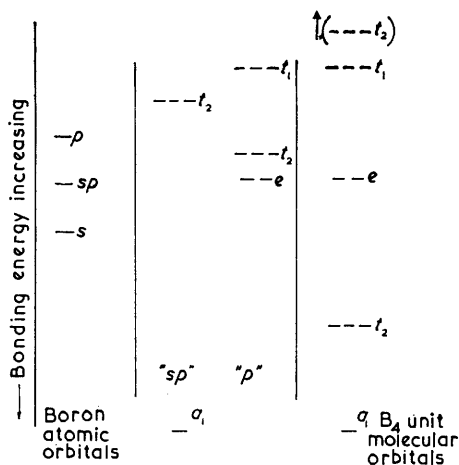
FIGURE 2. Energy-level diagram of the molecular orbitals formed from the interaction of boron atomic orbitals

Mutual Interaction of the Four Centrally Orientated Boron sp-*Hybrids.*—Let the four hybrid orbitals, ϕ_a, be numbered ϕ_9 to ϕ_{12}, so that ϕ_9 arises from the boron atom with p-orbitals ϕ_1 and ϕ_5, ϕ_{10} (ϕ_2 and ϕ_6), ϕ_{11} (ϕ_3 and ϕ_7), and ϕ_{12} (ϕ_4 and ϕ_8). The molecular orbitals will be:

$$a_1 \quad \psi_9 = \tfrac{1}{2}(\phi_9 + \phi_{10} + \phi_{11} + \phi_{12})$$
$$t_2 \begin{cases} \psi_{10} = \tfrac{1}{2}(\phi_9 + \phi_{10} - \phi_{11} - \phi_{12}) \\ \psi_{11} = \tfrac{1}{2}(\phi_9 - \phi_{10} + \phi_{11} - \phi_{12}) \\ \psi_{12} \phi \tfrac{1}{2}(-\phi_9 + \phi_{10} + \phi_{11} - \phi_{12}) \end{cases}$$

If the Coulomb integral for the sp-hybrid orbitals is α_{sp}, and the resonance integral between any two hybrids is β_5, then the energies of the molecular orbitals are,

$$E_9 = \alpha_{sp} + 3\beta_5,$$
$$E_{10} = E_{11} = E_{12} = \alpha_{sp} - \beta_5$$

From which it follows that a_1 is a strongly bonding molecular orbital concentrated around the centre of the tetrahedron, but t_2 orbitals are antibonding (shown diagrammatically in Figure 2, column " sp ").

Interaction of the t_2-*Molecular Orbitals.*—Molecular orbitals of irreducible representation t_2 have been described in both preceding sections. Interaction between these two sets of orbitals is therefore inevitable. Calculations similar to those described above suggest that the resonance integral will be large for elements such as boron where the energy difference between valency s- and p-atomic orbitals is relatively small. The relative energy levels of the molecular orbitals of the B_4 tetrahedron are shown qualitatively in the right-hand column of Figure 2. The a_1- and t_2-orbitals are strongly bonding but the e-orbitals are only slightly bonding. The bonding t_2-orbitals will be concentrated between the boron atoms (" B–B bonds ") when the two original sets of t_2-orbitals " sp " and " p " are similar in energy. Figure 3 gives a rough idea of the nature of part of one of the orbitals. Since each boron may be regarded as contributing one electron to the formation of a σ-bond with a chlorine atom only eight boron electrons are available to hold B_4 together. If these electrons are housed $(a_1)^2$, $(t_2)^6$, $(e)^0$ the structure will be electron-deficient with four vacancies in the bonding e-orbitals.

Chlorine–Boron Interaction ("π-Bonding").—Each chlorine atom has a pair of filled $3p$-orbitals at right angles to the boron–chlorine bond. It will be assumed that there is no interaction between the four chlorine atoms so that the eight molecular orbitals (e, t_1, t_2) that may be derived from the eight atomic orbitals will be energetically degenerate. The representations of these M.O.'s are such that they may interact with the orbitals of the boron tetrahedron. The various orbitals that result will be written: e, e^*, t_2, $t_2{}^0$, $t_2{}^*$ and t_1, $t_1{}^*$, arranged in order of decreasing binding energy in each group. Various possible situations may now be considered depending on whether the chlorine, or, more generally, the ligand p-orbitals are (a) much more, (b) about equally, or (c) less electronegative than the boron $2s$- and $2p$-orbitals. The effect of ligand interaction upon the molecular orbitals of the whole molecule in these cases is shown diagrammatically in Figure 4.
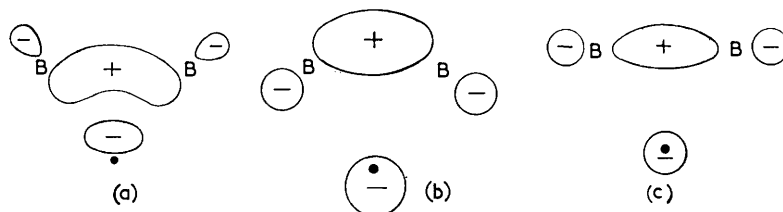

FIGURE 3. Diagrammatic representations of sections through t_2-orbitals containing the z-axis. (a) ψ_{10}, (b) ψ_3, (c) bonding orbital derived from interaction of ψ_{10} and ψ_3. (The bold dot represents the mid-point of the line joining the other two boron atoms)
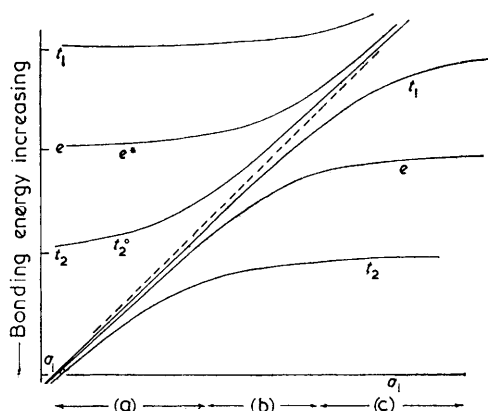

FIGURE 4. Energy-level diagram of the molecular orbitals of B_4X_4 ($t_2{}^*$ omitted) to show the effect of decreasing (from left to right) the electronegativity of X. The broken line relates the energy of the X orbital to the vertical scale. The molecular orbitals of the B_4 unit alone are indicated on the left. For a discussion of the effect in regions (a), (b), (c), see text

(a) The t_2-, e-, and t_1-orbitals will retain much ligand character, so that electrons in the e-orbitals in particular will not relieve the electron deficiency in B_4. The strongest interaction will probably involve t_2 and $t_2{}^0$ orbitals, since they are nearest in energy; the effect will be to make $t_2{}^0$ less bonding. Thus, ligands of this type in no way help to stabilise the central B_4 unit, and compounds which contain them will probably be unstable.

(b) The e-orbitals of B_4 are slightly bonding relative to the $2p$-atomic orbital of boron. Thus, the e-orbitals of ligands in this class will interact strongly with the B_4 e-orbitals. The new e-orbitals will be bonding relative to those in the original B_4 unit and will be filled with electrons shared with the ligands. Other ligand orbitals remain concentrated on the ligands ($t_2{}^0$ and t_1). Ligands of this type, then, not only relieve the electron deficiency of the B_4 tetrahedron as suggested by Longuet-Higgins, they also help to stabilise it.

(c) In this case the ligand p-orbitals are very much less bonding than any of the boron atomic orbitals, comparable with, say, the antibonding t_1-orbitals. The bonding orbitals (t_2 and e) in the boron tetrahedron will have their bonding power only slightly enhanced.

Ligand t_1- and t_2-orbitals will interact most strongly with the antibonding t_1- and t_2^0-orbitals of the boron tetrahedron. However, t_1- and t_2^0-orbitals will have much more boron character than in (b). Thus, whilst electron donation from the ligands is energetically advantageous, the orbitals themselves have much character that is antibonding to the boron tetrahedron. Ligands of this type would probably cause B_4X_4 to decompose to 4BX.

It seems that B_4Cl_4 is a molecule of either class (b) or perhaps (c). The presence of d-orbitals on the chlorine atoms which, because of their very diffuseness could overlap effectively with the molecular orbitals of the boron tetrahedron, would render orbitals of types e, t_1, and t_2 more bonding (if a B–Cl bond is a z-axis, d_{xz}- and d_{yz}-orbitals on the four chlorine atoms belong to representations e, t_1, and t_2). The formally isoelectronic $B_4O_4^{4-}$ might more truly belong to class (c) and the oxygen atoms have no d-orbitals to aid stability. The non-existence of this anion could thus be explained. Fluorine, on the other hand, is probably a ligand of class (a), in which case B_4F_4 should also be unstable.

FIGURE 5. The ultraviolet spectrum of B_4Cl_4
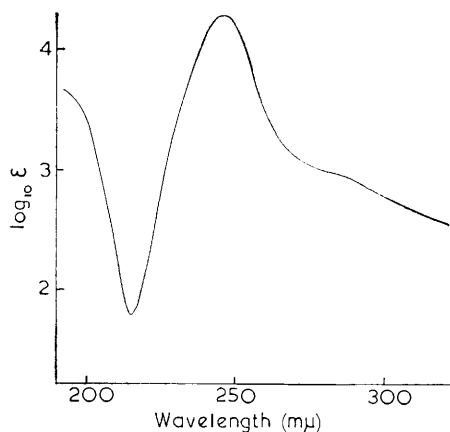
Related compounds such as $B_4(OR)_4$ and $B_4(NR_2)_4$ will have only four p-orbitals to interact with the boron tetrahedron. They do not belong to the symmetry group T_d, and so the above arguments do not apply to them.

Ultraviolet Absorption Spectrum of B_4Cl_4.—No matter to which of the above cases B_4Cl_4 belongs, the juxtaposition of molecular orbitals on the energy scale remains the same; a_1, t_2, and e are strongly bonding occupied orbitals. Other bonding orbitals are t_1 and t_2^0, and the lowest unoccupied molecular orbital has representation e^*. A naïve argument would then suggest that the longest wavelength of ultraviolet absorption in B_4Cl_4 should involve excitation from either a t_1- or a t_2-orbital to an e-orbital. In either case two possible excited states result, T_1 and T_2. It can be shown that all eight normal vibrational frequencies of B_4Cl_4 ($2a_1$, $2e$, $3t_2$, t_1) can interact with the permitted electronic transition to a T_2 state, and that six of these modes (not $2a_1$) will destroy the forbiddenness of the $A_1 \longrightarrow T_1$ transition. The observation of simple vibronic structure in either of these transitions cannot therefore be expected.

The ultraviolet spectrum is shown in Figure 5. It seems reasonable to associate the intense absorption at 245 mμ (log ε approx. 4·25) with a permitted transition, and the shoulder at about 285 mμ (log ε approx. 2·95) with a " forbidden " transition. The broad appearance of both peaks suggests complex concomitant vibrational excitation. In short, the observed spectrum is in agreement with that anticipated from theory.

Flash photolysis [7] of B_4Cl_4 shows that the absorption of 245 mμ radiation causes the decomposition of the molecule into BCl fragments. This reaction may be understood in an

[7] A. G. Massey and J. J. Zwolenik, *J.*, 1963, 5354,

elementary way by using the model proposed above. The excitation of an electron from a t_2^0-orbital to an e^*-orbital results [for case (b)] in an electron being transferred from the ligands to an antibonding orbital more associated with the B_4 unit. Furthermore, the presence of an electron in the antibonding e^*-orbitals will in part cancel the stabilising effect of ligand (B_4 interaction). Weakening of the whole B_4 structure is therefore expected, and this could easily lead to complete decomposition to 4BCl.

Experimental.—Tetraboron tetrachloride was obtained by a by-product from the discharge preparation of diboron tetrachloride. It was purified by vacuum-sublimation and shown to be >99% pure by mass spectrometry. The ultraviolet spectra were obtained from samples vacuum-sealed into dry quartz cells (1- and 10-cm. path length), using Perkin-Elmer 350 and Optika instruments.