Theoret. chim. Acta (Berl.) 4, 352—366 (1966)

University of Newcastle upon Tyne (Great Britain)

Self-Consistent Molecular Orbital Calculations on Organoboron Compounds

Part I. Halogenovinylboranes

By

D. R. Armstrong and **P. G. Perkins**

Calculations of the π-electronic structures and spectra of a series of halogenovinylboranes are presented. The Pariser-Parr-Pople method (L.C.A.O.–M.O.–S.C.F.) is used throughout and the agreement with experiment is good. The significance of the results with regard to the chemistry of the compounds is indicated.

π-Elektronen-Struktur und Spektren einer Reihe von Halogenvinylboranen werden mit der LCAO–MO–SCF-Methode von Pariser, Parr und Pople berechnet. Die Übereinstimmung mit experimentellen Daten ist gut. Die Bedeutung der Resultate für die Chemie dieser Verbindungen wird aufgezeigt.

Les calculations des niveaux d'énergie électroniques π et les spectres d'une série de halogenovinylboranes sont presentés. La méthode de Pariser-Parr-Pople (L.C.A.O.–M.O.–S.C.F.) est utilisée partout et l'agrément avec l'expériment est bon. L'importance des résultats dans la chimie des composés est indiquée.

It is now generally accepted that delocalisation of electrons from attached groups having orbitals of π-symmetry to a boron atom may occur and a previous communication [*1*] contained calculations of the π-electronic structures of two vinylboranes by the free-electron method. To simplify the analysis in these cases a non-branched chain only was considered, and it was assumed that substituents on the boron atom did not perturb the π-system. This paper presents the results of calculations by the more versatile Pariser-Parr-Pople L.C.A.O.–M.O.–S.C.F. technique [*16, 17*] on a series of compounds of general formula $(CH_2 = CH_x)BX_{3-x}$. The substituent X is F, Cl, Br or H and $x = 1, 2, 3$.

1. Method of Calculation

a) Groundstate

The molecular orbitals, ψ_i, are expressed as linear combinations of atomic orbitals, φ_μ, in the usual manner:

$$\psi_i = \sum_\mu \chi_{i\mu}\, \varphi_\mu \,. \tag{1}$$

The energies, ε_i, are the roots of the secular equation

$$|F_{\mu\nu} - \varepsilon S_{\mu\nu}| = 0 \tag{2}$$

where $F_{\mu\nu}$ is the element of the self-consistent Hamiltonian matrix referring to atoms μ and ν and is given by [*17*]

$$F_{\mu\mu} = H_{\mu\mu} + \tfrac{1}{2} P_{\mu\mu} \langle \mu\mu \mid \mathcal{G} \mid \mu\mu \rangle + \sum_{\mu \neq \nu} P_{\nu\nu} \langle \mu\nu \mid \mathcal{G} \mid \mu\nu \rangle \,, \tag{3}$$

$$F_{\mu\nu} = H_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu} \langle \mu\nu \mid \mathcal{G} \mid \mu\nu \rangle \,. \tag{4}$$

$H_{\mu\mu}$, $H_{\mu\nu}$, $P_{\mu\mu}$, $P_{\mu\nu}$ are the diagonal and off-diagonal elements of the core Hamiltonian matrix $\boldsymbol{H}$ and the spinless density matrix $\boldsymbol{P}$ respectively. The integrals, $\langle \mu\mu \mid \mathcal{G} \mid \mu\mu \rangle$ and $\langle \mu\nu \mid \mathcal{G} \mid \mu\nu \rangle$ (generally abbreviated to $\gamma_{\mu\mu}$, $\gamma_{\mu\nu}$), have a corresponding function in the electron repulsion matrix $\boldsymbol{G}$.

The values of $H_{\mu\mu}$ and $H_{\mu\nu}$ required were taken from the appropriate valence state ionisation potential data and the MULLIKEN-WOLFSBERG-HELMHOLTZ approximation [*13, 21*],

$$H_{\mu\nu} = K\, S_{\mu\nu} \, (I_\mu + I_\nu) \,. \tag{5}$$

The starting matrix $\boldsymbol{P}$ was generated by solving the Hückel problem for the molecule and the diagonal elements of $\boldsymbol{G}$ ($\gamma_{\mu\mu}$) obtained by the method of JULG [*11*] except for boron which contributes no electrons to the π-system. For this atom an alternative approach due to KAUFMAN [*5*] was employed. When two electrons are contributed to the π system by an atom the energy of one of these depends on its attraction to the nucleus and the repulsion of the other electron i. e.

$$H_{\mu\mu} = I - \gamma_{\mu\mu}$$

e. g. for chlorine $H_{\mu\mu} = -23.40$ eV. The two-centre repulsion integrals, $\gamma_{\mu\nu}$, were calculated from the corresponding $\gamma_{\mu\mu}$ and $\gamma_{\nu\nu}$ by MATAGA and NISHIMOTO's procedure [*12*],

$$\gamma_{\mu\nu} = \frac{14.397}{a + r_{\mu\nu}} \,, \tag{6}$$

and a refinement of this [*15*],

$$\gamma_{\mu\nu} = \frac{14.397}{\sqrt{a^2 + r_{\mu\nu}^2}} \,, \tag{7}$$

where

$$a = \tfrac{1}{2} \left[\frac{14.397}{\gamma_{\mu\mu}} + \frac{14.397}{\gamma_{\nu\nu}} \right] . \tag{8}$$

Overlap integrals were generally calculated from established master formulae [*14*]; however, for cases where bromine was involved (non-integral Slater effective quantum number) the overlaps were obtained by interpolation from BROWN's tables [*4*]. The appropriate valence state ionisation potentials were taken mainly from reference [*10*] and are listed in Table 1, to gether with the one-centre repulsion integrals.

Table 1

	$I_{(\mathrm{eV})}$	$\gamma_{\mu\mu}$ (eV)
C	–11.16	9.76
B	– 1.06	5.97
F	–18.07	14.83
Cl	–13.36	10.04
Br	–12.08	9.40

b) Excited states

The singlet and triplet states resulting from the excitation of an electron from a closed shell ground state may be written as linear combinations of all the excited configurations,

$$ {}^1\Psi_I = \sum_l \sum_k c_I^s\,(l\to k)\; {}^1\psi_{l\to k} \tag{9} $$

$$ {}^3\Psi_I = \sum_l \sum_k c_I^t\,(l\to k)\; {}^3\psi_{l\to k}\,. \tag{10} $$

The summations l and k range over occupied and unoccupied orbitals respectively. The energies of the final states and the state mixing coefficients are obtained by diagonalising a configuration interaction matrix with elements

$$ ({}^1\psi_{i\to k} \mid \mathscr{H} \mid {}^1\psi_{j\to l}) = \delta_{ij}\,\delta_{kl}\,(\varepsilon_k - \varepsilon_i) + 2\,\langle ik \mid jl\rangle - \langle ij \mid kl\rangle \tag{11} $$

$$ ({}^3\psi_{i\to k} \mid \mathscr{H} \mid {}^3\psi_{j\to l}) = \delta_{ij}\,\delta_{kl}\,(\varepsilon_k - \varepsilon_i) - \langle ij \mid kl\rangle \tag{12} $$

where

$$ \langle ij \mid kl\rangle = \sum_\mu \sum_\nu c_{i\mu}\, c_{k\mu}\, c_{j\nu}\, c_{l\nu}\, \gamma_{\mu\nu}\,. $$

The intensity of absorption of radiation on excitation to one of the above states as measured by its oscillator strength may be computed from

$$ f_n = 4.703 \cdot 10^{29}\, \nu\, \left| \int \Psi_0\, e r\, \Psi_n\, \mathrm{d}v \right|^2 . \tag{13} $$

c) Geometry

Although the geometry of none of these boranes is known, it is reasonable to assume that trivinylboron is planar and has the swastika configuration (Fig. 1a). All the monovinyl compounds belong to the point group C_s whereas the divinylboranes have three possible geometrical isomers. Previous calculations on divinylboranes [*8*] by the Hückel method have assumed the swastika configuration. In the present work calculations were carried out on both forms 1 (b) and 1 (c) to ascertain if it were possible to make a definite assignment of geometry. The boron-halogen bond distances were taken from [*18*]; the B–C bond was assumed to have length 1.55 Å and the C–C bond 1.35 Å [*1*].

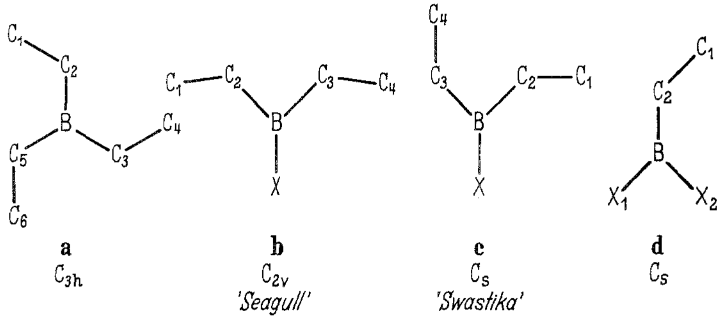

Fig. 1. Geometry of vinylborones

The electronic states of the molecules with symmetry C_{2v} belong to either A_1 or B_1 representations of the group, but on lowering the symmetry to C_s this distinction is eliminated and all transform as A'. Because of the absence of degeneracy each one electron excitation gives rise to a separate state and under both symmetries all the transitions from the totally symmetric ground state are space allowed and are polarized in the x or y directions ($y = C_2$ axis). The swastika form of trivinylboron has C_{3h} symmetry and its states are either A' or E'. The $0 \rightarrow 0$ transitions to the former are forbidden but strongly allowed to the latter and are polarized in the xy plane. Excitations from the filled orbitals to any of the first three empty levels give rise to three A' and three E' states. The energies of all six were calculated.

d) $n \rightarrow \pi^*$ *transitions*

For halogenoboranes transitions of the $n \rightarrow \pi^*$ type (^1U, ^3U) stemming from the in-plane non-bonding p-orbitals on the halogen are possible. These are forbidden by the local symmetry of the B–X bond and, moreover, should occur at rather higher energies than the lower excited π states because of the high ionisation potentials of halogen atoms. The energies of the two transitions from the non-bonding level to the first two π states in the halogenodivinylboranes were calculated. When two halogens are attached to boron there are two possible transitions to the lowest empty π orbital. Their energies are not identical since the environment of each halogen differs in the compound. Both these energies were calculated. In carrying this out the halogen one-centre two-electron integrals $\langle nn \mid \pi\pi \rangle$ were obtained from [22]

$$\langle nn \mid \pi\pi \rangle_{\mathrm{F}} = 0.8922 \, \langle \pi\pi \mid \pi\pi \rangle_{\mathrm{F}}$$

and

$$\langle nn \mid \pi\pi \rangle_{\mathrm{Cl}} = 0.8832 \, \langle \pi\pi \mid \pi\pi \rangle_{\mathrm{Cl}} \, .$$

For bromine the proportionality constant was given the value 0.9. The corresponding exchange integrals $\langle \pi n \mid \pi n \rangle_{\mathrm{X}}$ were set equal to

$$\tfrac{1}{2} \left[\langle \pi\pi \mid \pi\pi \rangle_{\mathrm{X}} - \langle nn \mid \pi\pi \rangle_{\mathrm{X}} \right] .$$

e) σ-*polarisation*

At present there is no general method available to take into account the effect of σ polarization in such molecules. Classically the halogens are considered to withdraw σ electron density from the boron atom and we have attempted to take this into account (calculation 3) for the halides by approximating the distribution of σ electrons by [20]

$$n_{\mathrm{hal.}} = \frac{2 \cdot \chi_{\mathrm{hal.}}}{\chi_{\mathrm{hal.}} + \cdot \chi_{\mathrm{boron}}} \tag{13}$$

where $n_{\mathrm{hal.}}$ is the number of σ electrons in the neighbourhood of the halogen and $\chi_{\mathrm{hal.}}$, χ_{boron} are the valence state electronegativities of the halogen and boron respectively [9]. The σ distribution is assumed to be unaffected by the π electrons. Eq. (13) allows a new Slater Z^* to be obtained for each atom whence the π valence state ionisation potentials or electron affinities (i.e. the diagonal elements of the core Hamiltonian matrix) can be calculated using the relation

$$I \text{ (or } E) = A \cdot Z^{*2} + B \cdot Z^* + C \tag{14}$$

A, B and C are evaluated by comparison of a series of isoelectronic species in the same valence state. The one-centre repulsion integrals may then be scaled in direct proportion to Z^*.

f) Programme for solution of molecular self-consistent field problems

The programme was written in Algol 60 for the University of Newcastle English Electric KDF 9 computer. The eigenvalues and eigenvectors of the Fock matrices are found by the Wilkinson-Householder method [*18*]. The density matrix is then constructed from the eigenvector sets, and together with the core matrix and repulsion matrix is used to form a new Fock matrix. The iteration proceeds until a density matrix self-consistent to 5 decimal places is obtained; about 10 iterations are generally required to satisfy this criterion. For the excited states the interconfigurational matrix elements are calculated from (11) and (12) and the configuration interaction matrix so constructed is diagonalised. The programme considers a prescribed set of single electron excitations and all configuration interaction between them. The oscillator strengths of the states are automatically calculated taking into account configuration interaction in the excited state. Finally if required the $n \rightarrow \pi^*$ transition energies are calculated using a similar technique to that employed for the π electronic states. For a molecule containing six π orbitals [e.g. $(C_2H_3)_2$ BCl] the time taken for the whole calculation is $\approx$ 3 min.

2. Results

Tab. 2 to 6 list the results obtained for the series of compounds studied. The oscillator strengths of the triplet states are zero because of spin orthogonality.

3. Discussion

a) Spectra

Experimental ultra-violet spectral data relating to the vinylboranes is very much lacking, no doubt due in part to the difficulties in preparation and handling of these reactive compounds. GOOD and RITTER [*8*] examined the spectra of trivinylboron and chlorodivinylborane and reported intense bands at 234 mμ and 222 mμ respectively. A more detailed analysis of these spectra* in the way indicated previously [*1*] yielded the peak positions and intensities shown in Tab. 7.

α) $\pi - \pi^*$ transitions. For both these compounds the lowest energy singlets predicted are strongly allowed and should therefore correspond to the lowest energy *intense* bands in the experimental spectra. Thus for $(C_2H_3)_2BCl$ the observed band centred at 5.572 eV is assigned to the $^1A_1 \rightarrow {}^1B_1$ transition and that at 5.983 eV to the first $^1A_1 \rightarrow {}^1A_1$.

Similarly for trivinylboron the low energy transition from the ground state to the $^1E'$ state involves two degenerate excitations from the mutually orthogonal components of the e'' orbital (Fig. 2). This leads to a doubled intensity, hence the band at 234 mμ may be satisfactorily assigned to $^1A' \rightarrow {}^1E'$. Transitions to the $^1A'$ states are formally forbidden since the transition density is symmetric to reflection in the xy plane but the z axis is not. Such a promotion may be achieved if the upper state is coupled with an in-plane degenerate (E') vibration. Those in which the carbon boron skeleton are involved will couple most strongly with excited π states. There are four of these normal modes in trivinylboron. Thus, in this case, the 0→0 transition is forbidden and a band appearing gains its intensity by vibronic coupling and borrowing from the neighbouring allowed $^1A' \rightarrow {}^1E'$ transition to which it is energetically close. Hence the intensity of the latter should be concomitantly reduced. The weak band seen at 215 mμ ($f = 0.04$) seems to be of this type and its peak corresponds to the Frank-Condon transition. Vibrational structure on the main band in this case can arise from coupling with totally symmetric vibrations (of which there are five). The vibrational spectrum of

---

* We are indebted to Prof. D. M. RITTER for making copies of his spectra available to us.

trivinylboron below 400 cm^{-1} has not been investigated but, by comparison with BCl_3, skeletal deformation modes should appear in this region. Such a low frequency A' mode may give rise to "hot" bands in the U.V. spectrum and could readily be tested experimentally.

Table 2. *Monovinylboranes* $(CH_2{=}CH)\,BX_2$

Calcn.	$(^1\Psi_I)$ E (eV)	f	$(^1\Psi_{II})$ E (eV)	f	$(^3\Psi_I)$ E (eV)	$(^3\Psi_{II})$ E (eV)	^1U E (eV)		^3U E (eV)	
X = F										
1	6.915	.541	8.923	.105	2.789	8.286	—	—	—	—
2	6.073	.509	8.269	.055	3.746	7.924	11.782	11.500	11.746	11.464
3	5.655	.448	7.444	.111	3.616	6.720	—	—	—	—
X = Cl										
1	6.966	.566	8.847	.099	2.972	8.507	—	—	—	—
2	6.084	.507	8.257	.262	3.756	7.627	8.253	7.973	8.211	7.932
3	5.849	.462	7.001	.472	3.694	6.043	—	—	—	—
X = Br										
1	6.931	.559	7.738	.155	2.790	7.444	—	—	—	—
2	6.044	.488	7.275	.421	3.752	6.606	6.880	7.140	6.845	7.125
3	5.848	.416	6.495	.591	3.704	5.585	—	—	—	—
X = H										
1	6.457	.437	8.428	.214	2.763	7.304	—	—	—	—
2	5.766	.459	7.651	.117	3.661	7.061	—	—	—	—

Calcn. 1. $\gamma_{\mu\nu}$ from 6
Calcn. 2. $\gamma_{\mu\nu}$ from 7
Calcn. 3. Allowing for σ drift.

The narrowness of the bands in the spectra of both $(C_2H_3)_3B$ and $(C_2H_3)_2BCl$ suggests that the nuclear configuration remains essentially the same on excitation

Table 3. *Divinylboranes* $(CH_2 = CH)_2\,BX$

	$E(^1\Psi_I)\ B_1$	f	$E(^1\Psi_{II})\ A_1$	f	$E(^1\Psi_{III})$	f	$E(^3\Psi_I) B_1$	$E(^3\Psi_{II}) A_1$	$E(^3\Psi_{III})$	$E[^1U_{(1)}]\ A_2$	$E[^1U_{(2)}]\ B_2$	$E[^3U_{(1)}]\ A_2$	$E[^3U_{(2)}]\ B_2$
X = F													
1a	6.186	.660	6.545	.007	7.556(A_1)	.010	2.748	2.798	6.761(A_1)				
b	6.149	.434	6.457	.114	7.412	.215	2.749	2.800	6.632				
2a	5.636	.815	6.170	.037	7.954(A_1)	.064	4.056	4.142	7.658(A_1)	10.712	13.204	10.662	13.204
b	5.704	.610	6.090	.251	7.685	.047	4.061	4.145	7.429	10.815	13.329	10.767	13.329
3a	5.386	.761	5.885	.011	7.842(A_1)	.085	3.990	4.099	7.366(A_1)				
b	5.424	.554	5.844	.241	7.569	.072	3.995	4.100	7.146				
X = Cl													
1a	6.266	.658	6.552	.002	7.545(A_1)	.078	2.757	2.798	6.795(A_1)				
b	6.225	.424	6.470	.144	7.406	.225	2.756	2.798	6.656				
2a	5.655	.860	6.089	.011	7.517(B_1)	.044	3.685	3.739	7.026(A_1)	7.026	9.168	6.960	9.168
b	5.740	.617	6.035	.322	7.401	.053	3.683	3.738	6.938	7.187	9.379	7.122	9.379
3a	5.530	.832	5.837	.001	7.306(B_1)	.080	3.642	3.696	6.338(A_1)				
b	5.585	.551	5.842	.370	7.245	.071	3.640	3.695	6.322				
X = Br													
1a	6.267	.654	6.485	.000	7.519(A_1)	.039	2.757	2.796	6.726(A_1)				
b	6.228	.417	6.420	.179	7.393	.232	2.756	2.796	6.604				
2a	5.658	.861	5.962	.000	7.474(B_1)	.046	3.686	3.730	6.505(A_1)	5.940	8.163	5.884	8.163
b	5.734	.574	5.957	.405	7.357	.052	3.684	3.729	6.510	6.101	8.376	6.045	8.376
3a	5.573	.842	5.729	.018	7.213(A_1)	.270	3.657	3.694	5.882(A_1)				
b	5.618	.478	5.786	.512	7.118	.080	3.655	3.693	5.909				
X = H													
1a	5.920	.645	6.323	.006	7.548(A_1)	.101	2.723	2.794	6.523(B_1)				
b	5.884	.434	6.248	.110	7.403	.203	2.722	2.794	6.417				
2a	5.399	.821	5.978	.028	7.314(B_1)	.093	3.591	3.710	6.673(B_1)				
b	5.451	.591	5.900	.220	7.193	.091	3.589	3.709	6.631				

Calcn. 1. $\gamma_{\mu\nu}$ from 6
Calcn. 2. $\gamma_{\mu\nu}$ from 7
Calcn. 3. allowance for σ drift.

a: C_{2v} (Seagull) — symmetries specified in the table

b: C_s (Swastika) — all electronic states A'

Table 4. *Trivinylboron*

Symmetry	E'		A'		A'		E'		A'		E'	
Calcn.	$E(^1\Psi_{\mathrm{I,\,II}})$	f	$E(^1\Psi_{\mathrm{III}})$	f	$E(^1\Psi_{\mathrm{IV}})$	f	$E(^1\Psi_{\mathrm{V,\,VI}})$	f	$E(^1\Psi_{\mathrm{VII}})$	f	$E(^1\Psi_{\mathrm{VIII,\,IX}})$	f
1	5.680	0.357	6.197	0	7.297	0	7.333	0.281	7.489	0	7.787	0.265
2	5.374	0.551	6.030	0	7.323	0	7.462	0.230	8.446	0	8.749	0.007
	$E(^3\Psi_{\mathrm{I,\,II}})$ E'		$E(^3\Psi_{\mathrm{III}})$ A'		$E(^3\Psi_{\mathrm{IV,\,V}})$ E'		$E(^3\Psi_{\mathrm{VI}})$ A'		$E(^3\Psi_{\mathrm{VII}})$ A'		$E(^3\Psi_{\mathrm{VIII,\,IX}})$ E'	
1	2.964	—	3.051	—	6.211	—	6.335	—	7.297	—	7.555	—
2	3.817	—	4.008	—	6.849	—	6.900	—	8.446	—	8.724	—

Table 5. *Electron densities and bond orders (from calc. 2)*

Compound	B	X_1	X_2	C_1	C_2	C_3	C_4	B–X_1	B–X_2	C_1–C_2	C_3–C_4	B–C_2	B–C_3
$(C_2H_3)_3B$	0.1399	—	—	0.9500	1.003	—	—	—	—	0.9749	—	—	0.2190
$(C_2H_3)_2BX$*													
X = H	0.0968	—	—	0.9469	1.005	1.010	0.9417	—	—	0.9805	0.9802	0.1943	0.1959
F	0.1806	1.897	—	0.9588	1.003	1.009	0.9521	0.4301	—	0.9793	0.9789	0.1995	0.2009
Cl	0.2470	1.822	—	0.9764	0.9896	1.003	0.9618	0.5523	—	0.9805	0.9802	0.1941	0.1957
Br	0.2668	1.799	—	0.9821	0.9851	1.001	0.9653	0.5805	—	0.9804	0.9801	0.1950	0.1964
$C_2H_3BX_2$													
X = H	0.0502	—	—	0.9377	1.012	—	—	—	—	0.9742	—	0.2254	—
F	0.2192	1.907	1.907	0.9599	1.007	—	—	0.4065	0.4059	0.9824	—	0.1847	—
Cl	0.3235	1.852	1.851	0.9822	0.9912	—	—	0.4960	0.4962	0.9839	—	0.1777	—
Br	0.3512	1.837	1.837	0.9892	0.9857	—	—	0.5145	0.5151	0.9836	—	0.1795	—

---

* Swastika form.

Table 6. *Electron densities and bond orders (from calc. 3)*

Compound	B	X_1	X_2	C_1	C_2	C_3	C_4	B–X_1	B–X_2	C_1–C_2	C_3–C_4	B–C_2	B–C_3
$(C_2H_3)_2BX$*													
X = F	0.2543	1.839	—	0.9594	0.9944	1.005	0.9474	0.5257	—	0.9748	0.9742	0.2191	0.2214
Cl	0.2967	1.779	—	0.9804	0.9823	0.9998	0.9617	0.6049	—	0.9779	0.9776	0.2061	0.2079
Br	0.3041	1.766	—	0.9861	0.9793	0.9980	0.9661	0.6187	—	0.9785	0.9783	0.2034	0.2049
C_2H_3 BX_2													
X = F	0.3699	1.839	1.839	0.9577	0.9950	—	—	0.5110	0.5103	0.9738	—	0.2220	—
Cl	0.4201	1.806	1.805	0.9883	0.9796	—	—	0.5494	0.5500	0.9795	—	0.1989	—
Br	0.4224	1.804	1.803	0.9940	0.9768	—	—	0.5516	0.5527	0.9800	—	0.1972	—

---

* Swastika form.

of one electron to the lowest empty orbital although as this has a node between each pair of carbon atoms slight rotation of the terminal CH_2 groups may well occur. The overall effect expected is simply a decrease in the C–C bond stretching force constant, and hence the $0 \rightarrow 0$ and the vertical (Frank-Condon) transitions should be very close or identical in energy.

In the light of the above the agreement between the observed and calculated positions of the bands in $(C_2H_3)_2BCl$ and $(C_2H_3)_3B$ is good, particularly when the 'refined' form of the MATAGA approximation [Eq. (7)] for repulsion integrals is employed and the allowance for σ electron polarisation is made. The latter produces a lowering in energy for all the electronic transitions. This results principally from an increase in the electron affinity of the boron atom which affects directly those one-electron levels containing boron in direct proportion to the square of its mixing coefficient. This is in accord with perturbation theory.

Table 7. *Spectra of vinylboranes*

	Symmetry	$^1B_1$ *E*	*f*	$^1A_1$ *E*	*f*	Mystery band[b] *E*	*f*
$(C_2H_3)_2BCl$	Obs. eV	5.572	7.02[c]	5.983	5.31[c]	5.099	1.0
	Obs. mμ	222.0		207.2		243.0	
	Calcd.[a] eV	5.585	0.551	5.842	0.370	—	—
	Calcd.[a] mμ	221.9		212.2			

	Symmetry	$^1E'$ *E*	*f*	$^1A'$ *E*	*f*	Mystery band[b] *E*	*f*
$(C_2H_3)_3B$	Obs. eV	5.308	0.329	5.765	0.040	4.702	0.032
	Obs. mμ	233.5		215.0		264.0	
	Calcd.[a] eV	5.374	1.100	6.030	0	—	—
	Calcd.[a] mμ	230.6		205.6			

---

[a] values chosen for best overall agreement

[b] the symmetry of this is unknown (see later)

[c] the *f* values observed are relative to the oscillator strength of the weakest band.

β) $\sigma - \pi^*$ transitions. The weak bands in the spectra of $(C_2H_3)_3B$ and $(C_2H_3)_2BCl$ at 264 mμ ($f = 0.032$) and 243 mμ ($f_{rel} = 1$) respectively have not yet been discussed. Similar bands appear in the methylvinylboranes and have been found difficult to assign [*2*]. BERRY [*3*] has discussed similar shoulders at longer wavelengths than the first main band in the U.V. spectra of alkylated ethylenes. He suggests that these should be assigned to transitions between the highest C–H σ-bonding levels and the lowest π orbitals. They should be weakly allowed.

In the present series of compounds it is reasonable to suppose that the vinyl C–H σ-system remains virtually unperturbed from compound to compound. Hence its electrons may be regarded as though they were non-bonding and located at a fixed position in the absolute energy scale. If this is accepted the energy of the

$\sigma - \pi$ transition under consideration depends only on the location of the first empty π orbital. In the special cases of the divinylboranes and trivinylboron the bonding orbital remains almost unaltered in energy with change of substituent so that the energy gap between the main and subsidiary bands should be approximately constant. The actual measured quantities [2] all fall in the region 0.45 – 0.6 eV.

γ) Configuration of the Divinylboranes. Both seagull and swastika geometries yield very similar band energies and they cannot be interdistinguished on this basis. The intensities, however, are much more revealing. As is not uncommon with this type of calculation the agreement between the observed and calculated oscillator strengths is mediocre but the relative intensity of the calculated bands to each other yields valuable information.

It would be expected that the change in dipole moment for the $^1A_1 \rightarrow {}^1A_1$ transition would be less in the seagull than the swastika form because the extension of the former is smaller in the y direction. On the other hand the effect would be reversed for the $^1A_1 \rightarrow {}^1B_1$ transition. From Tab. 2 the ratio of the oscillator strengths of these states is ~1:500 for the seagull but ~3:2 for the swastika form. In the experimental spectrum of chlorodivinylborane the above intensity ratio is ~4:3 and it is therefore concluded that the equilibrium configuration of the ground state of the molecule is chiefly the swastika form. The reason for the assumption of such a shape is not clear, but it may indicate the stereochemistry of the transition state in the reaction by which it is produced [$Sn(C_2H_3)_4 + BCl_3$]. Presumably in this state free rotation of the vinyl groups is restricted, otherwise a proportion of the more symmetrical seagull form would be expected in the end product.

The spectra of vinylboranes other than those discussed above are either uninvestigated or incomplete. It is reported that dichlorovinylborane possesses an intense band at 207 mμ [*7*] whilst in the corresponding fluoride this band undergoes a blue shift and only its long wavelength trailing edge has been noted. No intensity data for these compounds nor any spectra for the rest of those in Tab. 2 and 3 have as yet been published. In a previous paper [*1*] the calculated energies of the hydrovinylboranes were compared with the observed spectra of the methylvinylboranes. The interaction of the methyl group with the rest of the π electron system, though small, is not really negligible and a subsequent paper will deal with incorporation of its effect. The results for the unknown hydrovinylboranes in Tab. 2 and 3 show that their state energies should be, in general, lower than those observed in the corresponding methylvinylboranes. The weak $\sigma \rightarrow \pi^*$ bands have not been reported for the halogenomonovinylboranes, although they appear in the U.V. spectra of $C_2H_3BMe_2$ and C_2H_3BClMe [*2*]. It is apparent from Fig. 3 that both the filled and unfilled levels of $C_2H_3BH_2$ are shifted on substitution of halogen for hydrogen and thus the near equal energy separations of the $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands previously discussed need not be observed. If these bands do indeed arise from $\sigma - \pi^*$ excitations, as supposed, then their intensities should presumably be approximately proportional to the number of vinyl groups in the molecule.

b) Energy levels of the compounds

Figs. 2 and 3 illustrate the self-consistent ground state sets of eigenvalues of all the compounds. These are taken from calculation 2 in each case. The effect of substituting for a hydrogen on boron an atom capable of contributing to the π system is well seen.

In divinylboranes, if the π orbital which the substituent provides is of lower energy than the occupied bonding orbitals (e.g. F or Cl) then it raises the energy of these levels in proportion to the boron mixing coefficient. Hence halogen substitution increases the energy of the lowest empty and penultimate filled orbitals more than the alternate set. This is because the substituent affects only the orbitals which contain a large contribution from boron. The result is a hypsochromic shift in the spectrum. The perturbation is less simple in trivinylboron since the introduction of the vinyl group raises the symmetry to C_{3h} and so the incoming group mixes its orbitals with all the others under the C_3 rotation and concomitantly degeneracy is introduced. This means that the energies of all the orbitals are modified by vinyl substitution. The overall effect is that the two new vinyl orbitals and a pair of a_2 orbitals originating from the divinylboron chain form into two degenerate e'' pairs. Furthermore, of these pairs, the energy of the filled level is raised whilst that of the first empty orbital (which may be identified with

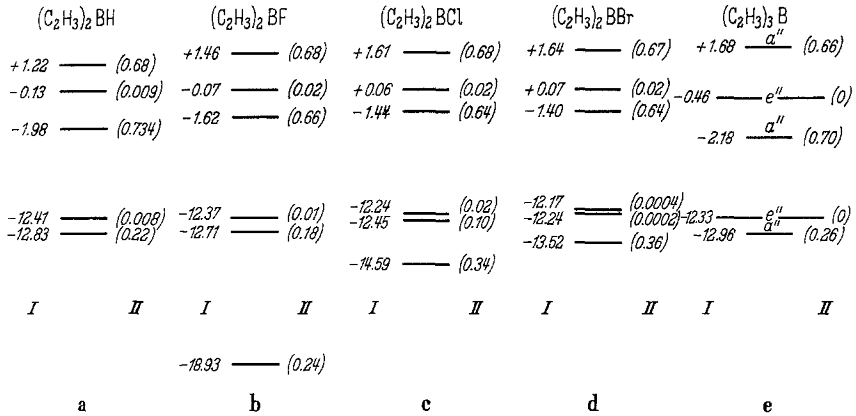

Fig. 2. Energies (I) and (boron mixing coefficients II) for divinylboranes

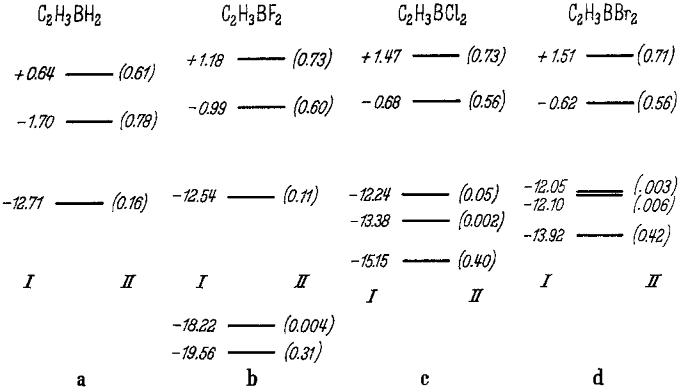

Fig. 3. Energies (I) and (boron mixing coefficients II) for monovinylboranes

the non-bonding level in the isoelectronic odd alternant hydrocarbon ion) is lowered. The aggregate effect readily interprets the bathochromic shift of the first main band of trivinylboron with respect to the divinylboranes.

Because of C_s symmetry, all the molecular orbitals of monovinylborane (Fig. 3a) are raised in energy by substitution at boron. Over the series F, Cl, Br the effect of the halogen becomes progressively greater on both filled and empty orbitals as it approaches them more closely in energy. The second order energy difference, however, *decreases* differentially for the lowest pair of levels, being least for the filled one. The one-electron scheme thus reveals how the prediction of almost identical spectra for $C_2H_3BCl_2$ and $C_2H_3BF_2$ arise and how the peaks in $C_2H_3BH_2$ and $C_2H_3BBr_2$ should be bathochromically shifted with respect to them.

c) Electron densities and bond orders

The electron densities on each atom and the bond orders between adjacent atoms for the series are listed in Tab. 5. All are taken from calculation 2. Those in Tab. 6 are from calculation 3.

Considerable π-electron density is contributed by the halogens to the boron atom in the divinylboranes. By contrast the vinyl group supplies little despite the lower valence state ionisation potentials of its carbon atoms. A comparison of the figures for trivinylboron and fluorodivinylborane shows this clearly, and suggests that an investigation of the efficacy of the former as an electron acceptor in donor-acceptor complex formation may be rewarding. Over the series of halogenated compounds the greatest density is contributed by bromine which has the lowest core Coulomb integral. When little density is transferred by the halogen to boron (e.g. F) there is a greater accumulation of the π charge on the carbon atoms linked to boron and also a greater B–C bond order. Hence it might be expected that a second halogen substituent would exaggerate the first effect and this is indeed the case. The charges on both carbon atoms are increased differentially in $C_2H_3BX_2$. The overall effect of the electronegative atom is to transfer electron density via the boron atom to the vinyl group. A substituent 'inert' to the π system (e.g. H) shows this effect at its greatest having both the lowest boron electron density and the highest differential charges on the carbon atoms. At the other extreme the transfer of electron density to boron by bromine in $C_2H_3BBr_2$ actually *reverses* the order of the charges on the two carbons. The C=C bond orders stay sensibly constant over the series but the change in B–X (or even B–C) bond order may be large enough to be detected by vibrational spectroscopy.

d) Reorganisation Energies

Possibly the chief factor influencing the thermodynamics of donor-acceptor complex formation by boron compounds is the energy required to reorganise the acceptor molecule from the planar to the hypothetical pyramidal configuration. This quantity is partly made up of the π delocalisation energy of the molecule in question which may be obtained directly from the present calculations. Thus it may be calculated from POPLE's equation [*17*]:

$$E_\pi(\text{SCF}) = \sum_{\mu<\nu} Z_\mu Z_\nu R_{\mu\nu}^{-1} + \tfrac{1}{2}\sum_{\mu\nu} P_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu}) .$$

The initial electronic energies are subtracted from the above quantity. For the carbon skeleton this is the self-consistent energy of an isolated vinyl group whilst for a halogen atom the relevant quantity is $(2\,I - \gamma_{\mu\mu})$. With this definition we obtained the vertical reorganisation energy of the bonds to boron, i.e. no account is taken of the energy changes resulting from increments in the bond lengths on reorganisation. A fuller discussion of these features in relation to the problem will be published at a later date. The vertical reorganisation energies are given in Tab. 8 and are taken from those calculations in which allowance was made for σ-polarisation of the boron-halogen bonds. The highest energies are calculated for compounds containing two halogen atoms. These decrease when vinyl groups are substituted reaching a minimum at $(C_2H_3)_3B$. Thus despite the fact that the B–C bond order is higher in trivinylboron than in any halogeno derivative the compound has a lower π energy. For the hydrovinylboranes the π energy increases regularly to a maximum at trivinylboron.

Table 8. *Reorganisation energies*

	R.E. (eV)				
X =	F	Cl	Br	H	C_2H_3
$C_2H_3BX_2$	3.775	3.765	3.600	0.335	0.995
$(C_2H_3)_2$ BX	2.335	2.428	2.372	0.665	0.995

It has previously been established that the order of reorganisation energies in the trihalides is $BF_3 > BCl_3 > BBr_3$ [*6*]. This also holds for the series $C_2H_3BX_2$ but not for $(C_2H_3)_2BX$. However, the compression energy of the σ bonds may well affect the above ordering of the energies and we consider that no final conclusion may yet be drawn. On the above basis it is clear that trivinylboron should be a stronger acceptor than any trihalide. A similar result has been established experimentally for triphenylboron in the gas phase [*9*].

The authors thank Dr. B. J. Duke for help with computing and one of us (D.R.A.) thanks the S.R.C. for a maintenance grant.

References

[*1*] Armstrong, D. R., and P. G. Perkins: Theoret. chim. Acta **4**, 69 (1966).
[*2*] — — Theoret. chim. Acta (in the press).
[*3*] Berry, R. S.: J. chem. Physics **38**, 1934 (1963).
[*4*] Brown, D. A.: J. chem. Physics **29**, 1086 (1957).
[*5*] Chalvet, O., and J. J. Kaufman: Tech. Rept. No. 8 of Office of Naval research, Contract Nonr. 3471(00), Task No. 356—433, (1962).
[*6*] Cotton, F. A., and J. R. Leto: J. chem. Physics **30**, 993 (1959).
[*7*] Coyle, T. D., S. L. Stafford, and F. G. A. Stone: J. chem. Soc. (Lond.) **1961**, 3103.
[*8*] Good, C. D., and D. M. Ritter: J. Amer. Chem. Soc. 84, 1162 (1962).
[*9*] Greenwood, N. N., and P. G. Perkins: Proc. 8th Internat. Conf. on Coord. Chem. (Vienna) 1964.
[*10*] Hinze, J., and H. H. Jaffe: J. Amer. chem. Soc. **84**, 540 (1962).
[*11*] Julg, A.: J. Chim. physique **55**, 413 (1958).
[*12*] Mataga, N., and K. Nishimoto: Z. phys. Chem. (Frankfurt) **13**, 140 (1957).
[*13*] Mulliken, R. S.: J. phys. Chem. **56**, 295 (1952).
[*14*] —, C. A. Rieke, D. Orloff, and H. Orloff: J. chem. Physics **17**, 1248 (1949).

[*15*] OHNO, K.: Theoret. chim. Acta **2**, 219 (1964).
[*16*] PARISER, R., and R. G. PARR: J. chem. Physics **21**, 466 (1953).
[*17*] POPLE, J. A.: Trans. Faraday Soc. **49**, 1375 (1953).
[*18*] Tables of Interatomic distances and configuration in molecules and ions, Special Public, No. 11. London: Chemical Society 1958.
[*19*] WILKINSON, J. H.: Numerische Mathematik **4**, 254 (1962).
[*20*] WILMSHURST, J. K.: J. chem. Physics **27**, 1129 (1957).
[*21*] WOLFSBERG, M., and L. HELMHOLTZ: J. chem. Physics **20**, 837 (1952).
[*22*] ZAULI, C.: Boll. Sci. Fac. Chem. Ind. (Bologna) **17**, 74 (1957).

(Received December 14, 1965)