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Self-Consistent Molecular Orbital Calculations on Organoboron Compounds

Part II. Methylvinylboranes

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The Pariser-Parr-Pople method has been used to calculate the π electronic structures and spectra of three methylvinylboranes. Two separate calculational models of the methyl group are considered and the agreement between observed and calculated spectral quantities is good. The reorganisation energies of these molecules are also evaluated.

Mit der Methode von Pariser, Pople und Parr werden Struktur und Spektren der π-Elektronensysteme von drei Methylvinylboranen berechnet, ebenso ihre Reorganisationsenergien. Für die Methylgruppe werden zwei verschiedene Modelle verwendet. Die Übereinstimmung zwischen berechneten und experimentellen Werten ist gut.

A l'aide de la méthode Pariser-Parr-Pople nous avons calculé les structures et les spectres π-électroniques de trois méthylvinylboranes. Nous considérons deux modèles du groupe méthyl; les spectres observés et calculés s'accordent bien. En plus, les énergies de réorganisation de ces molécules sont évaluées.

In a previous paper [*1*] self-consistent molecular orbital calculations on a series of halogenovinylboranes were presented. We here report the results of similar calculations on the three methylvinylboranes $CH_3B(C_2H_3)_2$, $(CH_3)_2BC_2H_3$ and $ClCH_3BC_2H_3$. Of these, the first two have been studied previously by the Hückel method [*7*] but in the calculations the effects of the methyl group were neglected. Here we have considered explicitly the participation of the methyl group in the π electron system of the rest of the molecule.

1. Models of the Methyl group

Conjugation of the C–H σ bonding electrons of a methyl group with the π electron system of an unsaturated molecule may be simulated in two distinct ways. The group may be considered (a) as the triply bonded $-C{\equiv}H_3$ species [*14*], (b) as a pseudoheteroatom [*11*].

In the former the H_3 entity is regarded as a pseudoatom having three orbitals and three electrons. The orbitals are formed from linear combinations of the three hydrogen 1*s* functions under C_3 symmetry thus:

$$\psi_1 = \frac{1}{\sqrt{3}}(s_A - s_B - s_C)$$

$$\psi_2 = \frac{1}{\sqrt{2}}(s_B - s_C)$$

$$\psi_3 = \frac{1}{\sqrt{6}}(2\,s_A - s_B - s_C)\,.$$

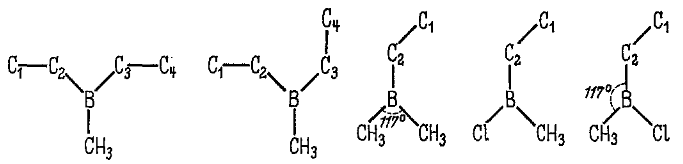
The first orbital has σ symmetry and forms a σ bond with the adjacent carbon; the second pair have the symmetry of a doubly degenerate pair of p orbitals respectively coincident with and orthogonal to the main π electron system. INUZUKA [9] and MORITA [12] have suggested appropriate valence state ionisation potentials and one-centre repulsion integrals for this model. We made the assumption that the methyl carbon atom is in either (α) an sp^3 V_4 state or (β) in a quasi dihedral state.

Table 1

	I (eV)	$\gamma_{\mu\mu}$(eV)
B	-1.06	5.97
Cl	-13.36	10.04
C	-11.16	9.76
(a) H_3[a]	-8.80	8.43
(b) C(Me)[a]	-14.61	11.67
(c) H_2[b]	-10.26	9.33
(d) C(Me)[b]	-11.19	9.71
CH_3(pseudoatom)	-13.12	11.67

[a] Ref. [9]; [b] Ref. [12].

The methyl group may also be considered as a single pseudoheteroatom which contributes two π electrons to the system. Such a model has been employed successfully in previous calculations on borazines [16]. The first valence state ionisation potential of the pseudoatom may be taken as the corresponding experimental quantity for methane. Similarly the one-centre repulsion term and effectiv enuclear charge are those pertaining to an electron on a carbon atom in the sp^3 V_4 state. For such a model the position of the pseudo p_π orbital is in question, i.e. a centre of charge must be assigned to the whole entity. This must necessarily be somewhat uncertain and in the calculations four different positions were tested. These were (α) at the carbon atom of the methyl group [16] and (β) $\frac{1}{3}$, $\frac{1}{2}$ and $\frac{2}{3}$ the distance from the C atom along a line collinear with the B–C axis and terminating at the centre of the plane of the three hydrogen atoms.



a 'seagull'(C_{2v}) b 'swastika' c *cis* Me-C1 d e *trans* Me-C1

Fig. 1. Geometrical configurations of Methylvinylboranes

For both models the core resonance integrals were calculated in the usual manner from the MULLIKEN-WOLFSBERG-HELMHOLTZ formula [13, 19]. The assumption that for the $-C{\equiv}H_3$ group these integrals may be obtained as for 'normal' p_π orbitals was investigated further. This was done by varying both

$\beta_{B-C\equiv}$ and $\beta_{C\equiv H3}$ over a range of values in a separate series of calculations on dimethylvinylborane. The input data for the compounds are summarised in Tab. 1 and their geometrical configurations are shown in Fig. 1. The following bond lengths were assumed in the calculations and were taken mainly from ref. [*18*]:

C=C: 1.35 Å; B–C (vinyl): 1.55 Å; B–Cl: 1.72 Å[1]; B–C (methyl): 1.55 or 1.56 Å.

2. Experimental Spectra

The positions and intensities of the bands in dimethylvinyl and methyldivinylborane have been reported previously [*2*, *7*]. They are given below together with the corresponding data for chloromethylvinylborane.

$Me_2BC_2H_3$: 195 mμ (6.325 eV) $f = 0.282$; 228 mμ (5.437 eV) $f = 0.0254$;

$ClMeBC_2H_3$: 204 mμ (6.071 eV) $f = 1.0$; 228 mμ (5.437 eV) $f = 0.1$
(the f values are relative);

$MeB(C_2H_3)_2$: 201 mμ (6.179 eV) $f = 0.1074$; 253 mμ (4.925 eV) $f = 0.0303$;
221 mμ (5.619 eV) $f = 0.3065$.

The two main bands in the spectrum of $MeB(C_2H_3)_2$ have previously been assigned to the $^1A_1 \rightarrow {}^1B_1$ and $^1A_1 \rightarrow {}^1A_1$ transitions [*2*] based on C_{2v} symmetry. In both the other compounds all excited states have A' symmetry. Bands similar to the weak lowest energy ones in the above spectra are thought to stem from either $\sigma \rightarrow \pi^*$ or $\pi \rightarrow \sigma^*$ excitations [*4*, *8*]. Later in this paper the two alternatives are considered further.

3. Spectral Results

a) $-C\equiv H_3$ *model*

The results obtained using this model of the methyl group are collected in Tab. 2. The Mataga approximation [*10*] for the two-centre repulsion integrals was employed in calculation 1 and the 'refined' form [*15*] in numbers 2—5. The latter four calculations incorporate all four combinations of the carbon and H_3 group parameters of Tab. 1 in the order $(a + b)$, $(a + d)$, $(b + c)$, $(c + d)$.

As in earlier work on the halogenovinylboranes [*1*] it is found that use of the Mataga expression for $\gamma_{\mu\nu}$ leads to transition energies which are generally ~ 0.5 eV too high. The 'refined' form of the equation, however, gives good agreement between observed and calculated spectra, this being optimised when carbon is assumed to be in the sp^3 V_4 state with the hydrogen atoms forming the trigonal H_3 rather than the dihedral H_2 entity. The predicted band energies are not very sensitive to the choice of these parameters however.

The energies calculated for the two different geometrical forms of $MeB(C_2H_3)_2$ and $ClMeBC_2H_3$ are very similar and do not serve to interdistinguish the isomers. The calculated relative intensity of the two main bands in $MeB(C_2H_3)_2$, when compared with that for the observed peaks indicate, as for the halogenovinylboranes, the swastika form for the compound. Only one spectral band has been observed for $ClMeBC_2H_3$ and so the same comparison may not be made here.

In order to test to what extent the calculated energies were affected by change in $\beta_{B-C\equiv}$ and $\beta_{C\equiv H3}$ the latter were systematically and independently varied over

Table 2. $-C\equiv H_3$ model

Calcn.	$E\ (^1\Psi_1)$	f	$E\ (^1\Psi_2)$	f	$E\ (^3\Psi_1)$	$E\ (^3\Psi_2)$
Dimethylvinylborane						
1	6.409	0.427	8.337	0.228	2.765	7.195
2	5.847	0.477	7.752	0.099	3.682	7.244
3	5.784	0.468	7.657	0.109	3.669	7.094
4	5.798	0.467	7.665	0.111	3.671	7.114
5	5.749	0.459	7.601	0.119	3.661	7.005
Chloromethylvinylborane						
1 t	6.737	0.484	8.630	0.135	2.780	7.851
c	6.752	0.551	8.617	0.126	2.778	7.832
2 t	5.964	0.472	8.061	0.074	3.725	7.566
c	6.005	0.554	8.017	0.035	3.721	7.537
3 t	5.944	0.471	8.005	0.075	3.720	7.495
c	5.985	0.551	7.965	0.035	3.717	7.468
4 t	5.948	0.468	8.009	0.077	3.721	7.502
c	5.989	0.555	7.965	0.037	3.718	7.472
5 t	5.932	0.466	7.970	0.079	3.717	7.451
c	5.975	0.554	7.931	0.038	3.715	7.423
Methyldivinylborane						
1 a	5.909	0.633	6.296	0.004	2.725	2.795
b	5.875	0.426	6.226	0.118	2.724	2.796
2 a	5.450	0.824	6.010	0.027	3.610	3.715
b	5.509	0.594	5.929	0.236	3.608	3.714
3 a	5.418	0.818	5.971	0.023	3.599	3.711
b	5.473	0.587	5.896	0.233	3.598	3.710
4 a	5.423	0.818	5.983	0.022	3.601	3.712
b	5.478	0.588	5.906	0.230	3.599	3.710
5 a	5.398	0.814	5.956	0.023	3.593	3.709
b	5.451	0.583	5.883	0.227	3.592	3.708

a — seagull; b — swastika; c — cis; t — trans.
$B{-}CH_3 = 1.56$ Å. Energies in eV.

the ranges -1.4 to -1.8 eV and -6.3 to -4.0 eV respectively. These values were incorporated with other standard parameters in a series of calculations on $Me_2BC_2H_3$. It was found that the transition energies were almost completely insensitive to the β values and changed by only 0.02 – 0.04 eV over the whole range considered.

b) Pseudoatom model

All the calculations employed the 'refined' MATAGA equation for the two-center integrals. The results are listed in Tab. 3. The agreement between the observed and calculated energies of the spectral bands is good and, furthermore, variation of the B–Me distance has little effect on the calculated quantities.

In summary it may be concluded that for neither the $-C\equiv H_3$ nor the pseudoatom model is the calculation of spectral quantities sensitive to the parameters selected for the methyl group. This illustrates the spectroscopic inertness of alkyl substituents on a boron atom as has previously been noted [*16*].

Table 3. *Methyl pseudoatom model*

Calcn.	B–CH$_3$ (Å)	β_{B-CH_3} (eV)	$E\,(^1\Psi_1)$	f	$E\,(^1\Psi_2)$	f	$E\,(^3\Psi_1)$	$E\,(^3\Psi_2)$
			Dimethylvinylborane					
1	1.968	−1.717	5.934	0.496	7.594	0.266	3.714	7.016
2	1.864	−1.999	5.988	0.500	7.767	0.295	3.729	7.066
3	1.769	−2.287	6.043	0.502	7.954	0.312	3.744	7.149
4	1.560	−3.050	6.168	0.504	8.401	0.292	3.780	7.482
			Chloromethylvinylborane					
1 t	1.968	−1.717	6.015	0.496	7.904	0.234	3.737	7.338
c			6.027	0.517	7.834	0.270	3.735	7.287
2 t	1.864	−1.999	6.039	0.501	7.996	0.263	3.743	7.339
c			6.045	0.510	7.940	0.301	3.741	7.295
3 t	1.769	−2.287	6.066	0.505	8.098	0.282	3.750	7.372
c			6.066	0.506	8.059	0.315	3.748	7.336
4 t	1.560	−3.050	6.136	0.514	8.363	0.291	3.769	7.584
c			6.130	0.506	8.373	0.290	3.767	7.574
			Methyldivinylborane					
1 a	1.968	−1.717	5.536	0.841	5.978	0.005	3.642	3.721
b			5.602	0.593	5.933	0.302	3.641	3.332
2 a	1.864	−1.999	5.578	0.848	6.009	0.005	3.657	3.725
b			5.649	0.598	5.964	0.313	3.656	3.725
3 a	1.769	−2.287	5.622	0.855	6.019	0.007	3.673	3.731
b			5.700	0.606	6.003	0.322	3.672	3.730
4 a	1.560	−3.050	5.797	0.878	6.250	0.262	3.735	3.763
b			5.838	0.634	6.116	0.332	3.713	3.749

a — seagull; b — swastika; c — cis; t — trans.

c) Weak bands

In considering the problem of the long wavelength weak bands which appear in vinylborane spectra, comparisons between the *total* energies of the ground and excited σ and π electronic states of the molecules should really be made. However, we have no knowledge of the former and can therefore only compare the self-consistent *one-electron* energies. This may not be as unsatisfactory as it seems at first sight since $\sigma \rightarrow \pi$ transitions are only weakly allowed even under the low symmetries of these molecules and the overlap of the ground and excited states is small. There is a distinct similarity between the $\sigma - \pi$ case and the $n \rightarrow \pi^*$ transitions which can theoretically occur in halogenoboranes and the exchange and coulomb integrals between the states should be similar. For such $n \rightarrow \pi^*$ excitations the former integrals are very small whilst the latter are in the region of 2 – 3 eV. It is not unreasonable to assume that they remain approximately constant for the $\sigma - \pi$ interactions in such a series of compounds and, if so, the one electron schemes may be intercompared directly.

The highest energy vinyl C–H σ bonding electrons are *equivalent* to a non-bonding pair and their energies should vary little over all the compounds; this is true for the filled π energy levels. Hence, if these bands are due to $\sigma \rightarrow \pi^*$ transitions, the first antibonding π^* eigenvalue should correlate with a weak spectral band for each compound. A linear relationship should then be expected between the observed energy of the bands in question and the energy of the lowest π^* antibonding level, which, if the σ levels were genuinely constant should have unity slope. Conversely, if the bands are due to $\pi \to \sigma^*$ transitions and the σ^* levels are taken as constant over the series then we should expect a linear plot between band energies and the highest π bonding levels.

Fig. 2 illustrates both relationships together with lines corresponding to constant σ and σ^* levels. The one-electron energies were abstracted from typical calculations. A good straight line is obtained only for the first alternative. The highest π bonding levels have an overall range on the abscissa of ~0.1 eV whereas

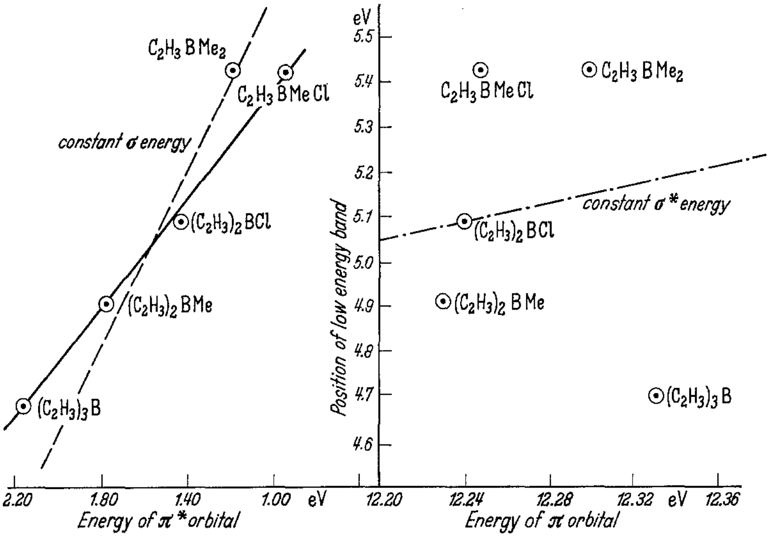


Fig. 2. Long wavelength weak bands

the antibonding orbitals spread over 1.1 eV. If the energy changes of the σ system from compound to compound parallel this behaviour then clearly the assumption of the constancy of energy of their *bonding* levels is sounder. On this evidence therefore the assignment of the 'stray' bands to $\sigma \to \pi^*$ excitations seems most likely.

4. Electron densities and bond orders

Considerable interest attaches to the question of to what extent the C–H σ bonding electrons of a methyl group may be delocalised into the empty orbitals of an acceptor atom. The effect may be seen quantitatively by considering the self-consistent density matrix and the relevant charges and bond orders are given in Tab. 4 which, for comparison, also lists the same quantities for trimethylboron.

In the $-C{\equiv}H_3$ model little delocalisation of electrons from the group to boron is revealed, most of the π charge on that atom originating either from the vinyl group or the chlorine atom. Such a result is in keeping with earlier studies [*1*] which showed that halogens transfer considerable charge to a boron atom accompanied by a high B–X bond order. When methyl is taken to be a single pseudoatom it makes a much greater contribution, in fact more π electron density originates from methyl than the vinyl group and is only exceeded by chlorine. The Me–B

Table 4. *Electron densities and bond orders*

		C_1	C_2	C_3	C_4	C(Me)	H_3	Cl	B	C_1–C_2	C_3–C_4	B–C_2	B–C_3	B–C(Me)	C≡H_3	B–Cl	CH_3
								–C≡H_3 model[a]									
$MeB(C_2H_3)_2$	a	0.9544	0.9957	0.9957	0.9594	1.248	0.7265	—	0.1145	0.9766	0.9766	0.2124	0.2124	0.1769	0.9519	—	—
	b	0.9571	0.9978	0.9939	0.9613	1.249	0.7265	—	0.1145	0.9765	0.9766	0.2127	0.2122	0.1769	0.9519	—	—
$Me_2BC_2H_3$		0.9689	0.9881	—	—	1.247	0.7288	—	0.0921	0.9782	—	0.2052	—	0.1755	0.9528	—	—
$MeClBC_2H_3$	t	0.9711	0.9955	—	—	1.247	0.7329	1.827	0.2272	0.9814	—	0.1901	—	0.1635	0.9548	0.5500	—
	c	0.9877	0.9798	—	—	1.247	0.7326	1.826	0.2273	0.9816	—	0.1886	—	0.1636	0.9547	0.5507	—
Me_3B		—	—	—	—	1.244	0.7315	—	0.0731	—	—	—	—	0.1737	0.9538	—	—
								Pseudoatom model[b]									
$MeB(C_2H_3)_2$	a	0.9688	0.9931	0.9688	0.9931	—	—	—	0.2046	0.9788	0.9788	0.2029	0.2029	0.4738	—	—	1.872
	b	0.9674	0.9946	1.003	0.9580	—	—	—	0.2048	0.9788	0.9785	0.2028	0.2040	0.4737	—	—	1.872
$Me_2BC_2H_3$		0.9727	0.9952	—	—	—	—	—	0.2574	0.9815	—	0.1909	—	0.4405	—	—	1.887
$MeClBC_2H_3$	t	0.9796	0.9912	—	—	—	—	1.841	0.2926	0.9828	—	0.1837	—	0.4207	—	0.5174	1.895
	c	0.9760	0.9949	—	—	—	—	1.842	0.2925	0.9828	—	0.1839	—	0.4207	—	0.5173	1.895
Me_3B		—	—	—	—	—	—	—	0.3007	—	—	—	—	0.4127	—	—	1.900

a — seagull; b — swastika; t — trans; c — cis.

[a] Taken from calc. 2b in each case.

[b] B–CH_3: 1.864 Å.

bond order is correspondingly higher. Trimethylboron illustrates this well; the charge conferred by the three methyls is four times greater for the pseudoatom model. The first model satisfies physical intuition rather better since it would be expected that a methyl group would not contribute more electron density to the acceptor than a vinyl group. Furthermore, the second model is imprecise with regard to the B–Me bond distance and this has a large effect on the magnitude of the bond orders and atom charges. The conclusion from either model is clear however: alkyl substituents may not be regarded as 'inert' to the π electron system when bonded directly to an acceptor atom.

5. Reorganisation energies

When a methyl group is attached to a boron atom electrons are delocalised into the vacant p_π orbital of the boron. This is clear from the present calculations (Tab. 4). However, it is the *energies* of the pseudo π bonds between the methyls and the central atom which are important in deciding the acceptor strength of the latter. It is well known that trimethylboron is a weak electron acceptor in donor-acceptor complex formation and the problem is thus to partition the energy barrier to coordination between that required to break the π bonds and that needed to overcome the steric impedance of the methyl groups. The former contribution may be calculated by Pople's equation [*17*] which yields the vertical reorganisation energies of the compounds. In this calculation we must subtract from E_π (S.C.F.) the appropriate initial energies corresponding to a completely localised model. For chlorine and the methyl pseudoatom this amounts to $(2I - \gamma_{\mu\mu})$ whilst for the vinyl and methyl ($-C\equiv H_3$) groups we must calculate the self-consistent energy of the isolated group. Hence the self-consistent reorganisation energy of the whole molecule is obtained, i.e. the π electronic energy of the bonds from boron to adjacent atoms or groups. Furthermore by separate calculation of the energy of the hypothetical molecule in which the π electrons are delocalised over only that part of the system not containing methyl groups then we may obtain the hyperconjugation energy. This results from the partial delocalisation of the electron pair from the methyl group to boron. The results for both methyl models are collected in Tab. 5 and 6. It may at once be seen that the two models yield very different estimates of the hyperconjugation energy of a methyl group, the pseudoatom giving values which are 2–3 times greater than those from the $-C\equiv H_3$ model. The calculated spectra give no indication of which should be the better model; as has been shown the excitation energies are somewhat insensitive to the parameters chosen (ionisation potential, $\gamma_{\mu\mu}$, B–X bond distances). However on more general grounds we consider that the pseudoatom is less reliable for absolute energy calculations as (a) the Me–B bond distance is uncertain with consequent variation in the bond resonance integral (the latter has a large effect on the calculated reorganisation energies), (b) on this basis the hyperconjugation energy of the methyl group is $\sim$3 times that of the vinyl group. This means that this energy forms the major part of the reorganisation energy of a methylvinylborane. This would hardly be expected since the carbon atoms of the two organic groups differ only in valence state. The $-C\equiv H_3$ model however yields π energies similar to those of the vinyl group. Thermodynamic measurements (gas phase dissociation) on selected compounds could help resolve the point.

Table 5. *π-electronic energies in* eV. $-C\equiv H_3$ *model*

		E_π (S.C.F.)	localised energy	reorganisation energy	semi-localised energy	hyperconjugation energy
		$I_C = -14.61$ eV		$I_{H_3} = -8.80$ eV		
$(C_2H_3)_2BMe$	a	91.7689	90.7910	0.9779	91.4564	0.3125
	b	91.7683		0.9773	91.4561	0.3122
$C_2H_3BMe_2$		103.9132	101.9532	0.9600	103.2884	0.6248
C_2H_3BMeCl	t	103.5617	101.3414	2.2203	103.2838	0.2779
	c	103.5588		2.2174	103.2824	0.2764
BMe_3		116.0533	115.1154	0.9379	—	0.9379
Me		38.3718	—	—	—	—
		$I_C = -14.61$ eV		$I_{H_3} = -10.26$ eV		
$(C_2H_3)_2BMe$	a	93.9308	92.9888	0.9420	93.6542	0.2766
	b	93.9304		0.9416	93.6539	0.2765
$C_2H_3BMe_2$		108.2420	107.3488	0.8932	107.6840	0.5580
C_2H_3BMeCl	t	105.7336	105.5392	2.1944	105.4816	0.2520
	c	105.7310		2.1918	105.4802	0.2508
BMe_3		122.5543	121.7088	0.8455	—	0.8455
Me		40.5696	—	—	—	—
		$I_C = -11.19$ eV		$I_{H_3} = -8.80$ eV		
$(C_2H_3)_2BMe$	a	85.8453	84.9496	0.8957	85.6150	0.2303
	b	85.8451		0.8955	85.6147	0.2304
$C_2H_3BMe_2$		92.0739	91.2704	0.8035	91.6056	0.4683
C_2H_3BMeCl	t	97.6430	95.5000	2.1430	97.4424	0.2006
	c	97.6406		2.1406	97.4410	0.1996
BMe_3		98.2817	97.5912	0.6905	—	0.6905
Me		32.5304	—	—	—	—
		$I_C = -11.19$ eV		$I_{H_3} = -10.26$ eV		
$(C_2H_3)_2BMe$	a	88.1187	87.2612	0.8575	87.9266	0.1921
	b	88.1186		0.8574	87.9263	0.1923
$C_2H_3BMe_2$		96.6188	95.8936	0.7252	96.2288	0.3900
C_2H_3BMeCl	t	99.9312	97.8116	2.1196	99.7540	0.1772
	c	99.9293		2.1177	99.7526	0.1767
BMe_3		105.1202	104.5260	0.5942	—	0.5942
Me		34.8420	—	—	—	—

Table 6. *π-electronic energies in* eV. *Methyl pseudoatom model*[a]

		E_π (S.C.F.)	localised energy	reorganisation energy	semi-localised energy	hyperconjugation energy
$(C_2H_3)_2BMe$	a	92.0290	90.3292	1.6998	90.9946	1.0344
	b	92.0294		1.7002	90.9941	1.0353
$C_2H_3BMe_2$		104.3791	102.0296	2.3495	102.3648	2.0143
C_2H_3BMeCl	t	103.7454	100.8796	2.8668	102.8448	0.9006
	c	103.7429		2.8633	102.8454	0.8975
BMe_3		116.6787	113.7300	2.9487	—	2.9487

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a — seagull; b — swastika; c — cis; t — trans.

[a] B–CH_3 bond length 1.864 Å.

The four sets of basic parameters for $-C{\equiv}H_3$ lead to values of hyperconjugation energy ranging from 0.2 to 0.3 eV (a total spread of ~2 kcal mole^{-1} for one methyl group) which uncertainty is maximised for trimethylboron. For this compound the total reorganisation energy, calculated for the H_3 group and sp^3 V_4 carbon, is 22 kcal mole^{-1}. This is very similar in magnitude to that calculated for trivinylboron [*1*] but is less than for any boron halide [*3*, *6*] or halogenovinylborane [*1*]. On this basis alone therefore Me_3B should be a stronger electron acceptor than the latter classes of compounds and comparable to $(C_2H_3)_3B$. The acceptor properties of the latter have not yet been investigated quantitatively but it is well established that trimethylboron is, in fact, a weaker acceptor than the boron halides [*5*]. The apparent anomaly may now be attributed to steric repulsions towards donor molecules alone. These stem from the out-of-plane methyl hydrogen atoms and a thermochemical comparison of the coordination complexes of this compound with those of trivinylboron, which acceptor has all its atoms in one plane, would be fruitful.

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