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Self-Consistent Molecular Orbital Calculations on Organoboron Compounds

Part IV: Diphenylboranes

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The Pariser-Parr-Pople L.C.A.O.–M.O.–S.C.F. method has been used to investigate the π electronic structures and spectra of a number of diphenylboranes. It was found necessary to include extensive configurational interaction in the calculations in order to obtain satisfactory agreement between the observed and calculated spectroscopic quantities. The implications of the shifts in the electronic absorption bands stemming from π electron conjugation for other phenyl- and vinyl metallic compounds are discussed.

π-Elektronen-Struktur und Spektren von Diphenylboranen werden mittels der PPP-Methode behandelt. Erst weitgehende Berücksichtigung von Konfigurationswechselwirkung führt zu hinreichender Übereinstimmung mit den beobachteten spektroskopischen Größen. Die Bedeutung der Verschiebung der elektronischen Banden von Phenyl- und Vinyl-Metall-Verbindungen wird diskutiert.

La méthode de Pariser-Parr-Pople L.C.A.O.–M.O.–S.C.F. a été utilisée pour étudier la structure électronique π et le spectre d'un certain nombre de diphénylboranes. Il a été nécessaire d'introduire une interaction de configurations étendue afin d'obtenir un accord satisfaisant entre les grandeurs spectroscopiques observées et calculées.

1. Introduction

In a previous communication [1] we reported calculations on a series of dihalogenophenylboranes by the self-consistent molecular orbital method. The present paper details the results of similar work on some diphenylboranes in which the third atom bonded to boron is chlorine, oxygen or nitrogen (see Fig. 1).

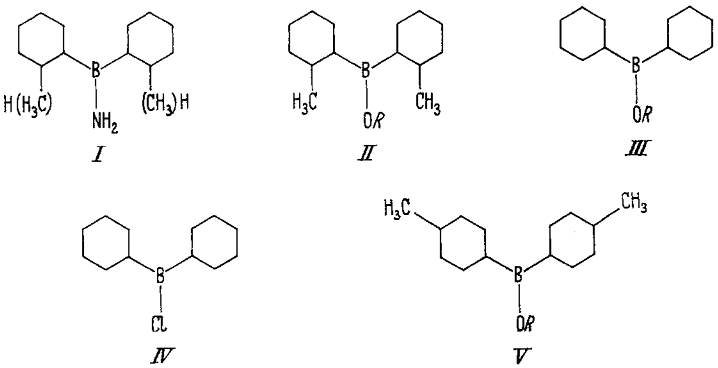

Fig. 1. Calculated Molecules (R = sec But.)

The aim of the substituent changes was to extend the scope of our work on organoboranes, previously principally concerned with those in which boron is bonded to a halogen or to a methyl group. In this way we may expect to ascertain theoretically the effect on the π electron distribution throughout the molecule of substituents with differing electron releasing characteristics. In the previous paper it proved convenient to base the discussion of the dihalogenophenylboranes on the perturbation of the one-electron orbitals of benzene. Hence presently it is appropriate to consider the electronic state energies of diphenyl, obtained under the same calculational scheme as that employed for the diphenylboranes.

2. Calculational details

The bond lengths appropriate to the compounds are:

$$\text{B–C} = 1.55\ \text{Å}\ [3]; \qquad \text{B–N} = 1.44\ \text{Å}, \qquad \text{B–O} = 1.39\ \text{Å},$$

$$\text{C}_{\text{Me}} - \text{C}_{\text{Ph}} = 1.52\ \text{Å}, \qquad \text{C–C}_{\text{in a phenyl ring}} = 1.397\ \text{Å}\ [17]\,.$$

The diagonal core Hamiltonian matrix elements and the one-centre repulsion integrals (in eV) for C_{Ph} were -11.16 and 9.76 respectively, but the corresponding quantities for boron, chlorine, oxygen, and nitrogen were modified to take account of the σ-electron distribution and calculated as in previous work [*2*]. The primary ionisation processes (before the latter modification) considered for oxygen and nitrogen were [*9*]

$$\text{O}_{\text{tri tri tri}^2\,\pi^2} \rightarrow \text{O}^{+}{}_{\text{tri tri tri}^2\,\pi} : E = -\,15.30\ \text{eV}\ ,$$

$$\text{N}_{\text{tri tri tri}\,\pi^2} \rightarrow \text{N}^{+}{}_{\text{tri tri tri}\,\pi} \ : E = -\,11.96\ \text{eV}\ ,$$

which, subsequently, by JULG's treatment [*11*] yielded the values 10.66 eV and 11.83 eV for γ_{NN} and γ_{OO}. In calculating the off-diagonal core matrix elements, for reasons advanced before [*1*], the standard C–C resonance integral was assigned the value -2.33 eV. The corresponding quantities for all bonds were then scaled to this value in the usual way.

The geometry of these molecules is itself an intriguing problem. The phenyl rings in triphenylboron are almost certainly not coplanar [*16*] which feature reduces its symmetry from D_{3h} to D_3 and we might expect this property to be inherent in the diphenylboranes also if the boron atom adopts a trigonal configuration. However, there is, as yet, no supporting experimental evidence for such a geometry. In an unsubstituted compound (i.e. on the phenyl ring) very little C–B–C angle widening is required to alleviate steric interference between the rings and any strain introduced by such a deformation will be somewhat compensated by retention of the greater π electronic energy of the planar molecule. However for diphenyl, in which a similar situation should obtain, the out-of-plane angle between the two phenyl rings is about 45° [*4*]. We therefore deemed it necessary to consider also a non-planar geometry for the diphenylboranes in parallel with the planar cases. This was accomplished on the assumption that the B–C bond resonance integral is proportional to the cosine of the angle α between a phenyl ring and the CBX plane i.e. $\beta^{\alpha}_{\text{B–C}} = \beta_{\text{B–C}} \cdot \cos \alpha$. In order to render the π electron problem tractable it must be assumed that the σ–π separability condition continues to hold so that integrals of the type $\langle \pi\pi \mid \sigma\sigma \rangle$ may be neglected.

In these calculations it is important to include interaction between all configurations generated from the four highest bonding and the four lowest antibonding orbitals of the borane and, indeed, it is only in this way that the electronic spectra of these compounds may be understood. These orbitals have their origins in the initially-degenerate e_{2u}, e_{1g} pairs from the benzene rings and consequently mutually interact strongly. A total of thirty two singlet and triplet states results and the energies of all were calculated for each case. The calculations were performed on the Newcastle University K.D.F. 9 computer by means of the automatic S.C.F. programme described elsewhere [*2*]. When the methyl group was considered as a substituent both the pseudoatom [*13*] and the $-C{\equiv}H_3$ [*14*] models were tested. It has not hitherto been easy to decide between these two models on the basis of calculations on methylboranes [*2*] because the methyl group is spectroscopically rather inert when bonded directly to boron. They should, however, be more 'active' when attached to phenyl rings in the *ortho*- or *para*-positions and hence may be interdistinguished in quality. The appropriate starting data for the two methyl models were taken from earlier work [*2*].

3. Results

The electronic structure and spectrum of planar diphenyl was re-investigated theoretically in order to aid in the evaluation and interpretation of the spectra of diphenylboranes. The results are given in Tab. 1 together with those of the recent work of Gondo [*7*]. The quality of the agreement between the calculated and observed singlet energies is very encouraging. Moreover, assuming that in the experimental spectrum, the bands have similar widths, the calculated oscillator strengths are in approximately the same ratio as the $\varepsilon_{\max}$ values found by experiment. The energy of the lowest triplet state of the molecule has been obtained by Kanda [*12*] from the phosphorescence spectrum of the compound and is 2.85 eV. This agrees unusually well with our figure for the $^3B_{3u}$ state (2.931 eV). This is

Table 1. *Electronic states of planar diphenyl* (eV)

Experimental spectrum[a]		Previous work (Gondo [*7*])			Present work				
E	$\varepsilon_{\max}$	^1E_n	symmetry[b]	f	^1E_n	symmetry	f	^3E_n	symmetry
4.16[c],4.18[d]		4.62	B_{3u}^+	0.000	4.542	B_{2u}	0	2.931	B_{3u}
					4.583	B_{1g}	0	3.497	A_g
5.02	16500	4.96	B_{2u}^+	0.555	4.779	B_{3u}	0.743	3.882	B_{1g}
					5.845	A_g	0	3.888	B_{2u}
					5.866	B_{1g}	0	3.898	B_{3u}
6.19	45000	5.66	B_{2u}^+	1.467	6.111	B_{3u}	1.300	4.099	A_g
					6.125	B_{2u}	1.050	4.592	B_{2u}
					6.378	A_g	0	4.583	B_{1g}
					6.715	A_g	0	6.378	A_g
					6.717	B_{3u}	0.002	6.662	B_{1g}
					6.865	B_{1g}	0	6.687	B_{2u}
					6.881	B_{2u}	0	6.715	A_g
					6.906	A_g	0	6.716	B_{3u}
		7.74	B_{3u}^+		7.168	B_{1g}	0	6.865	B_{1g}
7.4	35000	7.87	B_{2u}^+	0.842	7.306	B_{2u}	1.163	6.881	B_{2u}
		7.93	B_{2u}^+		7.793	B_{3u}	0.191	6.975	B_{3u}

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[a] data from various sources, summarised in [*7*].

[b] the long axis of the molecule is the y axis.

[c] solution.

[d] crystal.

separated from the corresponding $^1B_{3u}$ state (4.779 eV) by $\sim$15000 cm^{-1}, rather higher than is normally found.

The results obtained for the diphenylboranes are grouped in Tab. 2—7. Also tabulated are the experimental UV data published by NIKITINA and his co-workers [*15*]. Chlorodiphenylborane has been studied rather less thoroughly than the other compounds no doubt because of the difficulty inherent in the handling of this reactive material (it is hydrolysed readily to Ph_2BOH) and the only published information is that of GESKE [*6*]. He reported that the spectrum of the compound above 200 mμ consisted of a single broad band exhibiting a maximum at 230 mμ (5.39 eV).

Table 2. *Electronic states of Chlorodiphenylborane** (eV)

	Planar			Rings twisted 30°		
E_n	^1E_n	f	^3E_n	^1E_n	f	^3E_n
E_1	4.708 (B_1)	0.001	3.353 (B_1)	4.735 (A)	0.002	3.364 (B)
E_2	4.708 (A_1)	0.004	3.372 (A_1)	4.735 (B)	0.001	3.374 (A)
E_3	5.300 (B_1)	0.282	4.019 (B_1)	5.494 (B)	0.230	4.045 (B)
E_4	5.595 (A_1)	0.027	4.020 (A_1)	5.639 (A)	0.022	4.045 (A)
E_5	6.128 (B_1)	1.198	4.046 (B_1)	6.175 (B)	1.107	4.064 (B)
E_6	6.153 (B_1)	0.185	4.058 (A_1)	6.252 (B)	0.542	4.070 (A)
E_7	6.276 (A_1)	0.697	4.725 (A_1)	6.328 (A)	0.677	4.741 (A)
E_8	6.332 (A_1)	0.006	4.727 (B_1)	6.371 (A)	0.038	4.741 (B)
E_9	6.678 (B_1)	0.114	6.354 (A_1)	6.718 (B)	0.189	6.426 (A)
E_{10}	6.757 (B_1)	0.409	6.404 (B_1)	6.743 (B)	0.505	6.458 (B)
E_{11}	6.764 (A_1)	1.172	6.495 (A_1)	6.762 (A)	1.043	6.558 (A)
E_{12}	6.835 (A_1)	0.139	6.500 (B_1)	6.815 (A)	0.000	6.560 (B)
E_{13}	6.896 (B_1)	0.008	6.893 (A_1)	6.913 (B)	0.008	6.911 (A)
E_{14}	6.910 (A_1)	0.189	6.894 (B_1)	6.917 (A)	0.042	6.911 (B)
E_{15}	6.975 (A_1)	0.013	6.973 (B_1)	6.985 (A)	0.001	6.984 (B)
E_{16}	6.976 (B_1)	0.006	6.974 (A_1)	6.987 (B)	0.004	6.985 (A)

* for experimental data see text.

A survey of the figures in the tables reveals that the overall agreement between the experimental and calculated band energies is quite satisfactory. The calculated quantities are, moreover, almost insensitive to rotation of the phenyl rings. The ratio of the oscillator strengths of the first and second states is smaller than may be computed from the work of NIKITINA but it is nevertheless less than unity, as required. However, the ratio of the same quantity between the second and third states is much closer to that measured in all cases although it must be constantly borne in mind that the quantities measured are only extinction coefficients. The calculations also show that the intensities are not expected to be drastically altered by twisting of the B–Ph bonds and so we must conclude that the UV spectrum does not shed much light on the problem of the geometry of these molecules. Finally both the pseudoatom and the $-C{\equiv}H_3$ models appear to be equally suitable for representation of a methyl group and our calculations do not discriminate against either.

In all the above work the twisting angle was assumed to be 30°. It may, in

Table 3. *Electronic states of Hydroxydiphenylborane* (eV)

	Planar			Rings twisted 30°			Experimental spectrum	
E_n	^1E_n	f	^3E_n	^1E_n	f	^3E_n	E	ε_{max}
E_1	4.691 (B_1)	0.002	3.356 (B_1)	4.725 (A)	0.002	3.373 (B)	4.427 4.591 4.677	747 1 150 1 163
E_2	4.691 (A_1)	0.005	3.379 (A_1)	4.725 (B)	0.001	3.385 (A)		
E_3	5.302 (B_1)	0.326	4.012 (B_1)	5.415 (B)	0.277	4.045 (B)	5.208	17 500
E_4	5.552 (A_1)	0.030	4.012 (A_1)	5.600 (A)	0.026	4.045 (A)		
E_5	6.074 (B_1)	0.588	4.038 (B_1)	6.151 (B)	1.026	4.063 (B)	6.121	26 200
E_6	6.129 (B_1)	0.686	4.054 (A_1)	6.186 (B)	0.458	4.072 (A)		
E_7	6.207 (A_1)	0.598	4.714 (A_1)	6.254 (A)	0.557	4.732 (A)		
E_8	6.292 (A_1)	0.040	4.716 (B_1)	6.324 (A)	0.073	4.733 (B)		
E_9	6.668 (B_1)	0.165	6.294 (A_1)	6.710 (B)	0.309	6.361 (A)	6.773	30 300
E_{10}	6.764 (A_1)	1.205	6.353 (B_1)	6.744 (B)	0.483	6.400 (B)		
E_{11}	6.768 (B_1)	0.411	6.439 (A_1)	6.759 (A)	1.094	6.497 (A)		
E_{12}	6.833 (A_1)	0.137	6.444 (B_1)	6.812 (A)	0.000	6.499 (B)		
E_{13}	6.905 (B_1)	0.008	6.901 (A_1)	6.922 (B)	0.008	6.919 (A)		
E_{14}	6.919 (A_1)	0.174	6.902 (B_1)	6.926 (A)	0.045	6.919 (B)		
E_{15}	6.892 (A_1)	0.027	6.977 (B_1)	6.988 (A)	0.003	6.987 (B)		
E_{16}	6.982 (B_1)	0.008	6.978 (A_1)	6.990 (B)	0.006	6.988 (A)		

Table 4. *Electronic states of Aminodiphenylborane* (eV)

	Rings planar			Rings twisted 30°			Experimental spectrum	
E_n	^1E_n	f	^3E_n	^1E_n	f	^3E_n	E	ε_{max}
E_1	4.727 (B_1)	0.001	3.372 (A_1)	4.748 (A)	0.002	3.374 (A)	4.549	1 100
E_2	4.728 (A_1)	0.004	3.379 (B_1)	4.748 (B)	0.001	3.386 (B)		
E_3	5.438 (B_1)	0.256	4.041 (B_1)	5.533 (B)	0.205	4.059 (B)	5.165	18 000
E_4	5.559 (A_1)	0.043	4.041 (A_1)	5.622 (A)	0.032	4.059 (A)		
E_5	6.144 (B_1)	1.419	4.057 (A_1)	6.189 (B)	1.146	4.070 (A)		
E_6	6.170 (B_1)	0.005	4.072 (B_1)	6.279 (B)	0.588	4.081 (B)		
E_7	6.283 (A_1)	0.507	4.744 (A_1)	6.344 (A)	0.492	4.754 (A)		
E_8	6.329 (A_1)	0.237	4.746 (B_1)	6.368 (A)	0.283	4.755 (B)		
E_9	6.634 (B_1)	0.160	6.298 (A_1)	6.653 (B)	0.248	6.394 (A)		
E_{10}	6.691 (B_1)	0.352	6.373 (B_1)	6.732 (B)	0.389	6.444 (B)		
E_{11}	6.765 (A_1)	1.145	6.525 (A_1)	6.763 (A)	1.033	6.590 (A)		
E_{12}	6.828 (B_1)	0	6.528 (B_1)	6.816 (A)	0.003	6.592 (B)		
E_{13}	6.832 (A_1)	0.120	6.828 (A_1)	6.859 (B)	0	6.859 (A)		
E_{14}	6.839 (A_1)	0.217	6.828 (B_1)	6.861 (A)	0.011	6.859 (B)		
E_{15}	6.963 (B_1)	0.001	6.962 (B_1)	6.980 (B)	0.001	6.980 (B)		
E_{16}	6.963 (A_1)	0.002	6.962 (A_1)	6.981 (A)	0.000	6.980 (A)		

fact, be greater than this; e.g. recent work [*8*] has shown that, in triphenylbismuth, the Bi–C bonds are coplanar whilst the phenyl rings make an angle of 60° to this plane, although, because of the differences in electronic structure, direct comparison of this with the diphenylborane case is naïve. In order that the sensitivity of the calculations to this factor might be checked a further series was carried out for chlorodiphenylborane in which the angle α was successively set equal to 45° and 60°. We do not detail the treatment here but the overall result was that a variation of $< 3\%$ in the state energies is shown over the whole 0—60° range.

Table 5. *Electronic states of Aminodi(o-tolyl)borane* (eV)

	Methyl pseudoatom model						$-C{\equiv}H_3$ model						Experimental spectrum	
	Planar			Rings twisted 30°			Planar			Rings twisted 30°				
E_n	^1E_n	f	^3E_n	^1E_n	f	^3E_n	^1E_n	f	^3E_n	^1E_n	f	^3E_n	E	ε_{max}
E_1	4.631 (B_1)	0.044	3.384 (A_1)	4.661 (B)	0.034	3.389 (A)	4.679 (B_1)	0.009	3.361 (A_1)	4.703 (B)	0.006	3.364 (A)	4.459	1 810
E_2	4.642 (A_1)	0.005	3.386 (B_1)	4.669 (A)	0.001	3.391 (B)	4.681 (A_1)	0.004	3.366 (B_1)	4.704 (A)	0.001	3.681 (B)		
E_3	5.335 (B_1)	0.026	3.954 (B_1)	5.422 (B)	0.195	3.982 (B)	5.381 (B_1)	0.273	4.001 (A_1)	5.473 (B)	0.208	4.022 (A)	5.241	16 000
E_4	5.443 (A_1)	0.001	3.955 (A_1)	5.497 (A)	0.004	3.983 (B)	5.493 (A_1)	0.003	4.002 (B_1)	5.554 (A)	0.001	4.023 (B)		
E_5	5.989 (B_1)	0.375	4.044 (A_1)	6.031 (B)	0.882	4.055 (A)	6.059 (B_1)	0.401	4.039 (A_1)	6.098 (B)	0.947	4.052 (A)	6.076	45 500
E_6	6.034 (B_1)	0.650	4.050 (B_1)	6.133 (B)	0.429	4.060 (B)	6.085 (B_1)	0.880	4.049 (B_1)	6.199 (B)	0.671	4.059 (B)		
E_7	6.122 (A_1)	0.006	4.738 (A_1)	6.162 (A)	0.013	4.743 (A)	6.220 (A_1)	0.378	4.715 (A_1)	6.274 (A)	0.038	4.723 (A)		
E_8	6.202 (A_1)	1.104	4.742 (B_1)	6.256 (A)	1.127	4.745 (B)	6.244 (A_1)	0.611	4.716 (B_1)	6.289 (A)	0.978	4.723 (B)	6.439	60 000
E_9	6.451 (B_1)	0.691	6.147 (A_1)	6.476 (B)	0.841	6.213 (A)	6.577 (B_1)	0.551	6.257 (A_1)	6.597 (B)	0.582	6.344 (A)		
E_{10}	6.636 (B_1)	0.056	6.199 (B_1)	6.616 (A)	0.224	6.245 (B)	6.623 (B_1)	0.034	6.335 (B_1)	6.658 (B)	0.141	6.394 (B)		
E_{11}	6.659 (A_1)	0.176	6.396 (A_1)	6.665 (B)	0.097	6.476 (A)	6.721 (A_1)	1.005	6.434 (A_1)	6.705 (A)	0.629	6.501 (A)		
E_{12}	6.701 (A_1)	0.889	6.422 (B_1)	6.704 (A)	0.276	6.495 (B)	6.749 (A_1)	0.366	6.434 (B_1)	6.735 (A)	0.305	6.503 (B)		
E_{13}	6.710 (B_1)	0.015	6.705 (B_1)	6.713 (B)	0.017	6.708 (B)	6.787 (B_1)	0.000	6.787 (B_1)	6.803 (B)	0.000	6.802 (B)		
E_{14}	6.716 (A_1)	0.214	6.705 (A_1)	6.724 (A)	0.314	6.709 (A)	6.789 (A_1)	0.035	6.787 (A_1)	6.803 (A)	0.006	6.802 (A)		
E_{15}	6.926 (B_1)	0.000	6.922 (A_1)	6.956 (B)	0.001	6.953 (A)	6.851 (B_1)	0.000	6.850 (A_1)	6.878 (B)	0.000	6.878 (A)		
E_{16}	6.929 (A_1)	0.030	6.924 (B_1)	6.957 (A)	0.013	6.954 (B)	6.851 (A_1)	0.005	6.850 (B_1)	6.878 (A)	0.001	6.878 (B)		

Table 6. *Electronic states of Hydroxydi(p-tolyl)borane* (eV)

	Methyl pseudoatom model						$-C\equiv H_3$ model						Experimental spectrum	
	Planar			Rings twisted 30°			Planar			Rings twisted 30°				
E_n	^1E_n	f	^3E_n	^1E_n	f	^3E_n	^1E_n	f	^3E_n	^1E_n	f	^3E_n	E	ε_{max}
E_1	4.664 (A_1)	0.000	3.391 (B_1)	4.690 (A)	0.002	3.408 (B)	4.662 (A_1)	0.001	3.352 (B_1)	4.693 (A)	0.000	3.369 (B)	4.459	1400
E_2	4.665 (B_1)	0.000	3.416 (A_1)	4.691 (B)	0.002	3.421 (A)	4.662 (B_1)	0.000	3.377 (A_1)	4.693 (B)	0.001	3.383 (A)		
E_3	5.095 (B_1)	0.481	4.002 (B_1)	5.207 (B)	0.442	4.024 (B)	5.182 (B_1)	0.432	4.000 (B_1)	5.294 (B)	0.389	4.024 (B)	4.958	2450
E_4	5.365 (A_1)	0.077	4.014 (A_1)	5.420 (A)	0.072	4.024 (A)	5.450 (A_1)	0.057	4.000 (A_1)	5.500 (A)	0.053	4.024 (A)		
E_5	5.981 (B_1)	0.498	4.014 (B_1)	6.099 (B)	0.730	4.033 (B)	6.024 (B_1)	0.503	4.009 (B_1)	6.134 (B)	1.186	4.034 (B)		
E_6	6.112 (B_1)	0.658	4.021 (A_1)	6.129 (B)	0.670	4.044 (A)	6.118 (B_1)	0.702	4.025 (A_1)	6.140 (B)	0.240	4.044 (A)		
E_7	6.148 (A_1)	0.848	4.620 (A_1)	6.185 (A)	0.726	4.666 (A)	6.168 (A_1)	0.678	4.649 (A_1)	6.212 (A)	0.622	4.677 (A)		
E_8	6.198 (A_1)	0.004	4.622 (B_1)	6.225 (A)	0.042	4.666 (B)	6.236 (A_1)	0.011	4.651 (B_1)	6.265 (A)	0.039	4.678 (B)		
E_9	6.572 (B_1)	0.486	6.138 (A_1)	6.553 (B)	0.492	6.199 (A)	6.650 (B_1)	0.496	6.197 (A_1)	6.626 (B)	0.441	6.260 (A)		
E_{10}	6.637 (A_1)	0.493	6.206 (B_1)	6.643 (A)	0.451	6.243 (B)	6.650 (B_1)	0.121	6.262 (B_1)	6.691 (B)	0.361	6.303 (B)		
E_{11}	6.670 (B_1)	0.001	6.520 (B_1)	6.672 (B)	0.004	6.579 (B)	6.690 (A_1)	0.918	6.434 (B_1)	6.694 (A)	0.832	6.493 (B)		
E_{12}	6.678 (A_1)	0.108	6.522 (A_1)	6.676 (A)	0.083	6.580 (A)	6.775 (A_1)	0.230	6.435 (A_1)	6.755 (A)	0.178	6.493 (A)		
E_{13}	6.716 (B_1)	0.139	6.668 (A_1)	6.753 (B)	0.270	6.669 (A)	6.827 (B_1)	0.015	6.821 (A_1)	6.831 (B)	0.018	6.826 (A)		
E_{14}	6.819 (A_1)	0.597	6.668 (B_1)	6.798 (A)	0.337	6.670 (B)	6.850 (A_1)	0.313	6.821 (B_1)	6.836 (A)	0.080	6.826 (B)		
E_{15}	6.952 (B_1)	0.002	6.951 (B_1)	6.975 (B)	0.002	6.974 (B)	6.954 (A_1)	0.001	6.953 (A_1)	6.975 (A)	0.000	6.975 (B)		
E_{16}	6.954 (A_1)	0.016	6.951 (A_1)	6.975 (A)	0.003	6.974 (A)	6.955 (B_1)	0.002	6.954 (A_1)	6.975 (B)	0.001	6.975 (A)		

Table 7. *Electronic states of Hydroxydi(o-tolyl)borane* (eV)

	Methyl pseudoatom model						$-C{\equiv}H_3$ model						Experimental spectrum	
	Planar			Rings twisted 30°			Planar			Rings twisted 30°				
E_n	^1E_n	f	^3E_n	^1E_n	f	^3E_n	^1E_n	f	^3E_n	^1E_n	f	^3E_n	E	$\varepsilon_{\max}$
E_1	4.579 (B_1)	0.063	3.368 (B_1)	4.625 (B)	0.050	3.388 (B)	4.640 (B_1)	0.015	3.344 (B_1)	4.677 (B)	0.010	3.362 (B)	4.319, 4.459	1040, 1330
E_2	4.596 (A_1)	0.007	3.395 (A_1)	4.636 (A)	0.002	3.403 (A)	4.643 (A_1)	0.006	3.369 (A_1)	4.679 (A)	0.002	3.375 (A)	4.557	1310
E_3	5.204 (B_1)	0.308	3.918 (B_1)	5.306 (B)	0.257	3.961 (B)	5.248 (B_1)	0.340	3.972 (B_1)	5.357 (B)	0.281	4.009 (B)	5.241	14000
E_4	5.429 (A_1)	0.004	3.926 (A_1)	5.470 (A)	0.006	3.968 (A)	5.487 (A_1)	0.001	3.975 (A_1)	5.532 (A)	0.000	4.011 (A)		
E_5	5.917 (B_1)	0.023	4.025 (B_1)	5.976 (B)	0.643	4.049 (B)	5.993 (B_1)	0.033	4.018 (B_1)	6.053 (B)	0.685	4.044 (B)		
E_6	5.980 (B_1)	0.872	4.038 (A_1)	6.040 (B)	0.462	4.055 (A)	6.039 (B_1)	1.092	4.033 (A_1)	6.110 (B)	0.679	4.052 (A)		
E_7	6.037 (A_1)	0.180	4.722 (A_1)	6.070 (A)	0.131	4.731 (A)	6.137 (A_1)	0.560	4.691 (A_1)	6.178 (A)	0.473	4.706 (A)	6.121	39000
E_8	6.155 (A_1)	0.813	4.725 (B_1)	6.193 (A)	0.846	4.733 (B)	6.207 (A_1)	0.301	4.694 (B_1)	6.243 (A)	0.375	4.707 (B)		
E_9	6.453 (B_1)	0.647	6.086 (A_1)	6.484 (B)	0.882	6.134 (A)	6.573 (B_1)	0.411	6.238 (A_1)	6.610 (B)	0.672	6.297 (A)		
E_{10}	6.668 (A_1)	0.181	6.130 (B_1)	6.621 (A)	0.269	6.164 (B)	6.719 (A_1)	1.068	6.299 (B_1)	6.701 (A)	0.718	6.336 (B)	6.439	45500
E_{11}	6.697 (A_1)	0.940	6.347 (A_1)	6.704 (A)	0.471	6.412 (A)	6.734 (B_1)	0.246	6.356 (A_1)	6.713 (B)	0.207	6.417 (A)		
E_{12}	6.725 (A_1)	0.162	6.378 (B_1)	6.720 (B)	0.145	6.431 (B)	6.747 (A_1)	0.271	6.364 (B_1)	6.733 (A)	0.296	6.423 (B)		
E_{13}	6.729 (B_1)	0.003	6.719 (B_1)	6.727 (A)	0.160	6.719 (B)	6.835 (A_1)	0.022	6.832 (B_1)	6.841 (B)	0.007	6.838 (B)		
E_{14}	6.734 (B_1)	0.158	6.721 (A_1)	6.729 (B)	0.041	6.721 (A)	6.835 (B_1)	0.003	6.832 (A_1)	6.841 (A)	0.016	6.838 (A)		
E_{15}	6.990 (B_1)	0.010	6.981 (A_1)	7.000 (B)	0.005	6.996 (A)	6.900 (B_1)	0.007	6.892 (A_1)	6.910 (B)	0.004	6.908 (A)		
E_{16}	7.000 (A_1)	0.074	6.983 (B_1)	7.004 (A)	0.029	6.997 (B)	6.907 (A_1)	0.115	6.893 (B_1)	6.912 (A)	0.022	6.908 (B)		

4. Discussion

a) Diphenyl

A close correlation is expected between the first few states of diphenyl and of the diphenylboranes since both may be regarded as originating from a pair of chromophoric benzene rings interacting across a single C–C bond or *via* the empty p_π-orbital of a boron atom. The lowest electronic states of diphenyl are generated largely from the first four excited states of benzene (B_{2u}. B_{1u}, E_{1u} and E'_{1u}). The first ($^1B_{2u}$) correlates closely with the symmetric combination of the two locally excited $^1B_{2u}$ states of the two rings whilst the second ($^1B_{1g}$) matches the antisymmetric combination of these. The former transition possesses zero intensity because of the cancellation of the dipole contributions from each ring. The third state is of considerable importance in later discussion and it corresponds to the $E'_{1u} - E'_{1u}$ combination from the rings. A large measure of configuration interaction is present and its effect emerges clearly from Fig. 2 coupled with the state-mixing data listed in Tab. 8.

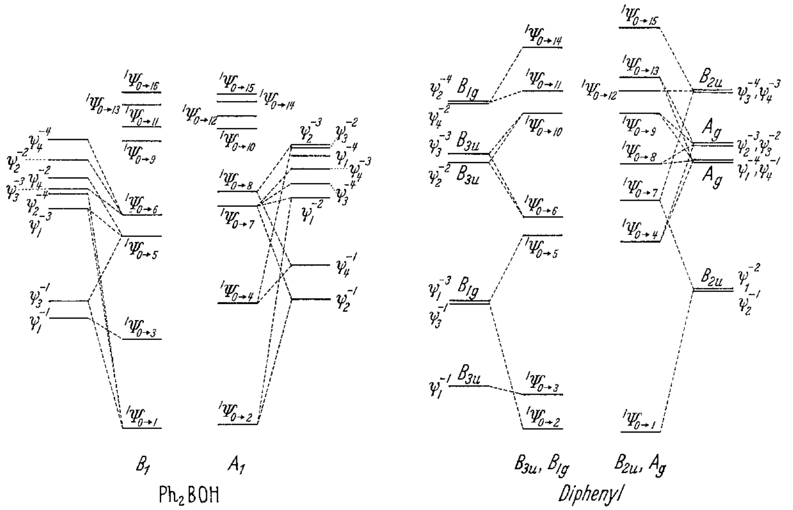

Fig. 2. Configuration Interaction (Singlet states)

Table 8. *Coefficients of principal spin configurations for diphenyl*

Transition	Coefficients				
$^1\Psi_{0\to1}$ (B_{2u})	$0.65\psi_{+1}^{-2}$	$0.65\psi_{+2}^{-1}$	$0.29\psi_{+3}^{-4}$	$0.29\psi_{+4}^{-3}$	$B_{2u} + B_{2u}$
$^1\Psi_{0\to2}$ (B_{1g})	$0.64\psi_{+1}^{-3}$	$0.30\psi_{+2}^{-4}$	$0.64\psi_{+3}^{-1}$	$0.30\psi_{+4}^{-2}$	$B_{2u} - B_{2u}$
$^1\Psi_{0\to3}$ (B_{3u})	$0.98\psi_{+1}^{-1}$				$E'_{1u} - E'_{1u}$
$^1\Psi_{0\to4}$ (A_g)	$0.47\psi_{+1}^{-4}$	$0.53\psi_{+2}^{-3}$	$0.53\psi_{+3}^{-2}$	$0.47\psi_{+4}^{-1}$	$B_{1u} + B_{1u}$
$^1\Psi_{0\to5}$ (B_{1g})	$0.71\psi_{+1}^{-3}$	$0.71\psi_{+3}^{-1}$			$E_{1u} - E_{1u}$
$^1\Psi_{0\to6}$ (B_{3u})	$0.73\psi_{+2}^{-2}$	$0.66\psi_{+3}^{-3}$			$B_{1u} - B_{1u}$
$^1\Psi_{0\to7}$ (B_{2u})	$0.71\psi_{+1}^{-2}$	$0.71\psi_{+2}^{-1}$			$E_{1u} + E_{1u}$ + CT states
$^1\Psi_{0\to8}$ (A_g)	$0.71\psi_{+1}^{-4}$	$0.71\psi_{+4}^{-1}$			CT states

The upper states of diphenyl are formed from mixtures of locally-excited and charge-resonance states (the latter involving charge transfer from ring to ring) and these may not be readily correlated with those of benzene.

b) Low-energy excited states of diphenylboranes

The four highest filled and lowest vacant molecular orbitals of the diphenylboranes result from linear combinations of the degenerate occupied ($\psi_{+1}, \psi_{+1'}$) and unoccupied ($\psi_{-1}, \psi_{-1'}$) orbitals of benzene. The new functions, which belong to the irreducible representations a_2 and b_2 are respectively symmetric and antisymmetric to rotation about the C_2 axis of the molecule. The remaining two π atomic orbitals which lie on this axis both belong to the representation b_2 and therefore mix only with the latter set. The orbital pattern is shown in Fig. 3.

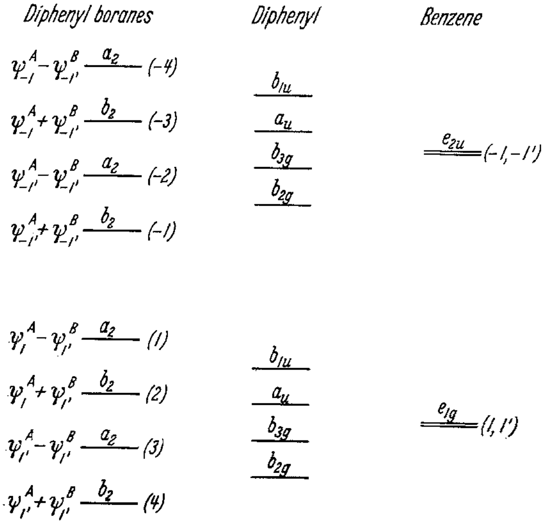

Fig. 3. MO-pattern

The close relation which exists between the diphenylboranes, benzene and diphenyl is obvious when the eigenvalues of the diagonalised $\mathcal{F}$-matrix are compared as in Fig. 4.

The effect of interposing a boron atom between the two rings of diphenyl is strikingly revealed. Firstly, whereas the penultimate three vacant orbitals of diphenyl (b_{3g}, a_u, b_{1u}) are strongly split, in diphenylboranes these levels differ little in energy from those of benzene. However, the first antibonding level (b_2) in the boranes is markedly depressed compared with that of benzene because it incorporates a high mixing coefficient for boron; it has similar energy to the corresponding b_{2g} level in diphenyl. By contrast none of the bonding levels of benzene is particularly perturbed by the introduction of a boron atom although for diphenyl they are split as before. On the basis of the one-electron schemes and the similar forms of the wavefunctions it would be expected that a direct correspondence should exist between the lower excited states of diphenyl and diphenylborane, particularly as there should also be a similar pattern of configuration interaction.

The third group bonded to boron constitutes a second important factor which can modify the one-electron energy scheme. If the electronegativity of this entity is increased the boron atom assumes a greater formal positive charge and this enhances the electron flow between the phenyl rings. The orbital energies, both bonding and antibonding, diverge and approach those of diphenyl. Substitution of a methyl in the benzene ring brings about a displacement of both bonding and antibonding levels to higher energies but no measureable effect on the spectrum is expected from this.

The most profound change in the electronic spectrum of benzene (or indeed any unsaturated organic substituent) stems from the ability of the p_π orbital of boron to aid in providing an empty low-lying b_2 level. Excited configurations of the molecules which do not involve this particular b_2 level would be expected to possess similar energies to those of benzene because of the otherwise general stability of the one-electron orbital pattern. This turns out to be the case.

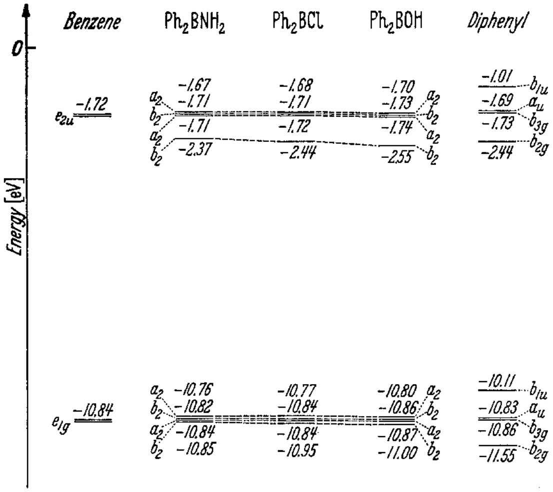

Fig. 4. Correlation diagram for diphenylboranes

Under the low symmetries of these molecules and because of the proximity of the energy levels, configuration interaction is extensive and strong. The point is brought out well by Tab. 9 and Fig. 2 in which the typical case of Ph_2BOH is analysed. For both diphenyl and Ph_2BOH the lowest two excited states are formed chiefly from the configurations ψ_{+1}^{-2}, ψ_{+2}^{-1}, ψ_{+1}^{-3}, ψ_{+3}^{-1}. Hence there is, for this borane, an approximate correlation of these states with the symmetric and antisymmetric combinations of the locally-excited $^1B_{2u}$ states of benzene. These have similar energies to each other and to both benzene and diphenyl. The oscillator strength of the symmetric combination is small, in keeping with opposition of the two locally-excited transition density dipole moments and it is the angular geometry of the boranes alone which allows f to have a non-zero value.

The lowest $^1B_{3u}$ state of diphenyl ($^1\Psi_{0\to 3}$) and the second $^1B_1$ state of hydroxydiphenylborane diverge in energy although both arise almost exclusively from the ψ_{+1}^{-1} configuration. The former is represented reasonably well by the antisymmetric combination of the intense ${}^1E'_{1u}$ benzene states but is considerably red-shifted with respect to them. The difference between the two cases stems from the interposition of the boron atom which diminishes the spectral shift. A second order effect is the shift of this state to lower energy when a more electronegative atom is substituted as the 'third group' on the boron.

Table 9. *Coefficients of the principal spin configurations composing the lowest eight electronic states*

Transition	Coefficients					
			Chlorodiphenylborane			
${}^1\Psi_{0\to1}$ (B_1)	$0.47\psi_{+1}^{-3}$	$0.43\psi_{+2}^{-4}$	$0.64\psi_{+3}^{-1}$	$0.42\psi_{+4}^{-2}$		
${}^1\Psi_{0\to2}$ (A_1)	$0.48\psi_{+1}^{-2}$	$0.63\psi_{+2}^{-1}$	$0.43\psi_{+3}^{-4}$	$0.42\psi_{+4}^{-3}$		
${}^1\Psi_{0\to3}$ (B_1)	$0.91\psi_{+1}^{-1}$	$0.21\psi_{+2}^{-2}$	$0.22\psi_{+3}^{-3}$	$0.29\psi_{+4}^{-4}$		
${}^1\Psi_{0\to4}$ (A_1)	$0.33\psi_{+1}^{-4}$	$0.36\psi_{+2}^{-3}$	$0.36\psi_{+3}^{-2}$	$0.79\psi_{+4}^{-1}$		
${}^1\Psi_{0\to5}$ (B_1)	$0.41\psi_{+1}^{-3}$	$0.40\psi_{+2}^{-2}$	$0.57\psi_{+3}^{-1}$	$0.42\psi_{+3}^{-3}$	$0.31\psi_{+4}^{-2}$	
${}^1\Psi_{0\to6}$ (B_1)	$0.30\psi_{+1}^{-3}$	$0.51\psi_{+2}^{-3}$	$0.46\psi_{+3}^{-1}$	$0.48\psi_{+3}^{-3}$	$0.28\psi_{+4}^{-3}$	
${}^1\Psi_{0\to7}$ (A_1)	$0.37\psi_{+1}^{-2}$	$0.73\psi_{+2}^{-1}$	$0.32\psi_{+3}^{-4}$	$0.34\psi_{+4}^{-3}$		
${}^1\Psi_{0\to8}$ (A_1)	$0.44\psi_{+1}^{-4}$	$0.44\psi_{+2}^{-3}$	$0.41\psi_{+3}^{-2}$	$0.57\psi_{+4}^{-1}$		
			Hydroxydiphenylborane			
${}^1\Psi_{0\to1}$ (B_1)	$0.46\psi_{+1}^{-3}$	$0.42\psi_{+2}^{-4}$	$0.66\psi_{+3}^{-1}$	$0.41\psi_{+4}^{-2}$		
${}^1\Psi_{0\to2}$ (A_1)	$0.47\psi_{+1}^{-2}$	$0.65\psi_{+2}^{-1}$	$0.42\psi_{+3}^{-4}$	$0.42\psi_{+4}^{-3}$		
${}^1\Psi_{0\to3}$ (B_1)	$0.93\psi_{+1}^{-1}$	$0.18\psi_{+2}^{-2}$	$0.19\psi_{+3}^{-3}$	$0.26\psi_{+4}^{-4}$		
${}^1\Psi_{0\to4}$ (A_1)	$0.30\psi_{+1}^{-4}$	$0.34\psi_{+2}^{-3}$	$0.34\psi_{+3}^{-2}$	$0.82\psi_{+4}^{-1}$		
${}^1\Psi_{0\to5}$ (B_1)	$0.51\psi_{+1}^{-3}$	$0.71\psi_{+3}^{-1}$	$0.40\psi_{+4}^{-2}$			
${}^1\Psi_{0\to6}$ (B_1)	$0.31\psi_{+1}^{-1}$	$0.64\psi_{+2}^{-2}$	$0.62\psi_{+3}^{-3}$	$0.20\psi_{+4}^{-4}$		
${}^1\Psi_{0\to7}$ (A_1)	$0.41\psi_{+1}^{-3}$	$0.74\psi_{+2}^{-1}$	$0.35\psi_{+3}^{-4}$	$0.35\psi_{+4}^{-3}$		
${}^1\Psi_{0\to8}$ (A_1)	$0.49\psi_{+1}^{-4}$	$0.46\psi_{+2}^{-3}$	$0.45\psi_{+3}^{-2}$	$0.55\psi_{+4}^{-1}$		
			Aminodiphenylborane			
${}^1\Psi_{0\to1}$ (B_1)	$0.47\psi_{+1}^{-3}$	$0.37\psi_{+2}^{-2}$	$0.28\psi_{+2}^{-4}$	$0.62\psi_{+3}^{-1}$	$0.27\psi_{+4}^{-2}$	$0.37\psi_{+4}^{-4}$
${}^1\Psi_{0\to2}$ (A_1)	$0.48\psi_{+1}^{-2}$	$0.45\psi_{+2}^{-1}$	$0.31\psi_{+2}^{-3}$	$0.43\psi_{+3}^{-4}$	$0.42\psi_{+4}^{-1}$	$0.32\psi_{+4}^{-3}$
${}^1\Psi_{0\to3}$ (B_1)	$0.88\psi_{+1}^{-1}$	$0.25\psi_{+2}^{-4}$	$0.23\psi_{+3}^{-3}$	$0.21\psi_{+4}^{-4}$		
${}^1\Psi_{0\to4}$ (A_1)	$0.31\psi_{+1}^{-4}$	$0.55\psi_{+2}^{-1}$	$0.34\psi_{+3}^{-2}$	$0.61\psi_{+4}^{-1}$		
${}^1\Psi_{0\to5}$ (B_1)	$0.32\psi_{+1}^{-1}$	$0.31\psi_{+1}^{-3}$	$0.55\psi_{+2}^{-2}$	$0.43\psi_{+3}^{-1}$	$0.51\psi_{+3}^{-3}$	
${}^1\Psi_{0\to6}$ (B_1)	$0.39\psi_{+1}^{-3}$	$0.60\psi_{+3}^{-1}$	$0.35\psi_{+3}^{-3}$	$0.52\psi_{+4}^{-2}$		
${}^1\Psi_{0\to7}$ (A_1)	$0.41\psi_{+1}^{-4}$	$0.61\psi_{+2}^{-1}$	$0.42\psi_{+3}^{-2}$	$0.41\psi_{+4}^{-3}$		
${}^1\Psi_{0\to8}$ (A_1)	$0.34\psi_{+1}^{-2}$	$0.33\psi_{+2}^{-1}$	$0.42\psi_{+2}^{-3}$	$0.66\psi_{+4}^{-1}$		

The fact that the *third* excited state originates from an almost pure ψ_{+1}^{-1} configuration is perhaps the most important single feature in the relationship between the electronic spectra of such compounds and their potentialities as electron acceptor molecules. Thus it is this *third* state (corresponding roughly in character to the ${}^1B_{1u}$ state of benzene) which gives most evidence of the perturbation by boron and which will undergo a bathochromic shift with respect to the original benzene band. This is in striking contrast to the situation in vinylboranes [*2*], where, in all cases, the ψ_{+1}^{-1} configuration is heavily weighted in the *first* excited state. This means that in the latter type of compound the presence of boron causes a strong red shift in the *first* band of ethylene which has been correctly taken to imply π bonding between the vinyl group and the boron p-orbital [*5*].

Other vinyl and phenyl metallic compounds frequently exhibit similar spectral shifts which, with heavy central elements, have been interpreted in terms of the mixing of d-orbitals of π symmetry on the central atom with the π molecular orbitals of the organic groups [*10*]. In view of the spectroscopic difference just noted between the above two classes of organoboranes it is evident that considerable care must be exercised when attempting, on the basis of UV data, to assess the part which a central atom plays in conjugation. It is essential to consider the appropriate excited state in order to come to a reliable conclusion. Conversely the absence of a red shift in the *first* band of an organometallic compound does not necessarily prove that there is no π interaction between the external groups and the central atom and it is necessary to examine all the bands closely.

c) Higher excited states of diphenylboranes

The fourth state of Ph_2BX is only weakly allowed and is related to the $^1B_{1u}$ + $^1B_{1u}$ combination of benzene states. The next twelve excited states are all close-lying and detailed interpretation in this region is difficult because of the complication of ring-ring excitations giving rise to charge-resonance states. The relative simplicity of the diphenyl case, in which the Laporte rule forbids transitions to half the states, is lost when the diphenylboranes are considered. These features are also likely to complicate the interpretation of spectral shifts in acceptors discussed earlier still further if the region under examination is that in which there is strong mixing between the locally excited and the charge-transfer states.

d) Electron densities and bond orders

The distribution of π electron density in these molecules is shown in Fig. 5. For brevity, only the results appertaining to the non-coplanar molecules and the pseudoatom model of the methyl group are given. It is immediately evident that the electron density resident on the boron atom varies little from compound to compound. Moreover it originates mainly from the heteroatom and not from the phenyl rings; drift from the latter might have been expected from the relative valence state ionisation data. The former accords well with our earlier calculations on the electron distribution in vinylboranes as does the fact that the order of the B–X bond is considerably greater than that of the B–C bond. Rotation of the phenyl rings by 30° out of the plane diminishes the B–C bond order only by $\sim$10%. The series of calculations carried out on chlorodiphenylborane to gauge the effect of varying the angle of twist of the rings shows that increase in this variable up to 60° reduces the π electron density on boron by only $\sim$25% whereas the B–C bond order becomes halved. The latter obtains because $\cos \alpha = \frac{1}{2}$ for a 60° rotation and so for any other desired case the planar bond order may be scaled down directly and obviates the need for a complete calculation.

The C_{Me}–C_{Ph} hyperconjugative bond orders differ by $\sim$4% when calculated on the basis of the two methyl models and are therefore almost independent of this factor. This contrasts strongly with calculated B–Me bond orders [*2*] where the one given by the pseudoatom is about 2—3 times greater than for the $-C{\equiv}H_3$ model. Methyl groups situated in o and p positions change the density on boron

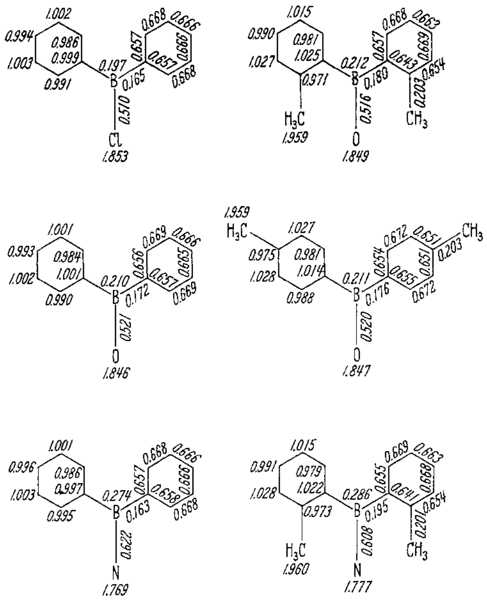

Fig. 5. Bond orders and Electron densities

only slightly and do not cause any radical redistribution in the B–O or B–N bonds. They do, however, exaggerate the differential charge distribution in the rings and activate the positions *o* and *p* to themselves towards electrophiles.

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