

Self-Consistent Molecular Orbital Calculations on Organoboron Compounds

V. Triarylboranes

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The PPP-SCMO-method is used to calculate the energies of the ground and lower excited states of triphenylborane and tri-*p*-tolylborane for which both planar and 'propellor' models are considered. It is found necessary to include a large measure of configuration interaction in the excited states in order to produce satisfactory agreement with published u.v. spectra. However the calculations are not diagnostic for the detailed geometry of these compounds. The electronic spectra may be interpreted in terms of ring exciton states and interring and phenyl→boron charge-resonance states. The π electron density on the central atom and the B-C π bond orders are small and so the phenyl rings are but little perturbed by their bonding to boron.

PPP-SCMO-Rechnungen wurden für Triphenyl- und Tri-*p*-tolylboran durchgeführt. Ohne ausgedehnte Konfigurationenwechselwirkung erhält man keine befriedigende Übereinstimmung mit veröffentlichten UV-Spektren. Die Deutung der Elektronenspektren geschieht mit Hilfe der Begriffe der einzelnen Ringanregung sowie des Ring-Ring- und des Ring-Bor-Ladungsaustausches. Ob die Molekeln in einer planaren oder einer Propeller-Konformation vorliegen, kann aufgrund dieser Rechnungen nicht entschieden werden. Bor- π -Ladung und B-C- π -Bindungsordnung sind gering; die Phenylringe werden durch ihre Bindung an Bor kaum beeinflusst.

La méthode SCMO-PPP a été utilisée pour calculer les énergies de l'état fondamental et des plus bas états excités du triphénylborane et du tri-*p*-tolylborane pour lequel on a considéré les modèles plan et "en hélice de bateau". L'inclusion d'une interaction de configurations étendue entre états excités est nécessaire pour obtenir un accord satisfaisant avec les spectres UV publiés. Mais les calculs ne permettent pas de préciser la géométrie détaillée de ces composés. Les spectres électroniques peuvent être interprétés en termes d'états excitoniques du cycle et d'états de résonance de charge entre cycles et entre le phényl et le bore. La densité électronique π sur l'atome central et les indices de liaison π sur les liaisons B-C sont faibles ce qui montre que les noyaux phényliques sont peu perturbés par leur liaison au bore.

1. Introduction

Previous papers [1] in this series have been concerned with the calculation of the electronic structures of a number of mono- and diaryl- and vinyl-halogenoboranes by the SCMO method. Trivinyl- and triphenylborane possess a C_3 rotation axis and hence occupy a unique position in these series because of the way in which the orbitals of the unperturbed organic group combine and give rise to the orbitals of the whole molecule. In this paper we present the detailed results of calculations on triphenyl- and tri-*p*-tolylborane by the LCAO SCF method [6].

Reference to this work has previously been made in a preliminary publication [7] and, moreover, whilst it was in progress, a study of the experimental electronic spectra of certain triarylboranes was published by RAMSEY [9].

2. Input Data and Geometry

All the input data (core Hamiltonian matrix elements, one- and two-centre electron repulsions integrals, and bond lengths) were consistent with those of our previous calculations [1]. In the present work the pseudoatom model of the methyl group was employed throughout, since it has previously been demonstrated [1] that the computed spectra of ring-substituted methyl arylboranes are almost independent of the particular calculational model of the methyl group.

The geometry of triphenylborane is an intriguing problem. Models indicate that the three rings cannot be coplanar with the B-C skeleton because of steric considerations. This situation may however be relieved in at least two ways, either (a) each ring could be inclined at some angle to the trigonal plane or (b) two of them could be perpendicular to this plane with the third lying in it. The heats of sublimation of the triphenyl derivatives of Group III are large [3] and are consistent with structures (in the crystal at least) in which the rings of separate molecules interact transannularly by virtue of dipole forces. Because of this and also crystal packing considerations we favour the former model. However the ring tilting angle is unknown and so a series of calculations to test models with differing ring inclination angles were carried out.

It was necessary to include configuration interaction in the excited states between all configurations formed from the six highest filled and the six lowest virtual orbitals. Initial calculations, which took into account four filled and four empty orbitals only, yielded excited state energies which were unsatisfactorily great in comparison with experimental data. On the other hand, extension of the configuration interaction treatment to include more than the above "6 to 6" led to an overall improvement in the state energies of only $\sim 0.5\%$.

3. Results

3.1. Orbital Energies

Triphenylborane

The sequence of orbitals for triphenylborane is illustrated in Figs. 1 and 2. It is convenient to analyse these under D_{3h} symmetry and to regard the phenyl ring twisting as an imposed perturbation leading to a descent in symmetry. The six highest filled and six lowest vacant molecular orbitals of triphenylborane are constructed essentially from linear combinations, under D_{3h} symmetry, of the benzene e_{1g} and e_{2u} orbitals respectively. The latter are denoted by ± 1 and $\pm 1'$ on Fig. 1. The combination of each of these orbital levels with its equivalent on the other phenyl rings results in a degenerate pair of new orbitals (e'') and an orbital of a_1'' or a_2'' symmetry. The forms of these orbitals can be approximately represented in terms of the degenerate pairs of benzene on phenyl rings *A*, *B*, and *C* as shown in Fig. 1. The energies of ten of the twelve new orbitals are similar to those of the original benzene contributors but two exceptional orbitals now appear, both of which are of a_2'' symmetry. The reason for the difference is that these latter

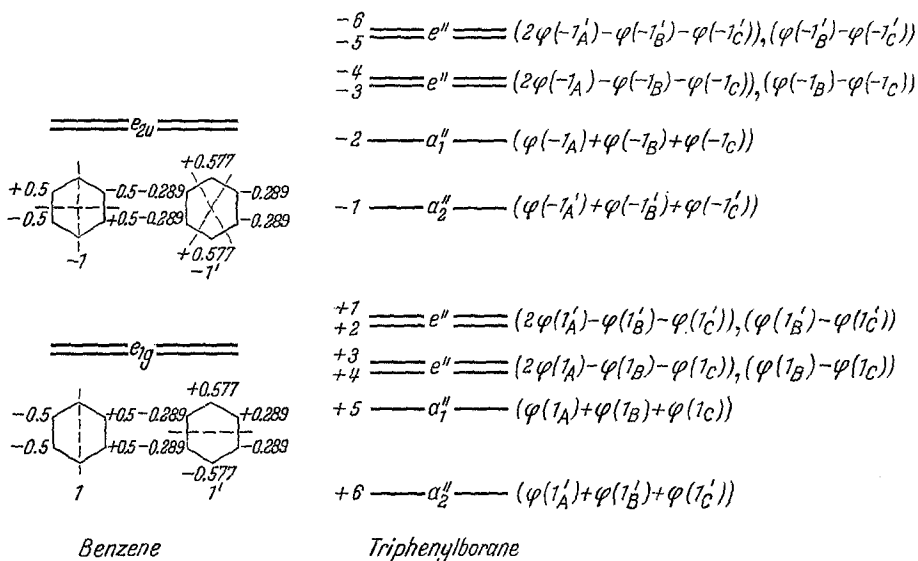


Fig. 1. MO-pattern

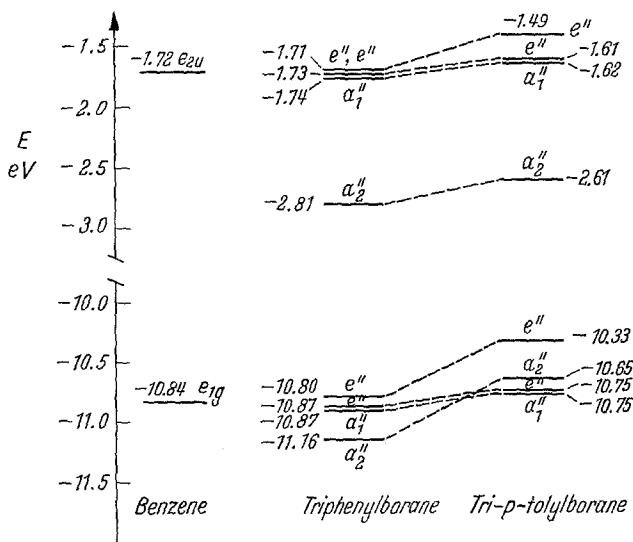


Fig. 2. One-electron energy level diagram for triarylboranes

two orbitals contain a large contribution from the (initially vacant) boron p_π orbital which transforms as a_2'' and hence they are lower in energy (in the absolute sense) than the e_{2u} , e_{1g} orbitals of benzene.

The reduction in energy is more marked for the antibonding orbital (ψ^{-1}) than for the filled one (ψ^{+6}). This would be expected since the initial energies of the empty boron p_π orbital and that of the e_{2u} levels in benzene are similar.

Tri-*p*-tolylborane

The methyl groups of tri-*p*-tolylborane affect the energies of the orbitals which incorporate the ± 1 benzene set and have only a second order effect on the $\pm 1'$ pair. Again this is as expected because the latter have effectively zero atomic coefficients on the three carbon atoms remote from boron and the energy level sequence for this compound is illustrated in Fig. 2. The orbital energies of tri-*p*-tolylborane are all raised with respect to the corresponding levels of triphenylborane and it transpires that the filled orbitals are perturbed by the methyl group rather more than are the empty ones because they are energetically closer to the π orbital of the methyl pseudoatom.

3.2. Ring Twisting Perturbations

The primary effect of concomitantly twisting all three phenyl rings is to decrease the overlap between the ring molecular orbitals and the boron p_π orbital. This affects directly the orbitals of a_2'' symmetry which bring about bonding between the two, and so the energies of these orbitals are raised and approach those of unperturbed phenyl rings. If the ring twisting angle were increased to 90° then there would be no π - π interaction at all.

RAMSEY [9] has suggested that, in the case of tri-*p*-tolylborane, one ring only is coplanar with the B-C skeleton whilst the remaining two are orthogonal to it. For such a system the eigenvalues would consist of (a) two effectively non-bonding sets from the orthogonal phenyl rings and (b) a third set of levels corresponding to those of a monophenylborane. Systems similar to the latter have been considered in previous papers [1] (Parts I and III). From a consideration of the trends of the one-electron energies in vinylboranes and dihalogenophenylboranes it would be expected that the energy gap between the highest bonding and lowest antibonding levels in PhBH_2 (as the system would effectively be) would be < 0.1 eV different from that in PhBF_2 , and, on this basis, the lowest electronic transition bands would have almost identical energy in the two cases. Data for the two systems PhBF_2 and Ph_3B can be compared and it is reasonable to assume that the conclusion therefrom will also be appropriate for the pair *p*- MePhBF_2 and (*p*- MePh) $_3\text{B}$. Experimentally the first transition bands of Ph_3B and PhBF_2 differ in energy by 0.1 to 0.37 eV [1, 9], which means that the observed red-shift between the two is too large to be consistent with RAMSEY's model. However this evidence is insufficient to make this feature certain.

3.3. Spectra

Electronic State Energies of Triphenylborane

Tabs. 1 and 2 list the computed energies and oscillator strengths of the singlet and triplet electronic states of triphenyl- and tri-*p*-tolylborane employing both the D_{3h} (planar) and D_3 (rings twisted by 30°) models. The experimental u.v. spectra are included in the table also and merit some comment. RAMSEY's paper details the only reliable information on the spectra of these compounds. Work on triphenylborane [4] previous to this suffered because the compound is very readily surface-oxidised in air and so was almost certainly contaminated with impurities

Table 1. *Electronic State Energies of Ph₃B (eV)*

| Planar model | | | Rings twisted 30° | | | Experimental | | | |
|--------------|--------|------------------|-------------------|--------|----------------|--------------|--------|-------------------|-------|
| Singlets | | | Singlets | | | Triplets | | | |
| No. | Energy | Symmetry | No. | Energy | Symmetry | No. | Energy | Symmetry | |
| | | | | | | | | | |
| | | | | | | | | \bar{E} | |
| | | | | | | | | ϵ_{\max} | |
| 1 | 4.649 | A ₂ ' | 1 | 4.693 | A ₂ | 1, 2 | 3.336 | E | 4.317 |
| 2, 3 | 4.651 | E' | 2, 3 | 4.693 | E | 3 | 3.364 | A ₁ | 4.496 |
| 4, 5 | 5.171 | E' | 4, 5 | 5.311 | E | 4 | 4.006 | A ₂ | 5.208 |
| 6 | 5.598 | A ₁ ' | 6 | 5.626 | A ₁ | 5, 6 | 4.006 | E | |
| 7 | 5.827 | A ₂ ' | 7 | 5.973 | A ₂ | 7, 8 | 4.030 | E | |
| 8, 9 | 5.948 | E' | 8, 9 | 6.030 | E | 9 | 4.050 | A ₂ | |
| 10, 11 | 6.060 | E' | 10, 11 | 6.081 | E | 10, 11 | 4.716 | E | 6.198 |
| 12 | 6.182 | A ₁ ' | 12 | 6.214 | A ₁ | 12 | 4.717 | A ₁ | |
| 13 | 6.484 | A ₂ ' | 13 | 6.584 | A ₂ | 13, 14 | 6.062 | E | |
| 14, 15 | 6.583 | E' | 14, 15 | 6.589 | E | 15 | 6.147 | A ₁ | |
| 16, 17 | 6.793 | E' | 16, 17 | 6.739 | E | 16 | 6.199 | A ₂ | |
| 18 | 6.820 | A ₂ ' | 18 | 6.834 | A ₂ | 17, 18 | 6.200 | E | |
| 19, 20 | 6.821 | E' | 19, 20 | 6.856 | E | 19 | 6.833 | A ₂ | |
| 21 | 6.825 | A ₁ ' | 21 | 6.860 | A ₁ | 20, 21 | 6.855 | E | |
| 22, 23 | 6.914 | E' | 22, 23 | 6.934 | E | 22 | 6.861 | A ₁ | |
| 24 | 6.924 | A ₁ ' | 24 | 6.936 | A ₁ | 23, 24 | 6.933 | E | |
| 25 | 6.944 | A ₂ ' | 25 | 6.947 | A ₁ | 25 | 6.938 | A ₁ | |
| 26 | 6.947 | A ₁ ' | 26 | 6.965 | A ₂ | 26 | 6.965 | A ₂ | |
| 27, 28 | 6.960 | E' | 27, 28 | 6.974 | E | 27, 28 | 6.972 | E | |
| 29, 30 | 6.976 | E' | 29, 30 | 6.984 | E | 29, 30 | 6.983 | E | |
| 31 | 6.981 | A ₁ ' | 31 | 6.989 | A ₁ | 31, 32 | 6.989 | E | |
| 32, 33 | 7.075 | E' | 32, 33 | 7.020 | E | 33 | 6.989 | A ₁ | |
| 34 | 7.104 | A ₂ ' | 34 | 7.070 | A ₂ | 34 | 7.061 | A ₂ | |
| 35, 36 | 7.118 | E' | 35, 36 | 7.075 | E | 35, 36 | 7.063 | E | |

Table 2. *Electronic State Energies of (MePh)₃B (eV)*

| Planar model | | | | Rings 30° twisted | | | | Experimental | |
|--------------|-----------------------------|----------|-----------|----------------------------|----------|-----------|----------------------------|--------------|-------------------|
| Singlets | | Triplets | | Singlets | | Triplets | | Spectrum | |
| State No. | Energy Symmetry | <i>f</i> | State No. | Energy Symmetry | <i>f</i> | State No. | Energy Symmetry | <i>E</i> | ϵ_{\max} |
| 1, 2 | 4.632 <i>E'</i> | 0.000 | 1, 2 | 4.665 <i>E</i> | 0.000 | 1, 2 | 3.369 <i>E</i> | 4.179 | 33000 |
| 3 | 4.634 <i>A'₂</i> | 0 | 3 | 4.666 <i>A₂</i> | 0.000 | 3 | 3.398 <i>A₁</i> | 4.395 | 19000 |
| 4, 5 | 4.976 <i>E'</i> | 0.429 | 4, 5 | 5.112 <i>E</i> | 0.413 | 4, 5 | 3.999 <i>E</i> | 4.978 | 20000 |
| 6 | 5.412 <i>A'₁</i> | 0 | 6 | 5.451 <i>A₁</i> | 0 | 6 | 4.003 <i>A₂</i> | 5.274 | 15000 |
| 7 | 5.762 <i>A'₂</i> | 0 | 7 | 5.927 <i>A₂</i> | 0.341 | 7, 8 | 4.003 <i>E</i> | | |
| 8, 9 | 5.932 <i>E'</i> | 0.658 | 8, 9 | 6.010 <i>E</i> | 0.617 | 9 | 4.022 <i>A₁</i> | | |
| 10, 11 | 6.027 <i>E'</i> | 0.184 | 10, 11 | 6.043 <i>E</i> | 0.173 | 10, 11 | 4.632 <i>E</i> | | |
| 12 | 6.066 <i>A'₁</i> | 0 | 12 | 6.093 <i>A₁</i> | 0 | 12 | 4.633 <i>A₂</i> | | |
| 13, 14 | 6.414 <i>E'</i> | 1.192 | 13, 14 | 6.420 <i>E</i> | 1.104 | 13, 14 | 5.906 <i>E</i> | | |
| 15 | 6.505 <i>A'₂</i> | 0 | 15 | 6.586 <i>A₂</i> | 0.368 | 15 | 5.979 <i>A₁</i> | | |
| 16, 17 | 6.568 <i>E'</i> | 0.001 | 16, 17 | 6.596 <i>E</i> | 0.000 | 16 | 6.292 <i>A₂</i> | | |
| 18 | 6.577 <i>A'₁</i> | 0 | 18 | 6.603 <i>A₁</i> | 0 | 17, 18 | 6.293 <i>E</i> | | |
| 19 | 6.657 <i>A'₂</i> | 0 | 19 | 6.669 <i>A₂</i> | 0.001 | 19, 20 | 6.596 <i>E</i> | | |
| 20, 21 | 6.722 <i>E'</i> | 0.588 | 20, 21 | 6.689 <i>E</i> | 0.463 | 21 | 6.603 <i>A₁</i> | | |
| 22 | 6.816 <i>A'₁</i> | 0 | 22 | 6.792 <i>A₂</i> | 0.021 | 22 | 6.668 <i>A₂</i> | | |
| 23 | 6.823 <i>A'₂</i> | 0 | 23, 24 | 6.796 <i>E</i> | 0.133 | 23, 24 | 6.777 <i>E</i> | | |
| 24, 25 | 6.841 <i>E'</i> | 0.249 | 25 | 6.808 <i>A₁</i> | 0 | 25 | 6.781 <i>A₂</i> | | |
| 26, 27 | 6.892 <i>E'</i> | 0.000 | 26, 27 | 6.852 <i>E</i> | 0.004 | 26, 27 | 6.818 <i>E</i> | | |
| 28, 29 | 6.933 <i>E</i> | 0.000 | 28, 29 | 6.933 <i>E</i> | 0.000 | 28, 29 | 6.962 <i>E</i> | | |
| 30 | 6.936 <i>A'₁</i> | 0 | 30 | 6.936 <i>A₁</i> | 0 | 30 | 6.963 <i>A₁</i> | | |
| 31 | 6.953 <i>A'₂</i> | 0 | 31 | 6.953 <i>A₂</i> | 0.001 | 31 | 6.975 <i>A₂</i> | | |
| 32, 33 | 6.958 <i>E'</i> | 0.011 | 32, 33 | 6.956 <i>E'</i> | 0.002 | 32, 33 | 6.976 <i>E</i> | | |
| 34 | 7.062 <i>A'₁</i> | 0 | 34 | 7.062 <i>A₁</i> | 0 | 34, 35 | 7.065 <i>E</i> | | |
| 35, 36 | 7.064 <i>E'</i> | 0.000 | 35, 36 | 7.064 <i>E</i> | 0.000 | 36 | 7.066 <i>A₁</i> | | |

containing B-O bonds. Secondly, it interacts markedly with any solvent possessing any degree of electron donor power and, in the limiting situation, a coordination complex is formed. Solution spectra are therefore always rendered somewhat suspect.

The calculated state energies obtained from models with ring tilting angles of 45° and 60° were in poorer agreement with the experimental data than those in which the twisting angle was 30° , and so only the latter are included in Tabs. 1 and 2 together with the corresponding figures for the planar models. For both compounds all thirty-six states are grouped in an energy range of ca. 2.5 eV and hence detailed correlation with the experimental results is not possible.

Comparison of the calculated and observed state energies shows that the agreement between the energy of the second band and the group of states ${}^1\Psi_{4,5}$ and between that of the third band and the group of states ${}^1\Psi_{7,8,9,10,11}$ is quite good. It is in fact, the first experimental band which exhibits the poorest agreement with the calculated figures (~ 0.3 eV difference); the latter do not predict as pronounced a red-shift from benzene as was observed.

Intensities of Triphenylborane

A comparison of the calculated and observed spectra immediately reveals one significant discrepancy. The present work predicts, for the planar form of triphenylborane, that (a) the first state is non-degenerate and hence formally forbidden (though it could be weakly allowed by ring twisting) and (b) the second and third states, which constitute the degenerate pair E' and to which transitions are allowed, should nevertheless be only weak. In the experimental spectrum it is reported that there are two superposed *intense* bands lying at 4.32 and 4.50 eV which have ϵ_{\max} values of 39000 and 35000 respectively and, moreover, each is twice as intense (on the ϵ_{\max} scale) as the next higher energy band ($\epsilon_{\max} = 19000$).

The first transition bands in the spectra of the mono- and diphenylhalogenoboranes, although symmetry allowed, are weak. This feature is explained by calculations which reveal that the excited configurations contributing to the final electronic state possess opposed dipole moments and thus tend to cancel mutually [1]. This is also the root cause of the predicted weakness of the transition to the ${}^1E'$ states of Ph_3B ; the excited configurations composing it have oppositely orientated dipole moments and hence the oscillator strength of the final state is reduced by configuration interaction.

There is thus marked disagreement between the experimental results and both the present calculations and the observed and calculated spectra of other phenylboranes. Our calculations do not suggest any way by which the first band of Ph_3B might be intensified. There are however three possible explanations for the intensity of this band; (a) it may be due to strong vibronic coupling, (b) to $\sigma \rightarrow \pi^*$ or $\pi \rightarrow \sigma^*$ transitions, (c) the purity of the compounds examined may be suspect.

With regard to (c): that such compounds are attacked and rendered impure by traces of oxygen or moisture even on transient exposure to the atmosphere is amply demonstrated by previous experimental work on triaryl systems [8]. However it must be said that the experimental precautions observed by RAMSEY in manipulating the boranes seem adequate to preclude any gross effects arising from this source.

The observed spectra are not sufficiently well-resolved to enable any real advance to be made in the direction of alternative (a). We may only note that, if vibronic coupling is genuinely responsible for the band intensities then i) the coupled vibration only appears in the *trigonal* B-C skeleton and not in the compounds with C_{2v} symmetry (the mono- and diaryl-boranes) and ii) vibronic levels should appear on the high energy side of the $0 \rightarrow 0$ band and we would expect rather better agreement with the calculated energy of the first band.

Alternative (b) merits further consideration. The energy order in which the σ molecular orbitals lie in these compounds has not yet been investigated but, for a planar model, they must all transform according to the irreducible representations a'_1 , a'_2 , and e' of D_{3h} . This means that the electronic states generated by excited $\sigma \rightarrow \pi^*$ or $\pi \rightarrow \sigma^*$ configurations must be of symmetry A_1'' , A_2'' , or E'' . Of these, transitions from the ground state to the A_2'' states only are allowed and are polarised vertically to the molecular plane. In a planar model the overlap between the ground and the allowed excited states might still be limited but it would be enhanced considerably if the symmetry were lowered to D_3 , and would thus intensify the associated electronic bands. Furthermore because σ orbitals are distributed over a larger energy range configurational interaction would exert a less potent effect here. Hence single orbital-orbital transitions which have unidirectional transition moments may well play the dominant rôle in determining the band intensities.

With regard to the two higher energy bands in the spectrum of triphenylborane the calculations suggest that the ratio of the intensities of these should be 1:5 and indeed this is close to that observed, although it should be borne in mind that only ϵ_{\max} values are available for comparison.

Energies and Intensities of Tri-*p*-tolylborane

The electronic states of tri-*p*-tolylborane are calculated to lie at lower energies than the corresponding states of triphenylborane, hence its spectral bands should be red-shifted with respect to the latter. This is confirmed and the overall agreement with experiment is satisfactory. The problem of the intense lowest energy band again arises and can only be explained as for the triphenyl compound.

4. Discussion

4.1. Electronic Spectra

In what follows the electronic states of the planar models are discussed. As might be expected for a molecule of such symmetry and possessing a large number of close-lying excited configurations, there is a high degree of configuration interaction in the excited states. Considerable improvement between the observed and calculated state energies was effected by allowing interaction between 36 configurations rather than 16 for both the singlet and triplet states. The coefficients of the principal spin configurations contributing to the excited states (i.e. the eigenvectors of the configuration interaction matrix) illuminate the structures of the excited states considerably and are particularly valuable in accounting for the intensities of the spectral bands. The relevant data for the lowest nine excited states are presented in Tabs. 3 and 4.

Table 3. Principal State Coefficients of Planar Triphenylborane

| Transition | Coefficients | | | | | |
|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| ${}^1\Psi_1(A'_1)$ | $0.65 \psi_5^{-1}$ | $0.35 \psi_1^{-4}$ | $0.35 \psi_2^{-3}$ | $0.30 \psi_2^{-6}$ | $0.30 \psi_2^{-5}$ | $0.30 \psi_6^{-3}$ |
| ${}^1\Psi_2(E')$ | $0.62 \psi_4^{-1}$ | $0.34 \psi_2^{-2}$ | $0.28 \psi_6^{-3}$ | $0.27 \psi_5^{-5}$ | $0.22 \psi_1^{-3}$ | $0.22 \psi_2^{-4}$ |
| ${}^1\Psi_3(E')$ | $0.62 \psi_3^{-1}$ | $0.34 \psi_1^{-2}$ | $0.28 \psi_6^{-4}$ | $0.27 \psi_5^{-6}$ | $0.22 \psi_2^{-3}$ | $0.22 \psi_1^{-4}$ |
| ${}^1\Psi_4(E')$ | $0.80 \psi_2^{-1}$ | $0.49 \psi_1^{-1}$ | | | | |
| ${}^1\Psi_5(E')$ | $0.80 \psi_1^{-1}$ | $0.49 \psi_2^{-1}$ | | | | |
| ${}^1\Psi_6(A'_1)$ | $0.81 \psi_6^{-1}$ | $0.29 \psi_5^{-1}$ | $0.28 \psi_4^{-3}$ | $0.28 \psi_3^{-4}$ | $0.22 \psi_2^{-5}$ | $0.22 \psi_1^{-6}$ |
| ${}^1\Psi_7(A_2)$ | $0.74 \psi_5^{-1}$ | $0.39 \psi_1^{-4}$ | $0.39 \psi_2^{-3}$ | $0.30 \psi_6^{-2}$ | | |
| ${}^1\Psi_8(E')$ | $0.68 \psi_4^{-1}$ | $0.31 \psi_5^{-1}$ | $0.30 \psi_2^{-2}$ | $0.26 \psi_5^{-5}$ | $0.22 \psi_6^{-3}$ | $0.21 \psi_4^{-6}$ |
| ${}^1\Psi_9(E')$ | $0.68 \psi_3^{-1}$ | $0.31 \psi_4^{-1}$ | $0.30 \psi_1^{-2}$ | $0.26 \psi_6^{-6}$ | $0.22 \psi_6^{-4}$ | $0.21 \psi_4^{-5}$ |
| | | | | | | $0.21 \psi_3^{-6}$ |
| | | | | | | $0.20 \psi_2^{-4}$ |
| | | | | | | $0.20 \psi_2^{-3}$ |
| | | | | | | $0.20 \psi_1^{-4}$ |
| | | | | | | $0.20 \psi_1^{-3}$ |
| | | | | | | $0.20 \psi_5^{-6}$ |
| | | | | | | $0.20 \psi_5^{-5}$ |

Table 4. Principal State Coefficients of Planar Tri-*p*-Tolylborane

| Transition | Coefficients | | | | | |
|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| ${}^1\Psi_1(E')$ | $0.57 \psi_5^{-1}$ | $0.42 \psi_2^{-2}$ | $0.34 \psi_2^{-3}$ | $0.32 \psi_5^{-6}$ | $0.29 \psi_2^{-4}$ | $0.29 \psi_1^{-3}$ |
| ${}^1\Psi_2(E')$ | $0.57 \psi_4^{-1}$ | $0.42 \psi_1^{-2}$ | $0.34 \psi_3^{-4}$ | $0.32 \psi_6^{-5}$ | $0.29 \psi_2^{-3}$ | $0.29 \psi_1^{-4}$ |
| ${}^1\Psi_3(A'_2)$ | $0.58 \psi_6^{-1}$ | $0.41 \psi_1^{-4}$ | $0.41 \psi_2^{-3}$ | $0.34 \psi_3^{-3}$ | $0.33 \psi_4^{-5}$ | $0.33 \psi_5^{-6}$ |
| ${}^1\Psi_4(E')$ | $0.82 \psi_2^{-1}$ | | $0.46 \psi_1^{-1}$ | | | |
| ${}^1\Psi_5(E')$ | $0.82 \psi_1^{-1}$ | | $0.46 \psi_2^{-1}$ | | | |
| ${}^1\Psi_6(A'_1)$ | $0.85 \psi_5^{-1}$ | $0.24 \psi_1^{-4}$ | $0.24 \psi_6^{-2}$ | $0.23 \psi_1^{-5}$ | $0.23 \psi_2^{-6}$ | |
| ${}^1\Psi_7(A_2)$ | $0.76 \psi_6^{-1}$ | $0.40 \psi_1^{-4}$ | $0.40 \psi_2^{-3}$ | $0.29 \psi_3^{-2}$ | | |
| ${}^1\Psi_8(E')$ | $0.77 \psi_5^{-1}$ | $0.32 \psi_2^{-2}$ | $0.23 \psi_1^{-3}$ | $0.23 \psi_2^{-4}$ | $0.22 \psi_3^{-3}$ | |
| ${}^1\Psi_9(E')$ | $0.77 \psi_4^{-1}$ | $0.32 \psi_1^{-2}$ | $0.23 \psi_1^{-4}$ | $0.23 \psi_2^{-3}$ | $0.22 \psi_3^{-4}$ | |
| | | | | | | $0.22 \psi_3^{-3}$ |
| | | | | | | $0.23 \psi_5^{-5}$ |
| | | | | | | $0.23 \psi_5^{-6}$ |
| | | | | | | $0.23 \psi_4^{-6}$ |
| | | | | | | $0.23 \psi_4^{-5}$ |
| | | | | | | $0.23 \psi_4^{-4}$ |
| | | | | | | $0.23 \psi_4^{-3}$ |
| | | | | | | $0.23 \psi_4^{-2}$ |
| | | | | | | $0.23 \psi_4^{-1}$ |

All the excited states of a D_{3h} model are A'_1 , A'_2 , or E' symmetry because the fourfold degenerate unsymmetrised direct product of e'' with itself reduces to these irreducible representations, as also do all other direct products of the orbital symmetry types.

It is again convenient to discuss the structures of the states under their relationship to the electronic states of benzene. The *three lowest states* of triphenylborane approximate to linear combinations of the locally excited ${}^1B_{2u}$ states of the phenyl rings and produce an A'_1 and an E' state. Each of these includes confi-

gurations in which the first antibonding orbital (-1) is occupied and so they should all be bathochromically shifted with respect to the original benzene ${}^1B_{2u}$ state. This is a consequence of the energy decrease which the boron p_π orbital undergoes as a result of mixing with the phenyl orbitals under D_{3h} symmetry (Fig. 2). These three transitions involve charge-transfer from the outlying phenyls to the central boron atom and hence a parallel situation exists to that assumed by RAMSEY in calculating the energies of these bands as simple CT bands. There are however two marked differences between his and our approaches: (a) the previous work assumed that the electron affinity of boron was zero and the ionisation potential of benzene 9.2 eV. In fact the π mixing with the phenyl rings alters the electron affinity of boron to 2.8 eV (if Koopmans' theorem is assumed to hold). The effect is, to some extent, offset by an increase of ~ 1.6 eV in the ionisation potential of the bonded phenyl rings but, even so, the calculated energy of the excited ionic state would be modified by ~ 1 eV. The close agreement with the experimental spectrum obtained by RAMSEY thus seems somewhat fortuitous. (b) it was also stated that, because the longest wave length band would have charge-transfer character it should therefore be intense. This argument, however, neglects the first-order configurational mixing.

We find that in triphenylborane the state ${}^1\Psi_2$ (one component of the allowed ${}^1E'$ state) is composed of $\sim 38\%$ of the configuration ψ_4^{-1} in which charge is transferred from two of the rings to the boron atom and concomitantly to the other ring. Charge is also redistributed more evenly in the rings and a symmetrical charge distribution in the excited state results. The oscillator strength of this single state is 0.102, but intermixed with it, in lesser proportion, are the subsidiary configurations ψ_2^{-3} , ψ_5^{-5} , ψ_5^{-6} , ψ_6^{-3} , and ψ_6^{-4} , which together constitute 25–30% of the final state. The configurations ψ_5^{-6} , ψ_2^{-3} do not involve the boron atom at all but are interring electron-transfer states with dipole moments opposed to that of ψ_4^{-1} ; on the other hand ψ_5^{-5} transfers charge in the same sense as does ψ_4^{-1} . Finally ψ_6^{-3} and ψ_6^{-4} both remove charge from boron back to the rings. A similar pattern of configuration interaction exists for ${}^1\Psi_3$ (the second ${}^1E'$ component) and the overall result for both is that their oscillator strengths are near zero.

Transitions to the lowest excited state of the first three, i.e. ${}^1\Psi_1$, (${}^1A'_2$) are forbidden under D_{3h} symmetry but become weakly allowed under D_3 by the small z component of transition moment which is introduced as a consequence of twisting the phenyl rings.

The succeeding three states (${}^1\Psi_{4,5,6}$) are of ${}^1A'_1$ and ${}^1E'$ symmetry and are related to the ${}^1B_{1u}$ state of benzene. Both components of the ${}^1E'$ state incorporate complementary proportions of the degenerate configurations ψ_1^{-1} and ψ_2^{-1} . The configuration ψ_1^{-1} brings about charge transfer to the boron atom from the rings, although there is no 'balancing out' of charge in the excited state because the ring orbitals involved are both derived from the $\pm 1'$ sets of benzene.

This electron transfer state is accompanied by a large local transition moment as would be expected. The complementary configuration, ψ_2^{-1} , is intermixed, and also transfers charge to boron but the simultaneous charge redistribution in the rings tends to oppose that of ψ_1^{-1} . The aggregate effect is to produce a band whose intensity is enhanced over that of benzene and, moreover, because of the strong participation of the first antibonding orbital (-1) it is bathochromically shifted

with respect to the parent benzene ${}^1B_{1u}$ state. The totally symmetric state arising in the group (${}^1\Psi_6$) is forbidden both under the group D_{3h} and D_3 as it correlates with the representation 1A_1 in the latter case. This state incorporates a very large contribution from the ψ_6^{-1} configuration, a situation which arises because the non-degenerate +6 orbital is displaced in the energy scale from the initial group of five bonding orbitals and so it is not markedly affected by configuration interaction.

The *higher states of triphenylborane* (${}^1\Psi_{7,8,9,10,11,12}$) are built from a large number of excited configurations and are not closely correlatable with the exciton states of benzene. However these six states do agree quite well in energy with the third band in the experimental spectrum and are related to the strongly allowed ${}^1E_{1u}$ and ${}^1E'_{1u}$ states of benzene which have been located at 6.76 eV [5]. Hence they are considerably red-shifted with respect to the latter (~ 0.6 eV). In triphenylborane these higher states are composed of a mixture of ring exciton states, interring, ring-boron, and boron-ring charge-resonance states. As the energies increase domination of states by particular configurations decreases and reappears strongly only in the highest states of the set (i.e. ${}^1\Psi_{30-36}$).

The corresponding *electronic states of tri-p-tolylborane* occur at lower energies than those of triphenylborane. This effect is more potent in those states which contain large proportions of the configurations ψ_1^{-n} , ψ_2^{-n} , ψ_6^{-n} , i.e. those originating from the $1'_A$, $1'_B$ and $1'_C$ orbitals on the phenyl rings. Hence the effect of the para-substituted methyl groups will be manifest principally in the 4th, 5th and 6th excited states because in these the configurations ψ_2^{-1} , ψ_1^{-1} , and ψ_3^{-1} figure largely. Experimentally this turns out to be the case although the experimental spectral shifts from Ph_3B are slightly smaller than predicted. The states of this compound can be analysed in a manner similar to that adopted for the triphenyl case.

4.2. Effect of Ring Twisting

When the phenyl rings are twisted the bond resonance integral is lowered and so the energy of the first vacant orbital is increased. This effect stems from the expression

$$\left(\frac{\partial \varepsilon}{\partial \beta_{rs}}\right) = 2c_r c_s$$

which arises from perturbation theory [2] and means that all transitions trowse to this orbital will be raised in energy as compared with the planar molecule. Hence the most powerful effect will be exerted on the low energy states. For a tilting angle of 30° the changes in the state energies are not particularly marked and the perturbation chiefly serves to allow certain of the transitions to the non-degenerate states which are polarised perpendicularly to the molecular plane. Hence we are forced to conclude that the experimental u.v. spectra do not aid in clarifying the geometry of such compounds. However, in the light of previous discussion regarding the one-electron energies, we consider that the large bathochromic shifts of the observed spectral bands of these triarylboranes relative to those of benzene argue against a structure in which only one ring is coplanar with the B-C skeleton and the other two orthogonal to it. For the latter configuration we should expect the electronic spectra to resemble closely those of monophenylboranes overlaid with unperturbed benzene bands.

4.3. *Electron Densities and Bond Orders*

Firstly, the phenyl ring bond orders are almost unchanged from those of benzene. The electron distribution in the non-planar compounds suggests that the overall π electron transfer to boron is limited and amounts to only 0.029 from each phenyl ring. This density originates mainly from the *o* and *p* positions in the phenyl ring and in tri-*p*-tolylborane it is augmented to a small extent by the methyl groups. The B-C bond orders are less in triphenyl- than in trivinyl-borane, the values for Ph₃B and Vi₃B being 0.172 and 0.219 respectively. This means that the energy barrier to rotation of the organic group will be smaller for the former compound and thus also the overall planar-tetrahedral vertical reorganisation energy.

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