

Calculation of $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ Transitions in Vinylboranes

D. R. ARMSTRONG and P. G. PERKINS

University of Newcastle upon Tyne, England

Received November 13, 1967

Calculations are presented of the energies of the ground and excited σ and π electronic states of ethylene and substituted vinylboranes. The Pople-Segal-Santry method was employed throughout. It is concluded that the excited state of lowest energy in ethylene has $\pi \rightarrow \sigma^*$ character whilst the lowest energy ultra-violet spectral bands of the latter compounds stem from $\sigma \rightarrow \pi^*$ transitions.

Valenzelektronenrechnungen nach Pople-Segal-Santry wurden für Äthylen und Vinylborane durchgeführt. Danach hat der niedrigste angeregte Zustand von Äthylen $\pi \rightarrow \sigma^*$ -Charakter, während die längstwellige UV-Bande der Vinylborane einem $\sigma \rightarrow \pi^*$ -Übergang entspricht.

Calculs de l'énergie pour les états fondamentaux et excités σ et π de l'éthylène et des vinylboranes substitués. Utilisation de la méthode de Pople-Ségal-Santry. L'état excité le plus bas pour l'éthylène résulte d'une transition $\pi \rightarrow \sigma^*$, alors qu'il résulte d'une transition $\sigma \rightarrow \pi^*$ pour les vinylboranes.

Introduction

Previous investigations of the electronic spectra of vinylboranes and methylboranes have dealt with bands arising from $\pi \rightarrow \pi^*$ transitions [1]. However, weakly allowed, low energy 'mystery bands' are also present in the spectra and, by analogy with similar bands which appear in the spectra of some alkenes [2], these have been tentatively assigned to $\sigma \rightarrow \pi^*$ transitions. On the other hand Robin, and Hart [7] using Gaussian type orbitals as basis sets, concluded that the weak bands in the alkenes stem from $\pi \rightarrow \sigma^*$ transitions. In this paper we present results for σ and π excited states calculated within the semi-empirical framework of the Pople-Segal-Santry method [5].

Method

The energies, ε_i , of the σ and π molecular orbitals are obtained by solution of the determinantal equation,

$$|\mathbf{F} - \varepsilon\mathbf{S}| = 0$$

where \mathbf{F} is the Hartree-Fock Matrix with elements,

$$F_{\mu\mu} = H_{\mu\mu} + (P_{AA} - \frac{1}{2} P_{\mu\mu}) \gamma_{AA} + \sum_{B \neq A} (P_{BB} - Z_B) \gamma_{AB}$$

$$F_{\mu\nu} = \beta_{AB}^0 S_{\mu\nu} - P_{\mu\nu} \gamma_{AB}.$$

In these equations μ represents an atomic orbital of atom A, ν one of atom B and \mathbf{P} is the usual bond order matrix; $H_{\mu\mu}$ is the Hamiltonian core matrix element referring to orbital μ and was computed from

$$H_{\mu\mu} = -I_{\mu} - (Z_A - 1) \gamma_{AA}$$

where Z_A is the core charge of atom A. The resonance integrals $H_{\mu\nu}$ were calculated from the expression

$$H_{\mu\nu} = K \beta_{AB}^0 S_{\mu\nu}.$$

Here β_{AB}^0 is obtained from the Pople constants [5]: the constant K was fixed so as to afford optimum agreement between the calculated and observed electronic spectrum of ethylene.

The electronic repulsion matrix, I , was assembled from the theoretical values for the s valence orbitals. The energy of the excited configuration ψ_i^{-j} is given by,

$${}^{1,3}E(\psi_i^{-j}) - E_0 = \varepsilon_j - \varepsilon_i - \langle ii | jj \rangle + \langle ij | ij \rangle \pm \langle ij | ij \rangle.$$

Finally a configuration interaction calculation was carried out in which excited states generated from all possible transitions from the six or seven highest filled to the six lowest vacant molecular orbitals were allowed to mix.

Results

In all, four compounds were studied, namely trivinylborane, divinylmethylborane, vinyldimethylborane and trimethylborane. The calculated electronic transition energies are listed in Table 1 together with the corresponding experimental energies. The nature of each transition and the degree to which it contributes are shown beside each calculated state. Agreement between the observed and calculated positions of the spectral bands is satisfactory, taking into account the approximations involved in the Pople method and the fact that wholly theoretical electron repulsion integrals make no allowance for electron correlation.

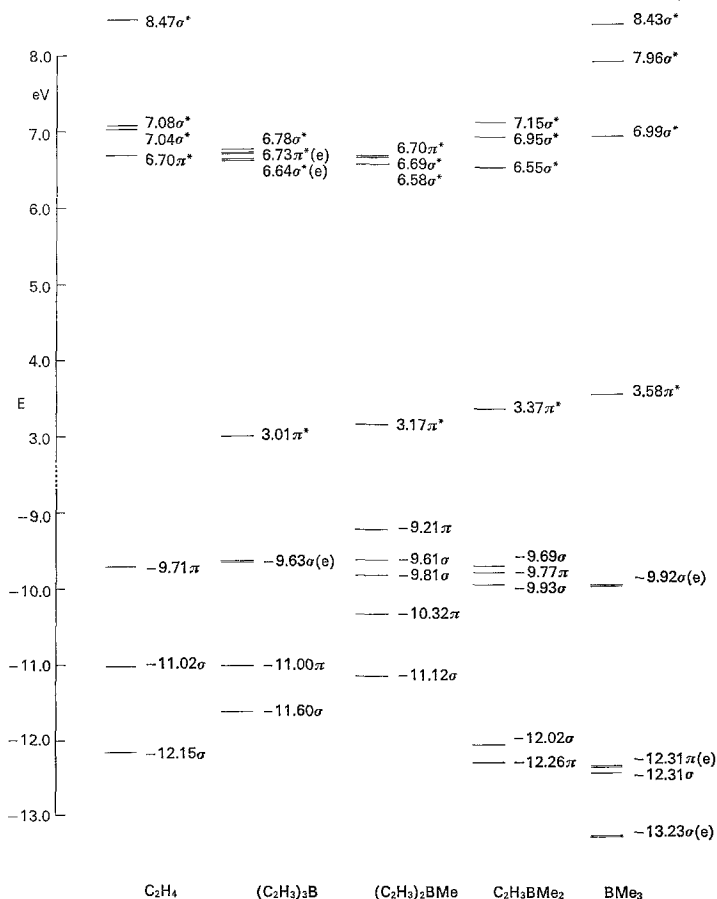


Fig. 1. σ and π energy levels of ethylene and vinylboranes

Table 1. Lowest σ and π Electronic States of Organoboranes

	First excited Singlet		Higher Singlets	
	Exptl.	Calc'd.	Exptl.	Calc'd.
$(C_2H_5)_3B$	4.702 ^a	5.49 ($\sigma \rightarrow \pi$; 0.98; ¹ E'')	5.308 ^a	6.48 ($\pi \rightarrow \pi^*$; 0.96, ¹ E')
$(C_2H_5)_2BMe$	4.925 ^a	5.34, 5.43 ($\sigma \rightarrow \pi^*$; 0.95, 0.95, Sym.)	5.619 ^a	6.34 ($\pi \rightarrow \pi^*$; 0.95, ¹ B ₁) 6.64 ($\pi \rightarrow \sigma^*$)
$C_2H_3BMe_2$	5.437 ^a	5.28, 5.43 ($\sigma \rightarrow \pi^*$; 0.95, 0.96, ¹ A'')	6.325 ^a	6.55 ($\pi \rightarrow \sigma^*$; 0.77, ¹ A'')
BMe_3	5.4 - 5.6 ^b	5.35 ($\sigma \rightarrow \pi^*$; 0.98; ¹ E'')	7.1 ^b	6.82 ($\pi \rightarrow \pi^*$; 0.95, ¹ A')
C_2H_4	~6.0 ^d	5.84 ($\pi \rightarrow \sigma^*$; ¹ B _{2g})	7.6 ^c	8.67 ($\pi \rightarrow \sigma^*$; 0.64, ¹ A'')
				8.99 ($\pi \rightarrow \pi^*$; 0.94, ¹ E')
				8.87 ($\sigma \rightarrow \pi^*$; 0.94, ¹ A'')
				7.01 ($\sigma \rightarrow \pi^*$; ¹ B _{2g})
				7.11 ($\sigma \rightarrow \pi^*$; ¹ B _{3g})

^a Ref. [4].^b Ref. [6].^c Ref. [3].^d Ref. [7].

Table 2. Total Electron Distribution in Organoboranes

	boron		vinyl carbon (1)		vinyl carbon (2)		vinyl hydrogens			methyl carbon			methyl hydrogens		
	σ	π	σ	π	σ	π	σ	π	c	σ	π	a	b	c	
$(C_2H_5)_3B$	2.641	0.300	3.062	1.071	3.275	0.829	0.946	0.926	0.911	—	—	—	—	—	
$(C_2H_5)_2BMe$	2.684	0.260	3.062	1.078	3.285	0.815	0.946	0.925	0.911	3.250	0.938	0.948	0.933	0.956	
$C_2H_3BMe_2$	2.731	0.213	3.061	1.083	3.293	0.999	0.938	0.924	0.911	3.253	0.939	0.956	0.931	0.948	
BMe_3	2.784	0.156	—	—	—	—	—	—	—	3.255	0.942	0.948	0.927	0.948	

The lowest energy excited states of all the boranes involve transitions from σ to π^* molecular orbitals. This contrasts with the ethylene case where the lowest excited singlet state is of B_{3g} symmetry and has $\pi \rightarrow \sigma^*$ character. The latter calculation also agrees with previous work [7] in that several $\sigma \rightarrow \pi^*$ transitions with energies lower than the well-known $\pi \rightarrow \pi^*$ state are revealed. In the vinylboranes the energies of the *filled* orbitals (both σ and π) are strikingly similar to those of ethylene (Fig. 1) whereas the energy of the first virtual π orbital is some 3 – 4 eV lower than that of ethylene. This stems from the strong mixing which takes place between the antibonding ethylene orbitals and the boron p_z orbital. The remaining π^* orbitals in these compounds do not differ significantly in energy from those in ethylene. This means that both the $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in the vinylmethylboranes will be considerably red-shifted with respect to ethylene whilst the $\pi \rightarrow \sigma^*$ states will be only slightly affected. Transitions of the $\pi \rightarrow \pi^*$ type in these compounds have been discussed in detail elsewhere [1].

We conclude that the low-energy weak bands observed in the spectra of vinylmethylboranes are due to transitions from $\sigma \rightarrow \pi^*$ levels. In all cases the particular σ orbitals involved are mainly centred on the boron-carbon skeleton and do not involve the C–H bonds. The present calculations thus substantiate the cruder argument advanced previously to support the same hypothesis [1].

Electron Distribution

The electron density distributions throughout the molecules (Table 2 and Fig. 2) exhibit an interesting feature: the *total* electron population on boron remains sensibly constant because when a methyl group is substituted for a vinyl

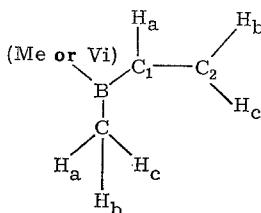


Fig. 2. Organoborane skeleton

group, the σ component in the density matrix increases whereas the π component decreases. The electron densities indicate that there is a movement of charge to the π orbital of boron. This is of the same magnitude as we have calculated from the Pariser-Parr-Pople method [4] which considers π electrons only.

Acknowledgement. We thank the Science Research Council for financial support.

References

1. ARMSTRONG, D. R., u. P. G. PERKINS: *Theoret. chim. Acta* (Berl.) **4**, 352; **5**, 11 (1966).
2. BERRY, R. S.: *J. chem. Physics* **38**, 1934 (1963).
3. MOSKOWITZ, J. W., and M. C. HARRISON: *J. chem. Physics* **42**, 1726 (1965).
4. PARISER, R., and R. G. PARR: *J. chem. Physics* **21**, 466 (1953).
5. POPLE, J. A.: *Trans. Faraday Soc.* **49**, 1375 (1953).
5. POPLE, J. A., D. P. SANTRY, and G. A. SEGAL: *J. chem. Physics* **43**, S 129 (1965).

6. RAMSEY, B. G.: *J. physic. Chem.* **70**, 4097 (1966).
7. ROBIN, M. B., u. R. R. HART: *Theoret. chim. Acta (Berl.)* **3**, 375 (1965).
— —, and N. A. KUEBLER: *J. chem. Physics* **44**, 1803 (1966).

Dr. P. G. PERKINS
Department of Chemistry
University of Newcastle upon Tyne
Newcastle upon Tyne, England