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

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Calculations are presented of the energies of the ground and excited $\sigma$ and $\pi$ 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.

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 $\sigma$ and $\pi$ excited states calculated within the semi-empirical framework of the Pople-Segal-Santry method [5].

Method

The energies, $e_i$, of the $\sigma$ and $\pi$ molecular orbitals are obtained by solution of the determinantal equation,

$$| F - \varepsilon S | = 0$$

where $F$ is the Hartree-Fock Matrix with elements,

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

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

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

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

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

$$H_{\mu \nu} = K \beta_{AB} S_{\mu \nu}.$$
Here $\beta_{2B}$ 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 $\psi_{i\rightarrow f}$ is given by,

$$1/2 E(\psi_{i\rightarrow f}) - E_0 = \varepsilon_f - \varepsilon_i + \langle ii | jj \rangle + \langle ij | ji \rangle \pm \langle ij | ij \rangle.$$  

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. $\pi$ and $\sigma$ energy levels of ethylene and vinylboranes](image-url)