Some Notes on the Electronic Spectra of Borazol

In their first paper on the semi-empirical antisymmetric molecular orbital configuration interaction (A. S. M. O.-C. I.) method for the calculation of the electronic spectra of unsaturated organic compounds, PARISER and PARR[1]) suggested that the method should be well suited for inorganic systems, especially those showing aromatic character. As a first step towards that direction we have used the method in the calculation of pi-electronic energy levels of borazol.

In order to calculate the energy levels of a molecule according to PARISER and PARR's scheme we need to know (i) the geometry of the molecule, (ii) the energy formulae over the atomic integrals, (iii) bicentric integrals of the type $(\mu\mu/\nu\nu)$ and (iv) the mono-centric integrals of the type $(\mu\mu/\mu\mu)$. The resonance integral, β, is considered an empirical parameter and is estimated from the experimental data.

(i) Geometry of the molecule: The electron diffraction investigation[2]) on borazol shows the molecule to be planar with all the ring bonds equal to 1·44 Å and the bond angles equal to 120°. (ii) Energy formulae: Since borazol is iso-pi electronic with and has the same symmetry as s-triazine, the energy formulae given by PARISER and PARR for s-triazine have been used in the calculation of various possible electronic transitions in borazol. (iii) Bicentric integrals: these were evaluated using uniformly charged sphere model formulae of Pariser and Parr. (iv) Mono-centric integrals· Pariser and Parr in their calculation evaluated the mono-centric integrals from the ionisation energy and the electron affinity of the atoms in their valence state. In the accepted structure of borazol, boron and nitrogen atoms are in the state B^- and N^+ respectively, for which experimental values of ionisation energies and electron affinities are not known.

It was found that if the mono-centric integrals were evaluated using Roothaan's equation or using the experimental ionisation energy and electron affinity of neutral boron and nitrogen, no adjustment of resonance integral, β, could reproduce the experimental data even approximately. On the other hand if the mono-centric (BB/BB) and (NN/NN) integrals are set equal to 6·84 eV and 10·27 eV respectively (i.e. about 2 eV less than the calculated values), and the resonance integral is evaluated spectrally from A_2 transition ($\beta = -3{\cdot}23$ eV), the agreement between the calculated and the experimental values are fair as shown by the following Table.

Transition	$^1E_1$	$^1A_1$	$^1A_2$
Energy (eV) experimental[4] .	7·70	6·86	6·50
Energy (eV) calculated . . .	7·98	6·80	6·50

It appears that in this case at least mono-centric integrals must be given rather low values as compared to the theoretical ones. The reason for this is not far to seek. If we are to consider borazol as a pi-electronic system, we must assume that the molecule has been formed from B^- and N^+ atoms. On the other hand, in order to justify the weakly polar character of the compound we must further assume that extensive charge reorganisation has taken place after molecule formation. Under these circumstances the "atoms-in-molecule" approximation is bound to fail. In fact it has been suggested[5] that for hetero-compounds mono-centric integrals in Pariser and Parr's scheme must be considered as empirical parameters.

Our sincere thanks are due to Prof. C. A. Coulson, Oxford, and Dr. S.L. Altman for valuable suggestions.

Department of Chemistry, University College of Science, Calcutta-9, India

Jashbhai Chandubhai Patel*) and Sadhan Basu

Eingegangen am 14. April 1960

---

*) Present Address: Patel Estate, Goregaon East, Bombay, India.

[1] Pariser, R., and R. Parr: J. Chem. Physics **21**, 466 (1953). — [2] Bauer: J. Amer. Chem. Soc. **60**, 524 (1938). — [3] Roothaan, C.C.T.: J. Chem. Physics **19**, 1445 (1951). — [4] Rector, C.W., G.W. Schaeffer and J.R. Platt: J. Chem. Physics **17**, 5 (1949). — [5] Peradejordi, J.: Calcul des Fonctions d'Onde Moléculaire, Colloques Internationaux de CNRS, 1958, p. 247.