The Electronic Structure of Boron Trifluoride

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Summary The electronic structure of BF_3 has been calculated by a self-consistent field method using an extended set of Gaussian-type basis functions.

THERE are a number of interesting aspects of the chemistry of boron trifluoride which can be correlated with its detailed electronic structure. Attempts to calculate the latter by the Pariser–Parr–Pople method[1,2] have, however, yielded only limited information, because only the π-electrons of the molecule were treated explicitly. In the present work we have circumvented the difficulties and approximations of the latter method by calculating the electronic structure of the compound *ab initio* using the self-consistent field method. This included all electrons described by extended basis sets of 64 Gaussian-type orbitals[3] comprising 7 GTO's for the *s*-orbitals of boron and fluorine and 3 for each 2*p*-orbital of the elements. We summarise the main results of the treatment below.

Molecular Energies

We assumed the experimental value, 1·31 Å, for the B–F bond length. The calculated equilibrium value, r_e, using a smaller (5,2) basis set and varying the interatomic distance to produce minimum total energy, was 1·306 Å. The molecular energies; electronic, nuclear, and total were −433·657006, +111·204919, and −322·452087 au., respectively, for the (7,3) basis. The total binding energy of the molecule, corrected for correlation effects[4] and zero-point energy was calculated to be 437 kcal.mole^{-1}. This compares well with the recent experimental value[5] of 459·5 kcal.mole^{-1}.

The planar–pyramidal *reorganisation energy*, which accounts for both σ and π effects due to bond stretching and angle bending has not previously been obtained with any degree of rigour. A further calculation on the C_{3v} (reorganised) form of the molecule produced a value of 34·2 kcal.mole^{-1} for this quantity. Similarly, by restricting the π electrons in the calculation to the fluorine atoms the "vertical" reorganisation energy was found to be 50·4 kcal.mole^{-1}. This is the π energy of the B–F bond alone and agrees well with that calculated by Armstrong and Perkins[1] by the semi-empirical method.[2] Since the π energy exceeds the reorganisation energy it is clear that there must be a regain of σ energy amounting to 16·2 kcal.mole^{-1} on reorganisation. This turns out to stem mainly from new '$\sigma \rightarrow \pi$' interactions in the pyramidal form.

The highest bonding orbital has energy −18·24 ev and is of σ type whilst the lowest virtual orbital is centred mainly on boron and is of $a_2''(\pi)$ symmetry. The latter result is the same as predicted by the π-only calculation.[1]

Charge Distribution

As might be expected electronic charge is displaced towards the fluorines, and boron has a nett charge of +1·419 units. The p_π orbital of boron is, however, partly filled and has a population of 0·318 electrons (*cf.* 0·309[1]).

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