The Electronic Structure of Borazine

By D. R. ARMSTRONG
(*Computing Laboratory, The University, Newcastle upon Tyne*)
and D. T. CLARK*
(*Department of Chemistry, The University, Durham*)

Summary Non-empirical LCAO–MO–SCF calculations have been performed on planar (D_{3h}) and non-planar (C_2) configurations of borazine; it is shown that the planar structure is energetically preferred by a substantial margin.

THE electronic structure of borazine has attracted the attention of chemists because of its isoelectronic relationship with the prototype for aromatic systems, benzene. Early electron diffraction studies[1] indicated a planar D_{3h} structure and subsequent semi-empirical treatments of bonding have assumed this configuration.[2] However, a recent re-examination of the structure,[3] in an electron diffraction study gave the somewhat surprising result that an equally good fit to the experimental data could be obtained with a non-planar "twist boat" configuration possessing C_2 symmetry. An all valence electron CNDO/2–SCF–MO investigation of the two models indicates a small (1·6 kcal./mole) energetic preference for the planar D_{3h} configuration and does not rule out the possibility of the non-planar C_2 form. We now report that on the basis of a non-empirical LCAO–MO–SCF investigation the non-planar C_2 model for borazine can be ruled out and that the planar D_{3h} configuration is energetically preferred by a substantial margin. The calculations have been carried out using the IBMOL IV computer program.† The basis set consisted of $7s$ and $3p$[4] atomic Gaussian functions for both boron and nitrogen atoms and $3s$ atomic Gaussian functions for the hydrogens. The 114 basis functions were then reduced to 42 contracted Gaussians.

The energies for both models are presented in Table 1.

TABLE 1

Energies of the two configurations of borazine (*in a.u.*)

	Planar D_{3h}	Non-planar C_2
Electronic energy	−436·7149	−437·1257
Nuclear energy	196·1889	196·6742
Total energy	−240·5260	−240·4515

The planar D_{3h} model is lower in energy than the non-planar C_2 model, and the magnitude of the energy difference, 40·5 kcal./mole, effectively rules out the non-planar configuration. Bending the N–H bonds out of the plane considerably reduces the π delocalization of the lone pairs on nitrogen and this is energetically expensive. This is readily shown by calculating the vertical reorganization energy in going from borazine (I) to a structure (II) in which the lone pairs are localized on the nitrogens. The energy difference (I) → (II) amounts to 119 kcal./mole.

A further point of comparison between the non-empirical and semi-empirical calculations is the assignment of the highest occupied orbital. The CNDO/2 calculation indicates that the highest occupied orbitals are σ type (E') with π type (E'') orbitals 0·93 ev lower in energy. Although

---

† A Veillard "IBMOL Version 4" Special I.B.M. Technical Report, San Jose, California, 1968.

the energy difference between the highest occupied σ and π orbitals is almost the same for the non-empirical calculation (0·89 ev) the assignment is reversed and the π orbitals (E'') have the highest energy (12·70 ev). It seems unlikely that correlation energy corrections would reverse this assignment and in fact the photoelectron spectrum of borazine has been interpreted[5] in this way, with the first ionization corresponding to removal of a π electron.

TABLE 2

Electronic population for the planar D_{3h} *model of borazine*

Nitrogen	σ	6·144
	π	1·591
	Total	7·735
Boron	σ	4·118
	π	0·409
	Total	4·527
Hydrogen (N)		0·701
Hydrogen (B)		1·037

The results of a Mulliken population analysis for planar D_{3h} borazine are shown in Table 2. This reveals that the nitrogen atoms possess large negative charges (—0·735*e*) arising from a large σ electron drift (1·144*e*) from the boron atoms (0·422*e*) and from hydrogens (0·299*e*) attached to nitrogen. Superimposed on this is a substantial π electron transfer from nitrogen to boron (0·409*e*). This is an overall positive charge (0·473*e*) on the boron atoms with a σ contribution of (0·884*e*).

(*Received, November* 25*th,* 1969; *Com.* 1791.)

---

[1] S. H. Bauer, *J. Amer. Chem. Soc.*, 1938, **60**, 524.

[2] *Cf.* (a) R. Hoffman, *J. Chem. Phys.*, 1964, **40**, 2474; (b) D. W. Davies, *Trans. Faraday Soc.*, 1968, **64**, 2881; (c) J. F. Labarre, M. Graffeuil, J. P. Faucher, M. Pasdeloup, and J. P. Laurent, *Theor. Chim. Acta*, 1968, **11**, 423.

[3] W. Harshbarger, G. Lee, R. F. Porter, and S. H. Bauer, *Inorg. Chem.*, 1969, 8, 1683.

[4] D. R. Whitman and C. J. Hornbach, *J. Chem. Phys.*, 1969, **51**, 398.

[5] Dr. D. R. Lloyd, University of Birmingham, personal communication.