

The Electronic Structure of Aminodiborane

D. R. ARMSTRONG

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, Scotland, U.K.

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The electronic structure of aminodiborane (ADB) is presented. The charge distribution reveals that there is electron donation to the amino group from the diborane moiety. The main component of the B–N bond is the in-plane interaction between the boron p_x orbital, perpendicular to the B–B bond (y axis), and the nitrogen p_y orbital. The π bonding within the BBN ring is negligible. Tilting the BH_2 groups by 16.8° from a plane perpendicular to the C_2 axis stabilises the molecular energy by 24.2 kJ mol^{-1} .

Introduction

One of the products arising from the reaction of ammonia and diborane is aminodiborane (ADB)¹. Due to previous experimental difficulties and instrumental deficiencies, the structure has only recently been obtained by a microwave spectroscopic determination¹. The results of this investigation revealed several interesting points. It is found that ADB has substantially different structural parameters from those of the closely related diborane. In particular, the B–B and the B–H_{br} bonds are much longer in ADB, while the BH_2 groups of $B_2H_5NH_2$ are tilted by 16.8° from the plane perpendicular to the C_2 symmetry axis. The B–N bonds span 15.58 nm , a length which seems to indicate that there are boron–nitrogen coordination bonds present. A further point of note is the value of the $\angle BNB$ angle which measures 76° and will, it is thought, cause steric hindrance between the bonds. The electronic distribution throughout the molecule is, therefore, of interest and the purpose of this publication is to present the results of calculational probes into its structure.

Method

The calculations were performed within a non-empirical LCAO–MO–SCF framework. A double-zeta basis set was constructed in which each atomic orbital was represented by two Slater orbitals. Each Slater orbital was simulated by a contracted set of four Gaussian orbitals². The orbital exponents were extract-

ed from the work of Clementi³, while the molecular dimensions of $B_2H_5NH_2$ were obtained from reference 1.

Results and Discussion

The gross atomic and overlap populations are presented in Table I. It can be seen that the nitrogen atom is negatively charged, with the extra electrons originating from the amino hydrogen atoms (0.359 e/atom) and the diborane group (0.227 e). A breakdown of the nitrogen p -orbital population reveals that the p_x orbital lying along the C_2 axis contains 1.39 electrons, while the second p orbital in the plane, p_y , attracts 1.60 electrons. The p_z orbital, perpendicular to the BBN plane, is filled by 1.35 electrons. It is surprising

TABLE I. The Electronic Energy and Distribution of the Tilted and Non-tilted Geometry of $B_2H_5NH_2$.

	$B_2H_5NH_2$ Tilted	$B_2H_5NH_2$ Non-tilted
Electronic Energy (au)	-179.69462	-179.90007
Nuclear Energy (au)	72.09346	72.30812
Total Energy (au)	-107.60116	-107.59195
Electron Densities		
B s	2.913	2.916
p	1.969	1.963
total	4.882	4.879
N s	3.610	3.602
p	4.335	4.324
total	7.945	7.926
H _{br}	1.040	1.055
H(N)	0.641	0.646
H(B)	0.992	0.992
Bond Populations		
B–N	0.217	0.190
B–H	0.880	0.880
B–H _{br}	0.436	0.440
N–H	0.684	0.690
B–B	0.002	0.023

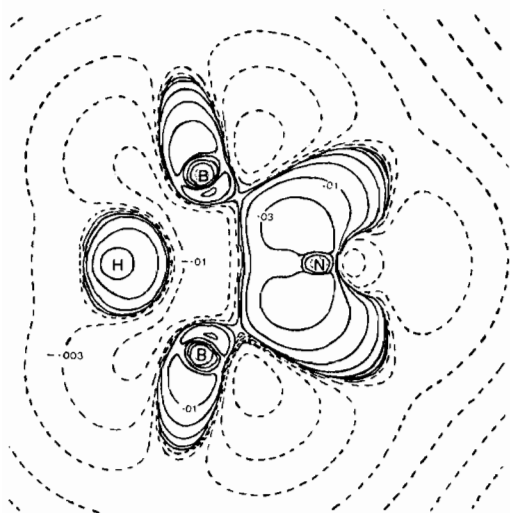


Figure 1. Electron density difference contours for $B_2H_5NH_2$, a section containing the BBN triangle. The broken lines indicate negative electron density differences, while the unbroken lines represent positive electron density differences.

that the p orbital, which at first glance would appear not to be involved in the bonding, is the most heavily populated. The BH_2 portions each bear a positive charge (0.134), with boron possessing the majority of this charge. The p -orbital populations of boron show a variable occupation, with the p_y and p_z orbitals possessing 0.56 and 1.02 electrons, respectively, while the p_x orbital contains 0.39 electrons. The more heavily populated boron p orbitals are involved in boron-hydrogen bonding. The hydrogen atom bears a small negative charge. This charge distribution confers on ADB a dipole moment of 2.92D, which is in reasonable agreement with the experimentally obtained value of 2.67D¹.

The bond populations indicate that the bonding in diborane is modified by substitution of an amino group for a bridging hydrogen atom. The boron-boron bond, although weak in diborane (0.147), becomes non-existent in ADB. The boron-hydrogen bridging bonds are more populated in $B_2H_5NH_2$ (.436) than B_2H_6 (.381). The $B-H_t$ bond populations, however, are not altered by substitution. The B-N bonds are not too heavily populated and are certainly smaller than expected for single B-N bonds. It is the $B_{p_x}-N_{p_x}$ and $B_{p_x}-N_s$ portions which are the important constituents. Therefore, the bonding interactions are concentrated in the plane of the ring as the π -bonding components of the BBN triangle are antibonding. Further information about the bonding situation is obtained from an electron density atom difference plot of a section con-

taining the BBN triangle (Figure 1). The amino group does not participate in three-centre BBN bonds as we find that the increase in electron density adjacent to the B-N bonds occurs outwith the BBN triangle. There is a diminution of electron density between the boron atoms, while there is a build-up of electron density over most of the B-H_{br} bonds.

The highest filled orbital of ADB with an energy of -0.476 au is an antisymmetric combination of the p_z orbitals on the boron atoms plus a symmetry-related combination of the orbitals of the terminal hydrogen atoms which are bonded to boron. The first virtual orbital is largely composed of a combination of boron p orbitals lying in the BBN plane and tangential to the BBN triangle. Hence, both nucleophilic and electrophilic reagents are likely to react with ADB via the boron atoms if their mode of attack involves the use of the first virtual and highest filled orbital, respectively.

In order to rationalise the tilted configuration adopted by the BH_2 groups, a second calculation was performed in which the BH_2 groups occupied a plane perpendicular to the C_2 axis. It is found that the non-tilted geometry is less stable than the tilted configuration by 24.2 kJ mol⁻¹. The electronic distribution of the non-tilted geometry was critically examined for any reason for the relative instability of the structure. The atomic populations of both species are found to be similar. The overlap population data, however, reveal that the B-N bonds are less populated, while the B-H_{br} and B-B bond populations are increased by the adoption of a non-tilted position by the BH_2 groups. Scrutiny of the components of these bond populations indicates that, when tilting occurs, the boron s orbitals become less involved in B-B bonding and more implicated in B-N bonding. Inclination of the BH_2 groups also affects the interactions of the boron p_y orbitals, which vary in the opposite direction to that of the boron s orbital although the changes in bond populations are not as great as those occurring with the boron s orbital. Tilting of the BH_2 groups provides boron sites which are more pyramidal and therefore produces environments which have a closer resemblance to the situation in traditional donor-acceptor compounds of boron. Hence, stronger boron-nitrogen bonds are obtained.

References

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