# Electronic Structure of Aziridine–Borane

**John A. Kroll[1] and Donald D. Shillady***

*Contribution from the Chemistry Department, Virginia Commonwealth University, Richmond, Virginia 23220.* *Received August 26, 1972*

**Abstract:** A very minimal gaussian lobe basis has been used to analyze the electron populations in aziridine–borane. Calibration against STO results for $BH_3NH_3$ shows good agreement. Comparison is made with CNDO/2 and INDO results for the same molecule. It is concluded that the BN bond in aziridine–borane is very covalent due to substantial donation of the amino lone pair to the $BH_3$ group in classical dative bond fashion, but that a smaller effect is also present in which endocyclic charge transfer occurs from the endo methylene protons to the endo borane proton. The *ab initio* energy in this very minimal basis was found to be −158.10167 hartrees and the dipole moment 6.294 D compared with the experimental value of 4.45 D.

Aziridine–borane is a very interesting compound which is isoelectronic with methylcyclopropane, but which has been under study as a potential radical scavenger and radioprotective agent[2,3] due to its strong reducing tendency. The published chemistry of this type of alkylamine–borane is less extensive than that of the corresponding isoelectronic hydrocarbons, but the work of Akerfeldt, *et al.*,[2] makes it clear that analogies to cyclopropylmethyl cation[4] rearrangements must be made very carefully, if at all.

The work we are reporting here is at a preliminary level due to our limited computational resources, and certainly our calculations can be improved upon. However, the molecule is a sufficient size that it may be some time before more accurate work is carried out and in the mean time our analysis should be helpful in understanding the overall charge distribution and bonding in the aziridine–borane ground state.

We have used three methods in studying aziridine–borane. Both the CNDO/2 and INDO semiempirical methods of Pople, *et al.*,[5] were used based on the CNINDO program of Dobosh.[6] We have also carried out *ab initio* SCF–LCAO–MO calculations in a very minimal gaussian lobe basis set adopted from the work of Sambe.[7] In order to reduce the computation to a manageable level, we have used a basis so minimal that we measure its success by its ability to nearly match a minimal basis set of exponential Slater-type orbitals (STO). In this sense we believe we have been successful, but of course an extended basis set of the Whitten double-$\zeta$[8] level would bring great improvements in the energy. Nevertheless, we believe our charge densities are essentially credible, especially since our comparison to Palke's[9] STO treatment of borazane ($BH_3NH_3$) is quite reasonable.

## Computational Methods

The CNINDO program has been described elsewhere in great detail,[5] and we will merely report the atomic charge densities and the dipole moments we found. We should say, however, that we do not regard these values lightly as the accumulated evidence of a wide variety of molecular systems treated by both CNDO/2 and INDO methods[5] shows substantial credibility.

The *ab initio* SCF calculations used what we call our (4G) basis set. This means that Sambe[7] hydrogenic mimics of four contracted gaussians were used for the 1s and 2p (two spheres per lobe for a total of four spheres per orbital) functions. For the 2s orbitals only a single gaussian of exponent 0.02 was scaled, while the hydrogen 1s orbitals used only the Sambe 2 gaussian mimic. We note in passing that Clark[10] used a similar 1s (2G) orbital in his treatment of cyclopropane and obtained reasonable results. Thus we expect our energy is not quite as good as what one might obtain from Pople's[11] 4G STO gaussian mimics, but we believe our charge densities show essentially the same trends. The *ab initio* work was carried out on the VCU IBM 370/145 using a program written by one of us (D. S.) which has been described elsewhere;[12] the only modification being that all the gaussian integrals were computed using the IBM intrinsic DERF and we believe our integrals are numerically accurate to $\pm 1 \times 10^{-14}$ au. The diagonalization tolerance was $\pm 1 \times 10^{-10}$ and double-precision arithmetic was used throughout.

The Sambe[7] mimics were scaled as if they were nodeless STO's using the orbital exponents optimized for $BH_3$–$NH_3$ by Palke's[9] and Clementi's [13]best atom $\zeta$'s for the carbon atoms. A value of 1.2 was used as the effective screening constant for the four hydrogen 1s (2G) mimics in the $-CH_2-$ groups.

## Borazane ($BH_3$–$NH_3$) Calibration

A recent series of calculations by Palke[9] provided optimized screening constants for the aminoborane portion of the molecule. We also repeated two of Palke's calculations using our basis for comparison. We chose his staggered and eclipsed "experimental"

---

[1] Submitted in fulfillment of undergraduate Senior Research, 1971–1972.

[2] S. Akerfeldt, K. Wahlberg, and M. Hellstrom, *Acta Chem. Scand.*, 23, 115 (1969).

[3] (a) H. Ringertz, *ibid.*, 23, 137 (1969); (b) R. L. Williams, *ibid.*, 23, 149 (1969).

[4] H. S. Tremper and D. D. Shillady, *J. Amer. Chem. Soc.*, **91**, 6341 (1969).

[5] J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

[6] P. A. Dobosh, Program No. 141, CNINDO, available from the Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind. 47401.

[7] H. Sambe, *J. Chem. Phys.*, 42, 1732 (1965).

[8] J. L. Whitten, *ibid.*, **44**, 359 (1966).

[9] W. E. Palke, *ibid.*, **56**, 5308 (1972).

[10] D. T. Clark, *Theor. Chim. Acta*, **15**, 225 (1969).

[11] R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 52, 5001 (1970).

[12] D. D. Shillady and C. Trindle, *Int. J. Quantum Chem.*, 1972 Sanibel Symposium, in press.

[13] E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).

geometries. Our charge densities and dipole moments are very close to his as shown in Table I and even our rotational barrier of 0.004726 au is very close to his 0.004675 au. Considering the brevity of our 1s (2G) functions, which each have an error of about 0.02 au compared with an STO 1s function, and limited 2p functions, the agreement between our total energy and Palke's is surprisingly good. While neither our nor Palke's dipole moment is very good, the calculation by Peyerimhoff and Buenker[14] used a much larger basis set and configuration interaction and they were only able to reduce the dipole moment to 5.71 D compared with the experimental value of 4.92 D.[15] Since the $CH_2$ groups are not as highly involved in the dative bond as B and N, we believe the Clementi $\zeta$'s are adequate for carbon in aziridine–borane, but the use of Palke's optimized exponents and the ability of our small basis to mimic STO's lead us to believe that we have done nearly as well as our basis will allow in our representation of the dative bond in aziridine–borane as well as borazane.

**Table I.** $BH_3NH_3$ Basis Set Comparison

| Orbital | $\zeta$ | Palke[9] population | Atom totals | This work population | Atom totals |
|---|---|---|---|---|---|
| H(B) 1s | 1.080 | 1.195 | H(B) 1.195 | 1.181 | H(B) 1.181 |
| B 1s | 4.683 | 1.993 | | 1.992 | |
| B 2s | 1.428 | 0.811 | | 0.894 | |
| B $2p_z$ | 1.449 | 0.486 | | 0.467 | |
| B $2p_x/2p_y$ | 1.449 | 0.811 | B 4.912 | 0.792 | B 4.937 |
| N 1s | 6.672 | 1.997 | | 1.995 | |
| N 2s | 2.019 | 1.479 | | 1.664 | |
| N $2p_z$ | 2.061 | 1.393 | | 1.355 | |
| N $2p_x/2p_y$ | 2.061 | 1.131 | N 7.131 | 1.107 | N 7.228 |
| H(N) 1s | 1.234 | 0.790 | H(N) 0.790 | 0.763 | H(N) 0.763 |
| Energy (staggered), au | | −82.461127 | | −82.043595 | |
| Energy (eclipsed), au | | −82.456452 | | −82.038869 | |
| Barrier, au | | 0.004675 | | 0.004726 | |
| Dipole (staggered), D | | 6.673[a] | | 6.789 | |
| Dipole (eclipsed), D | | 6.775[a] | | 6.828 | |

[a] For slightly different "equilibrium" geometry.

## Structure of Aziridine–Borane

Although the nmr work of Williams[3b] shows only a broad peak for the $^1H$ resonance due to the $-BH_3$ group, which is probably rotating in solution, the crystal structure of Ringertz[3a] shows a shortened B–H bond for the proton in the plane of symmetry. We adopted the $C_s$ structure with this shortened bond and the atomic coordinates we used are given in Table II. We carried out CNDO/2 and INDO calculations on both the crystal structure and a hypothetical structure with equivalent B–H bond lengths. We noted that the non-equivalent H atom charge in Table III is not as different as one might expect for a shorter bond, indicating interplay of this bond with the three-membered ring. Thus we chose the crystal structure for the *ab initio* calculation in the belief that this is the preferred geometry of the molecule at low energy.

**Table II.** Nuclear Coordinates of Aziridine–Borane (Bohrs)[a]

| Atom | No. | *X* | *Y* | *Z* |
|---|---|---|---|---|
| B | 1 | 0.0 | 0.0 | 0.0 |
| N | 2 | 0.0 | 0.0 | 2.944222 |
| H′(B) | 3 | −1.914963 | 0.0 | −0.442102 |
| H(B) | 4 | 1.112459 | −1.556878 | −0.812218 |
| H(B) | 5 | 1.112459 | 1.556878 | −0.812218 |
| H(N) | 6 | 1.768663 | 0.0 | 3.884631 |
| C | 7 | −1.891349 | 1.379514 | 4.369649 |
| C | 8 | −1.891349 | −1.379514 | 4.369649 |
| H(C) | 9 | −2.441471 | −2.186144 | 2.729895 |
| H(C) | 10 | −2.441471 | 2.186144 | 2.729895 |
| H′(C) | 11 | −1.841337 | −1.959645 | 6.266080 |
| H′(C) | 12 | −1.841337 | 1.959645 | 6.266080 |

[a] We have used 1 Bohr = 0.529172 Å.

**Table III.** Semiempirical Results for Aziridine–Borane

| Atom | Crystal structure CNDO/2 charge | Crystal structure INDO charge | Tetrahedral $BH_3$ group CNDO/2 charge | Tetrahedral $BH_3$ group INDO charge |
|---|---|---|---|---|
| B | 3.1528 | 3.1186 | 3.1494 | 3.1156 |
| N | 4.9082 | 4.8752 | 4.9105 | 4.8778 |
| H′(B) | 1.1086 | 1.1279 | 1.1124 | 1.1321 |
| H(B) | 1.1053 | 1.1267 | 1.1046 | 1.1255 |
| H(N) | 0.9082 | 0.9247 | 0.9050 | 0.9211 |
| C | 3.9881 | 3.9333 | 3.9882 | 3.9336 |
| H(C) | 0.9176 | 0.9451 | 0.9179 | 0.9453 |
| H′(C) | 0.9501 | 0.9717 | 0.9506 | 0.9723 |
| Valence shell energy, au | −35.814 | −34.682 | −35.827 | −34.695 |
| Dipole moment, D | 6.7438 | 6.8781 | 6.7380 | 6.8588 |

## Discussion of Results

In Table III we show the results of the CNDO/2 and INDO calculations and in Table IV we show the *ab initio* results. Note first that the semiempirical calculations both predict the crystal structure conformation to be lower in energy than the conformation with equivalent B–H bond lengths of 1.08 Å and tetrahedral angles.

**Table IV.** Aziridine–Borane *Ab Initio* Results[a]

| Orbital | $\zeta$ | Population | Atom total |
|---|---|---|---|
| B 1s | 4.683 | 1.993 | |
| B 2s | 1.428 | 0.779 | |
| B $2p_z$ | 1.449 | 0.436 | |
| B $2p_x$ | 1.449 | 0.870 | |
| B $2p_y$ | 1.449 | 0.883 | B 4.961 |
| N 1s | 6.672 | 1.995 | |
| N 2s | 2.019 | 1.667 | |
| N $2p_z$ | 2.061 | 1.210 | |
| N $2p_x$ | 2.061 | 1.024 | |
| N $2p_y$ | 2.061 | 1.122 | N 7.018 |
| H′(B) 1s | 1.08 | 1.167 | H′(B) 1.167 |
| H(B) 1s | 1.08 | 1.136 | H(B) 1.136 |
| H(N) 1s | 1.246 | 0.756 | H(N) 0.756 |
| C 1s | 5.673 | 1.995 | |
| C 2s | 1.608 | 1.266 | |
| C $2p_2$ | 1.568 | 1.170 | |
| C $2p_x$ | 1.568 | 1.018 | |
| C $2p_y$ | 1.568 | 0.983 | C 6.432 |
| H′(C) 1s | 1.200 | 0.725 | H′(C) 0.725 |
| H(C) 1s | 1.200 | 0.757 | H(C) 0.757 |

[a] Energy, au, −158.101697, experimental dipole moment 4.45 D,[1] dipole moment, D (0.284, 0.0, 6.288) = 6.294 total.

---

(14) S. D. Peyerimhoff and R. J. Buenker, *J. Chem. Phys.*, **49**, 312 (1968).

(15) J. R. Weaver, S. G. Shore, and R. W. Parry, *ibid.*, **29**, 432 (1958).

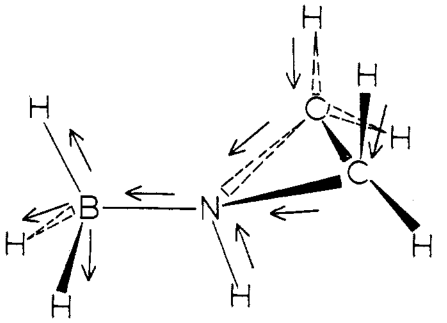

Figure 1.

This is why we chose the crystal structure geometry for the nonempirical calculations. The main points of agreement in all three calculations using the crystal structure are that the borane hydrogens have excess electron population and the amino hydrogen has a decided deficiency of electron density. The same trend is apparent in both this work and Palke's for $BH_3NH_3$. This has been interpreted previously by Peyerimhoff and Buenker[14] as being due to essentially the transfer of electron density from one set of hydrogens on N to the other set on B with the amino lone pair providing the B–N $\sigma$ bond *covalently* rather than by ionic transfer from $NH_3$ to $BH_3$ of the amino lone pair of electrons to form $(NH_3)^+(BH_3)^-$.

Our nonempirical charge totals indicate a slightly negative N and a slightly positive B with fairly negative ring C atoms. Our interpretation is that the B–N dative bond is very covalent and the charge transfer occurs in other bonds so as to keep the B–N bond covalent and hence strongly bound. We see the same trend of hyperconjugative transfer of electron density from the one amino hydrogen, as in borazane, to the $BH_3$ hydrogens. However, in aziridine–borane this effect is somewhat offset by the ability of the ring C atoms to maintain electrons in the ring system. In fact, our ring ($CH_2$) populations of 6.432 for carbon and the hydrogen values of 0.725 and 0.757 are quite close to the values Clark[10] obtained for cyclopropane using a very similar basis, 0.758 for H and 6.484 for C, although a minimal STO calculation by Stevens, *et al.*,[16] yielded values of 0.942 for H and 6.115 for C in the same molecule. Probably our C charges are more characteristic of the basis set than a true effect.

The main point of disagreement between the CNDO/2 and INDO results and the nonempirical results is in the respective charges on B and N. Strictly speaking the charge densities are computed differently due to the zero-differential-overlap approximation in CNDO/2 and INDO and deorthogonalization[17] might rectify the discrepancy. We did not carry out deorthogonalization because we felt the nonempirical results were more useful. It is now our belief that CNDO/2 and INDO are indeed valuable at a "suggestive" level, but that our (4G) results are qualitatively more correct even though they are admittedly crude compared with what one might expect with an extended basis. Thus, we believe that both B and N are very nearly neutral.

We note that the low $2p_y$ C–C population suggests that one source of the excess charge on the borane H atoms might be from the C–C $\sigma$ bond. However, assuming a strong similarity between our basis and that which Clark[10] used for aziridine, we see that the same short bond and even nearly the same C charges are found in aziridine itself; the electron density is shifted to the nitrogen in aziridine and Clark obtained 7.514 electrons on N ($\angle CNC = 60°$). Since we found only 7.018 electrons associated with N in the aziridine–borane complex, approximately 0.5 electrons have been donated to $BH_3$ by N in classical fashion. Evidently the low value of the $2p_y$ C–C population is a characteristic of aziridine itself rather than of the complex.

We note another effect which is not seen in aziridine alone; that of the difference in the endo and exo hydrogens on the $-CH_2-$ groups. Even when Clark[10] protonated the nitrogen lone pair in aziridine, the methylene hydrogens remained essentially equivalent in electron population. However our results show a difference of about 0.03 electrons less on the endo protons compared with the exo protons. The excess charge on the borane protons is about 0.439 electrons, but allowing for a boron deficiency of 0.039 yields a net of 0.400 electrons in excess on the $BH_3$ moiety. While this excess is nicely accounted for by the electron contribution from N, as expected classically, our results indicate that the net transfer is evidently enhanced along an "inner path" from the endo methylene protons to the unique borane proton. This interpretation is based on our populations on these three protons and the experimental observation of one short B–H bond.[2] This is indicated by the directional bonds in Figure 1.

We are not aware of any esca or uv data for the aziridine–borane complex so that we have no comparison available for the one-electron energy levels (available upon request). However, using Koopman's theorem, the lowest virtual orbital is 0.6773 hartrees above the highest occupied molecular orbital. Thus the lowest electronic transition could well be in the vacuum uv or at least the near uv. The nature of this transition in our basis set would be mainly back transfer of charge from the out-of-plane B–H $\sigma$ bonds to the ring $\sigma$-bond system. Both orbitals are ungerade with respect to the reflection plane of the $C_s$ point group. The intensity of the lowest triplet should be determined mainly by spin–orbit interactions since there are few symmetry restrictions to vibronic overlap or intensity borrowing from other spin-allowed transitions in such a low symmetry molecule. That is, there are very few special restrictions due to symmetry for the lowest singlet–triplet transition and spin–orbit coupling should be the dominant (most restrictive) mechanism. Thus this lower energy transition may occur in the near-uv or visible with an oscillator strength of the order of $10^{-6}$ using the ${}^3n \rightarrow \pi^*$ transition of monomeric acetic acid (also $C_s$ symmetry) from previous calculations[18] for a very rough comparison.

Unfortunately the above general analysis only indicates that it may be difficult to look at the electronic spectrum without resorting to the vacuum uv region. We have saved the computed two-electron integrals for future work in which we hope to carry out a small configuration-interaction calculation to determine the energy and oscillator strength of the lowest singlet

---

(16) R. M. Stevens, E. Switkes, E. A. Laws, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 93, 2603 (1971).

(17) D. D. Shillady, F. P. Billingsley, and J. E. Bloor, *Theor. Chem. Acta*, 21, 1 (1971).

(18) D. D. Shillady, Ph.D. Thesis, University of Virginia, 1970.

transition. This remains as future work when computer time becomes available.

### Conclusions

A very minimal basis of gaussian lobe functions has been used to analyze the electron populations in aziridine–borane. Simply put, the endo C–H protons on the ring and the amino proton relinquish electron density to the borane protons while the B–N bond is established as clearly covalent between B and N, which remain essentially neutral. The computed dipole moment of 6.294 D is high compared with the experimental value of 4.85 D but comparison with other minimum basis STO work on $BH_3NH_3$ indicates that the dipole would probably be high in either basis. It is worth noting that the computed dipole for aziridine–borane is less than that of borazane in agreement with experiment.

**Acknowledgments.** Much credit is due the Director of the Computer Center at Virginia Commonwealth University, Dr. Richard Grove, and his systems programmer, Mr. David Brydon, for making computer time available for this project. Dr. Carl Trindle of the University of Virginia was also helpful in setting up the *ab initio* program. We also thank the referee for making several interesting suggestions which helped interpret our results.

---

# An Electron Diffraction Study of *trans*-Cyclooctene

**R. M. Gavin, Jr.,* and Z. F. Wang**

*Contribution from the Department of Chemistry, Haverford College, Haverford, Pennsylvania 19041.* *Received July 8, 1972*

**Abstract:** The results of an electron diffraction study of *trans*-cyclooctene in the gas phase strongly imply that the molecule assumes a chair conformation rather than a crossed conformation. Models of both conformations were refined by least-squares analysis of the radial distribution curve. The standard deviation obtained from the chair model, 0.0533, was considerably lower than that for the crossed model, 0.0868. Structural parameters for both models are reported along with a discussion of the limitations intrinsic in the analysis. Bond lengths found are not appreciably different from those of noncyclic unstrained hydrocarbons. The effect of ring strain is apparent in the bond angles and the dihedral angles. Some internal bond angles are distorted 5–7° from comparable parameters found in unstrained molecules and there is a 23° twist about the double bond. The results obtained are compared with previous results reported from X-ray diffraction studies and from theoretical calculations. Difference curves obtained from the single isomer refinements imply that assuming a mixture of the chair and crossed geometries in the sample would not improve the fit of the data.

The molecular structure of *trans*-cyclooctene has been a subject of considerable interest since the highly strained molecule was synthesized in 1953 by Cope, *et al.*[1] Interest has centered on the manner in which ring strain is distributed among the internal coordinates, especially the twist about the carbon–carbon double bond, and whether the optically active molecule assumes a chair configuration, I, or a crossed configuration, II. A sketch of the two configurations is given in Figure 1.

Cope and coworkers[2] separated enantiomers and assigned an absolute configuration to the (−) species using chemical means, but they were not able to distinguish between conformations I and II. Manor, Shoemaker, and Parkes[3] performed an X-ray study of the complex used to separate enantiomers, dichloro[(−)-*trans*-cyclooctene][(+)-$\alpha$-methylbenzylamine]platinum(II), and confirmed the assignment of Cope.[2] Bowen[4] has reported the structure of a derivative of *trans*-cyclooctene, 9,9-dibromo-*trans*-bicyclo[6.1.0]nonane which also supports the work of Cope. A geometry with the crossed configuration was found in both X-ray studies.

Attempts have been made to use the circular dichroism spectrum of *trans*-cyclooctene to assign electronic transitions in the molecule and to provide supportive evidence for assignments of transitions in the ethylene molecule.[5–8] It has not been possible to come to definite conclusions about the transitions involved, however, because of a lack of accurate structural parameters on which to base calculations of rotational strengths. Most calculations have been made assuming a twist of 10° about the double bond, an angle obtained from measurements of the distortion in Dreiding molecular models.

Predictions of the conformation of the molecule have been made from molecular force-field calculations. Three results have been reported to date,[9–11] all using

---

(1) A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Amer. Chem. Soc.*, **75**, 3212 (1953).

(2) A. C. Cope, C. R. Ganellin, H. W. Johnson, Jr., T. V. Van Auken, and H. J. S. Winkler, *ibid.*, **85**, 3276 (1963); A. C. Cope and A. S. Mehta, *ibid.*, **86**, 5626 (1964).

(3) P. C. Manor, D. P. Shoemaker, and A. Parkes, *ibid.*, **92**, 5260 (1970).

(4) B. J. Bowen, Thesis, University of Texas, Austin, Texas, 1969; *Diss. Abstr. B*, **30** (4), 1617 (1969).

(5) M. Yaris, A. Moscowitz, and R. S. Berry, *J. Chem. Phys.*, **49**, 3150 (1968).

(6) A. I. Scott and A. D. Wrixon, *Chem. Commun.*, 43 (1970).

(7) O. Schnepp, E. F. Pearson, and E. Sharman, *J. Chem. Phys.*, **52**, 6424 (1970).

(8) R. D. Bach, *ibid.*, **52**, 6423 (1970).

(9) N. L. Allinger and J. T. Sprague, *J. Amer. Chem. Soc.*, in press.

(10) P. C. Manor, Thesis, Massachusetts Institute of Technology, 1968.

(11) G. Buemi, G. Favini, and F. Zuccarello, *J. Mol. Struct.*, **5** 101 (1970).