

STO-3G SCF RESULTS FOR VINYLBORANE

James E. Williams, Jr. and Andrew Streitwieser, Jr.

Department of Chemistry, University of California, Berkeley, California 94720

(Received in USA 10 September 1973; received in UK for publication 5 November 1973)

A recent interpretation of the photoelectron spectrum of trivinylborane has raised the question of the extent of boron-carbon π -conjugation in vinylboranes.¹ We present some results of our *ab initio* study of two conformations of vinylborane and show that such conjugation is significant; no previous *ab initio* studies on this system are known to us.

Using the minimal STO-3G basis set developed by Pople,² we have computed SCF molecular orbital wave functions for vinylborane in its planar conformation (I) and a twisted conformation (II) in which the planes of the vinyl and BH_2 groups are mutually perpendicular. The bond lengths and angles in the vinyl group are given the experimental values.³ Bond angles about borane were assumed to be 120° and the BH bond length was set at the value found experimentally for the terminal BH bonds in diborane.⁴ The orbital exponents used for the atoms in the vinyl and BH_2 groups are those found optimal for ethylene⁵ and for borane,⁶ respectively. The B-C bond length was set at 1.52 \AA , the value found experimentally in phenyl-dichloroborane.⁷ The total energies found are: I, -102.0361 au ; II, -102.0222 au .

In the twisted vinylborane there can be no interactions involving the π -bond of the vinyl group with the boron p_π atomic orbital. Only hyperconjugation effects are possible in II, and are expected to be relatively small. Correspondingly, the rotation barrier about the C-B bond, as given by the energy difference between I and II, should provide a fair measure of C-B π -bonding. Although the present STO-3G calculations are with a minimal basis set, such calculations are nonempirical and generally reproduce rotational barriers quite well.⁸ The computed energy difference is $8.8 \text{ Kcal mol}^{-1}$ (37 KJ mol^{-1}), favoring the planar structure, and indicates a significant π -interaction. This value may be compared

to experimental values of about 5 Kcal mol⁻¹ (21 KJ mol⁻¹) in 1,3-butadiene⁹ and about 23 Kcal mol⁻¹ (96 KJ mol⁻¹) in allyl cation.¹⁰ The computed C-B π -interaction is also affirmed by the lowering of the π -orbital energies of I, -9.86 eV, and II, -8.86 eV; that is, the mixing of the boron p_{π} atomic orbital into the C-C π -MO results in an energy lowering of 1.00 eV.

The Mulliken population analyses¹¹ show a B-C π -overlap population of 0.100 and a C-C π -population of 0.360 in I. In II, the C-C π -population is somewhat larger, 0.394, whereas the C-B populations in the MO's of π -symmetry are small, 0.026. The atomic and overlap populations are summarized in Table I.

Although convenient and frequently useful, Mulliken population analyses do have important limitations that generally arise from the way in which electron densities over broad regions of space are assigned to specific atoms and orbitals. As a result, Mulliken population analyses are basis-set dependent. An alternative representation is a direct plot of an appropriate electron density function. Such a plot is shown in Figure 1 of the π -electron density in I in a plane 0.5 au (0.265 Å) above the molecular plane. The electron density is given as the z-coordinate for every point in the xy plane. The peaks show the concentration of π -electron density near each nucleus but the saddle points show the relative extent of electronic overlap or covalent bonding. The plot shows that B-C π -bonding is significant but smaller than C-C π -bonding. The plot also shows, as do the Mulliken populations in Table I, that the electron density transferred from the C-C π -bond to boron comes principally from the β -carbon; the central atom has the largest π -density, a result expected from perturbation arguments and apparent in even simple Hückel treatments of allylic cation systems. It should be noted that the choice of a plane for the plot in Figure 1 is arbitrary. The molecular plane, of course, is the nodal plane of the π -system but any plane parallel to and above or below the nodal plane would show essentially the same features. Similar plots with other systems have shown that the choice of a plane 0.5 au above the molecular plane gives hills and valleys of convenient proportions.

Acknowledgement: This work was supported in part by National Science Foundation Grant no. GP-29383.

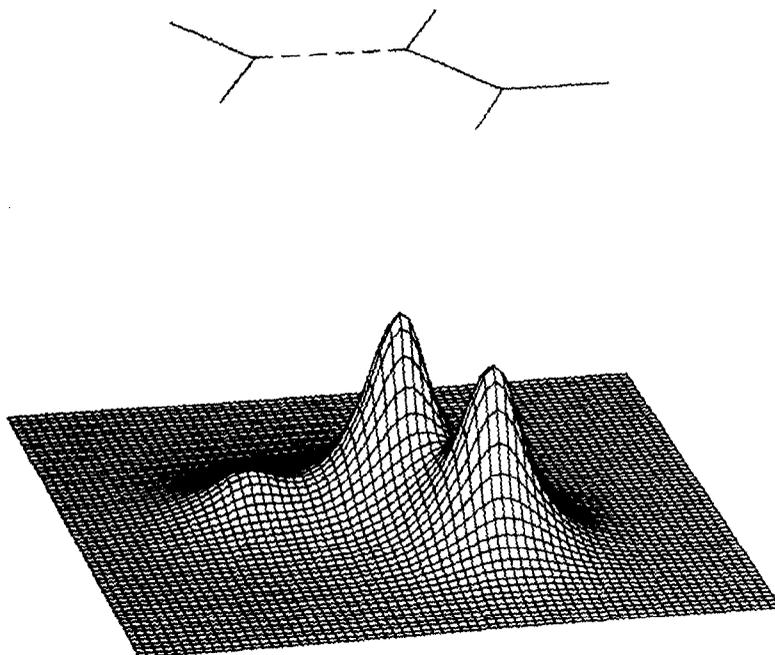


Fig. 1. Electron density function for a plane 0.5 au above the molecular plane of vinylborane, $\text{CH}_2=\text{CHBH}_2$. The C-B bond is indicated as a dashed line.

TABLE I. Atomic and Overlap Populations for Planar and Twisted Vinylborane.

	Atomic Populations			Overlap Populations	
	<u>B</u>	<u>C₁</u>	<u>C₂</u>	<u>B-C₁</u>	<u>C₁-C₂</u>
I, Planar					
π	0.128	0.999	0.872	0.100	0.360
Total	4.761	6.190	6.102	0.898	1.168
II, Twisted					
π	0.033	0.970	1.021	0.026	0.394
Total	4.726	6.178	6.158	0.854	1.196

References

1. A. K. Holliday, W. Reade, R. A. W. Johnstone, and A. F. Neville, J. Chem. Soc. (D), 1971, 51.
2. W. J. Hehre, R. F. Stewart and J. A. Pople, J. Chem. Phys., 1969, 51, 2657.
3. M. D. Newton, W. A. Lathau, W. J. Hehre, and J. A. Pople, ibid., 1970, 52, 4064.
4. L. S. Bartell and B. L. Carroll, ibid., 1965, 42, 1135.
5. W. J. Hehre and J. A. Pople, J. Amer. Chem. Soc., 1970, 92, 2191.
6. W. J. Hehre, R. Ditchfield, R. F. Stewart and J. A. Pople, J. Chem. Phys., 1970, 52, 2769.
7. L. E. Sutton, "Tables of Interatomic Distances", Chem. Soc. Special Publication, No. 11, 1956.
8. L. Radom and J. A. Pople, J. Amer. Chem. Soc., 1970, 92, 4786; L. Radom, W. J. Hehre and J. A. Pople, ibid., 1971, 93, 289; W. J. Hehre, L. Radom, and J. A. Pople, ibid., 1972, 94, 1496.
9. A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", Wiley, New York, 1961.
10. From a comparison of the difference in heats of formation of propyl and allyl cation (7 Kcal mol^{-1}) (J. L. Franklin, et al., "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions", NBS Publication 26, 1969, pp. 43, 45) with the corresponding difference for the hydrocarbons ($30 \text{ Kcal mole}^{-1}$) or the bromides (31 Kcal mol^{-1}) (J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, London, 1970). This argument assumes that the increased stabilization of allyl cation compared to n-propyl cation relative to the respective alkanes or bromides may be attributed entirely to allylic conjugation.
11. R. S. Mulliken, J. Chem. Phys., 1955, 23, 1833, 1841, 2338, 2343.