Qualitative Molecular Orbital Study of Ethane and Diborane

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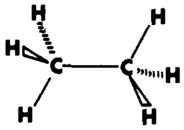
Abstract: Qualitative molecular orbital pictures and correlation diagrams are presented for staggered and bridged ethane and diborane. From qualitative arguments alone it is possible to explain the striking structural differences between these two molecules. The bridged structure of diborane is accommodated quite naturally by molecular orbital theory. Mechanisms and relative energy changes for the dimerization of CH_3 and BH_3 are also examined qualitatively. It can be shown that these processes should occur with zero or negligible activation energy and that $D(H_3C{-}CH_3) > D(H_3B{-}BH_3)$.

Qualitative molecular orbital theory has been used to give a highly pictorial understanding of the shapes and other properties of many molecules.[1,2] The rough features of molecular orbitals and their relative energies can be inferred from nodal surfaces, simple symmetry considerations, and the properties of atomic orbitals contributed by the atoms involved. Changes in molecular geometry produce changes in overlap among the atomic orbitals that make up the molecular orbitals. These overlap changes, which can be readily deduced from simple molecular orbital pictures, in turn produce changes in molecular orbital energies. The object in this paper is to present another example of the kind of information one can get about molecular properties from molecular orbital theory in a qualitative way.

Shapes of Ethane and Diborane

The shapes of ethane C_2H_6 and diborane B_2H_6 are strikingly different. Ethane with 14 valence electrons is staggered while diborane with 12 electrons is bridged.[3] Lowe has given a qualitative molecular orbital (MO) explanation of why ethane is staggered rather than eclipsed.[4] His argument is that out-of-phase interactions between atomic orbitals (AO's) on opposite ends of the molecule outweigh the in-phase interactions and the out-of-phase interactions are at a minimum in the staggered conformation.



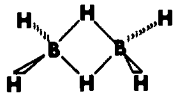


Figure 1 is a qualitative correlation diagram relating valence MO energy levels for two AH_3 molecules (perhaps methyl radicals) with those for a staggered A_2H_6 molecule (say ethane). Also included in Figure 1 are schematic pictures of the MO's as made up of AO's. The pictures for the AH_3 MO's and their relative energies have been discussed elsewhere.[1] The A_2H_6 MO's are easily constructed by taking in-phase and out-of-phase combinations of each AH_3 MO pair. The out-of-phase combinations are higher in energy, relative to separated AH_3 fragments, and the in-phase combinations are lower. The relative order of the staggered A_2H_6 energy levels in Figure 1 generally follows in a straightforward way from qualitative considerations alone. Only in the case of the relative positions of the $1e_g$ and $3a_{1g}$ orbitals is there any uncertainty about energy order. These orbitals should be close in energy and their relative position should be highly dependent on the A–A distance; the closer the two principal atoms, the lower the energy of $3a_{1g}$ (the in-phase combination) and the higher that of $1e_g$ (out-of-phase). *Ab initio* SCF–MO calculations for ethane give the order as shown in Figure 1, with $3a_{1g}$ below $1e_g$.[5,6] In a calculation for B_2H_6 in the staggered form but with the longer, bridged B–B distance (1.77 Å compared with 1.54 Å for ethane), Buenker, Peyerimhoff, Allen, and Whitten find $3a_{1g}$ above $1e_g$.[5]

Figure 2 is a qualitative correlation diagram showing what happens to A_2H_6 MO's and their relative energies for the conversion of the staggered ethane structure (of D_{3d} symmetry) to the bridged diborane shape (D_{2h}). For simplicity in Figure 2 the lowest energy pair of valence orbitals has not been included. These orbitals, related to $2a_{1g}$ and $2a_{2u}$ in Figure 1, have no significance for the ethane–diborane structural transformation. In fact, only two MO's undergo significant energy changes. First, consider the $3a_{1g}$–$3a_g$ orbital. On rocking from the staggered form to the bridged shape, four hydrogens move to terminal positions and two to bridging positions. The 1s AO's on the four hydrogens which have moved to the terminal positions of the D_{2h} structure are in more favorable overlap with the p–σ atomic orbitals on the principal atoms than they were in the D_{3d} geometry (from 32% of the maximum in D_{3d} to nearly 50% in D_{2h}).[7] Figure 3 shows overlap percentages between p orbitals and hydrogen 1s orbitals disposed at tetrahedral angles about the A atom. The 1s AO's on the two hydrogens that move into the bridge start from 32% of maximum overlap and move to locations offering each about 70% of the maximum overlap with two p–σ orbitals. This amounts to a considerable increase in in-phase overlap among constituent atomic

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[1] B. M. Gimarc, *J. Amer. Chem. Soc.*, **93**, 593 (1971).

[2] B. M. Gimarc, *ibid.*, **93**, 815 (1971).

[3] L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. **11** (1958); No. **18** (1965).

[4] J. P. Lowe, *J. Amer. Chem. Soc.*, **92**, 3799 (1970).

[5] (a) R. J. Buenker, S. D. Peyerimhoff, L. C. Allen, and J. L. Whitten, *J. Chem. Phys.*, **45**, 2835 (1966); (b) L. C. Allen, "Why Three Dimensional Hückel Theory Works and Where it Breaks Down" in "Sigma Molecular Orbital Theory," O. Sinanoglu and K. B. Wiberg, Ed., Yale University Press, New Haven, Conn., 1970, p 227.

[6] E. Clementi and D. R. Davis, *J. Chem. Phys.*, **45**, 2593 (1966); R. J. Buenker, S. D. Peyerimhoff, and J. L. Whitten, *ibid.*, **46**, 2029 (1967); W. H. Fink and L. C. Allen, *ibid.*, **46**, 2261 (1967); L. Pedersen and K. Morokuma, *ibid.*, **46**, 3941 (1967); R. M. Stevens, *ibid.*, **52**, 1397 (1970); C. R. Brundle, M. B. Robin, H. Basch, M. Pinsky, and A. Bond, *J. Amer. Chem. Soc.*, **92**, 3863 (1970).

[7] This overlap is proportional to the cosine of the angle between the p-orbital axis and the A–H bond. Maximum or 100% overlap obtains if the hydrogen were on the axis of the p orbital. For more about overlap arguments see ref 1.

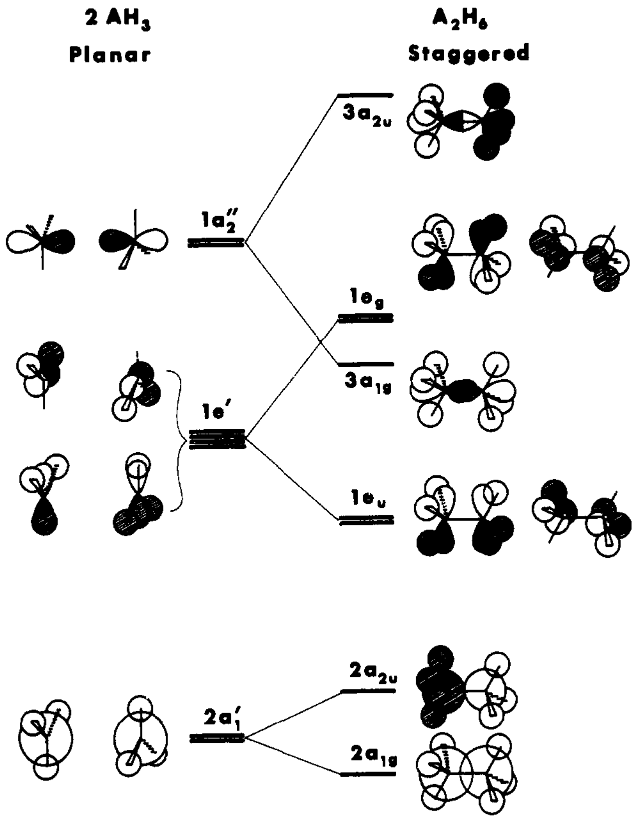

Figure 1. Molecular orbital pictures and relative energies for a staggered A_2H_6 molecule and two planar separated AH_3 fragments. Open and cross-hatched areas represent orbitals or parts of orbitals of different phase.

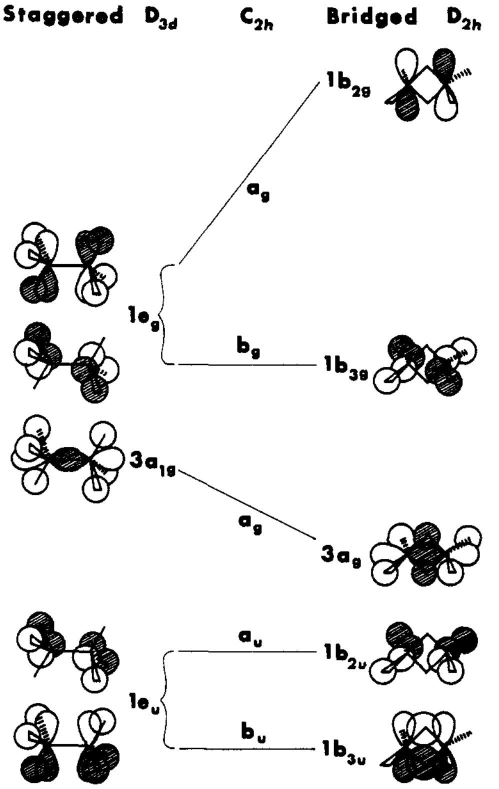

Figure 2. Molecular orbital pictures and qualitative correlation diagram for an A_2H_6 molecule in staggered D_{3d} and bridged D_{2h} shapes.

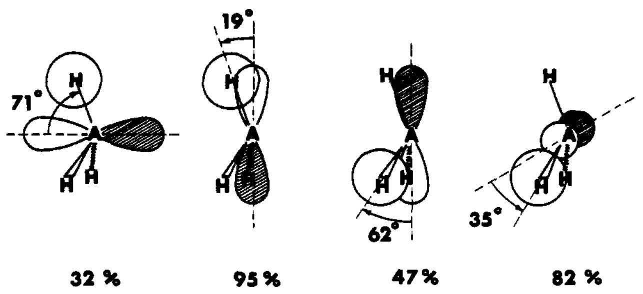

Figure 3. Percentages of maximum overlap and angles between p-orbital axes and A–H bonds for hydrogens tetrahedrally disposed about an atom A.

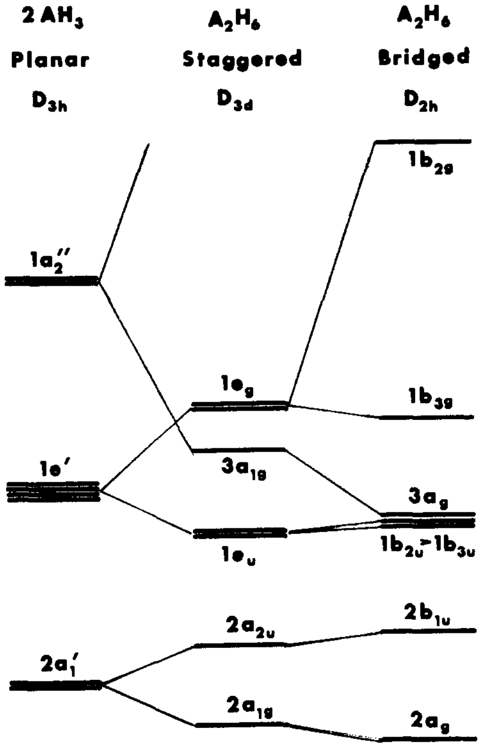

Figure 4. Extended Hückel correlation diagram for staggered and bridged A_2H_6 and two planar AH_3 molecules.

orbitals in $3a_g$ relative to $3a_{1g}$ and the increased overlap lowers the energy of $3a_g$ as Figure 2 shows. Next, observe the $1b_{2g}$ molecular orbital of the bridged form. This orbital is related to one of the members of the degenerate $1e_g$ pair of staggered geometry. In its $1e_g$ form, two hydrogen 1s orbitals overlap at about 95% of maximum with p–π atomic orbitals while each of four others overlap about 50%. In the bridged structure all six hydrogens lie on nodal surfaces of $1b_{2g}$, eliminating all hydrogen 1s contributions to $1b_{2g}$ and greatly raising the energy of $1b_{2g}$ relative to $1e_g$. This increase in $1b_{2g}$ energy is considerably greater than the decrease in that of $3a_g$. Energies of the other molecular orbitals in Figure 2 change little. The overlap changes between $1e_g$ and $1b_{3g}$ are small, as they also are between $1e_u$ and $1b_{2u}$. Individual overlaps in $1e_u$–$1b_{3u}$ do change but in a mutually cancelling way. Four hydrogen 1s orbitals in $1e_u$ (47% overlap) drop out of the $1b_{3u}$ orbital all together; the terminal hydrogens lie on a nodal surface. But two of the 1s orbitals in $1e_u$, already in good overlap, move to comparable positions in $1b_{3u}$ but with each 1s orbital overlapping two p–π orbitals. Figure 4 is a correlation diagram based on extended Hückel calculations for ethane, giving semiquantitative justification to the arguments presented and summarized in Figures 1 and 2. The order of energy levels for the bridged structure in Figures 2 and 4 agrees with that obtained from *ab initio* SCF–MO calculations.[5,8]

The energies of only two MO's in Figure 2 affect the structures of ethane and diborane. Diborane, with 12 valence electrons, has $1b_{3g}$ as its highest occupied MO. The $3a_{1g}$–$3a_g$ orbital is therefore responsible for holding diborane in the bridged shape. The highest occupied orbital in ethane is $1e_g$–$1b_{2g}$, the steeply rising energy of which forces ethane to be staggered.

In order to account for the bridged structure of diborane, the electron pair bond concept of valence-bond theory must be amended to allow some electron pairs to be delocalized over two bond regions. Molecular orbital theory, even in its most elementary form, can accommodate quite naturally such diverse structures as those of diborane and ethane without modifying assumptions.

Besides B_2H_6 and C_2H_6, a few more molecules belong to the series A_2H_6. Dialane, Al_2H_6 (12 valence electrons), has been detected mass spectrometrically.[9] Since it is isoelectronic with diborane it presumably has the bridged structure. From Figures 2 and 3, one would predict that $B_2H_6^+$, known from mass spectra, would also be bridged. Disilane, Si_2H_6, and digermane, Ge_2H_6, are isoelectronic with ethane and have the staggered shape.[3] The 13-electron ions $B_2H_6^-$ and $C_2H_6^+$ are known experimentally.[10] The $1e_g$–$1b_{2g}$ orbital energy rises so rapidly that even one electron occupying it should suffice to hold these ions in the staggered form. *Ab initio* SCF–MO calculations for $C_2H_6^+$ predict staggered geometry.[11]

Notice that in this form of qualitative MO theory no assumptions about hybridization are made. Hybrid orbitals are not the most convenient for energy considerations. In the course of the molecular deformations described, the atoms may be moved but the p AO's remain locked parallel to the same Cartesian reference axes for all structures. It is not necessary to tilt or twist p orbitals; this would just add confusion to some fairly simple rules for estimating energy changes. It is possible to choose different AO basis sets which make different arguments more convenient and an example of this will occur later on.

In the discussion above two differences between the structures of B_2H_6 and C_2H_6 have been neglected. It was assumed that no change occurs in the distance between the principal atoms as a result of the staggered-bridged conversion. In fact, the B–B distance in diborane is 0.23 Å longer than the C–C bond length in ethane. Lengthening the distance between principal atoms in the bridged structure would have the effect of lowering the energies of all the B–B antibonding orbitals while raising those of the bonding orbitals. These energy changes would be small compared with those produced by the angular structural changes and the conclusions about molecular shape would remain unchanged. The other neglected structural difference is the opening of the angle between the terminal hydrogens from $\angle HCH = 109°$ in ethane to $\angle H_tBH_t = 120°$ in diborane. The 11° angle change produces overlap changes amounting to 5 to 8%, negligible compared with overlap differences between the D_{3d} and D_{2h} structures and too small to affect conclusions about molecular shape.

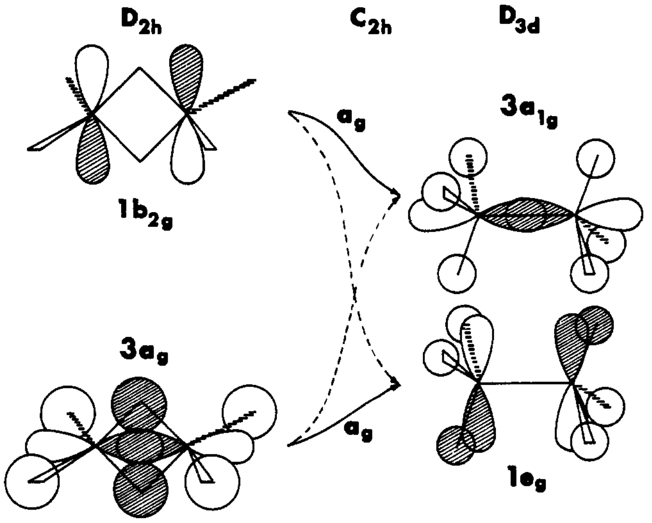

Figure 5. Orbital mixing in intermediate C_{2h} geometry. Solid lines show actual connections of MO's if $3a_{1g} > 1e_g$, dashed lines link MO's of related AO composition. Mixing occurs to avoid crossing (dashed lines) of orbitals with the same symmetry (a_g).

Several other papers bear on the arguments, illustrations, and conclusions presented here and it is appropriate to review them at this point. Lowe provides sketches of the valence MO's of staggered ethane but he does not relate them to those of bridged diborane.[12] Lloyd and Lynaugh accompany their discussion of the photoelectron spectrum of B_2H_6 with pictures of diborane orbitals but they do not compare them with those of ethane.[13]

Buenker, Peyerimhoff, Allen, and Whitten present a D_{3d}–D_{2h} correlation diagram based on *ab initio* SCF–MO calculations.[5] In those calculations they started with diborane in the bridged D_{2h} form and by moving only the hydrogens produced a staggered D_{3d} structure. In the D_{3d} structure and for the long B–B separation, the energy of $3a_{1g}$ lies above that of $1e_g$. Now in terms of their AO compositions $1b_{2g}$ is related to one of the $1e_g$ pair and $3a_g$ to $3a_{1g}$, as shown in Figure 2. Since $1b_{2g}$ is above $3a_g$, $3a_{1g}$–$3a_g$ must mix with $1e_g$–$1b_{2g}$ because of the common a_g symmetry for the intermediate geometry, and this mixing connects $3a_{1g}$ to $1b_{2g}$ and $1e_g$ to $3a_g$ (Figure 5). By assuming that the B–B bond length is equal to the ethane C–C distance, this mixing is avoided, and correlation diagram (Figure 2) is simpler, but at the same time it retains all of the qualitatively significant features. Figure 5 shows the two different correlations. Allen, *et al.*,[5] observed that all of the orbital energies in the correlation diagram they contructed from *ab initio* calculations on B_2H_6 in D_{2h}, C_{2h}, and D_{3d}

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(8) L. Burnelle and J. J. Kaufmann, *J. Chem. Phys.*, **43**, 3540 (1965); W. E. Palke and W. N. Lipscomb, *ibid.*, **45**, 3948 (1966); E. Switkes, R. M. Stevens, W. N. Lipscomb, and M. D. Newton, *ibid.*, **51**, 2085 (1969); E. A. Laws, R. M. Stevens, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **94**, 4461 (1972).

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(12) J. P. Lowe, *J. Amer. Chem. Soc.*, **94**, 3718 (1972).

(13) D. R. Lloyd and N. Lynaugh, *Phil. Trans. Roy. Soc. London, Ser. A*, **268**, 97 (1970).

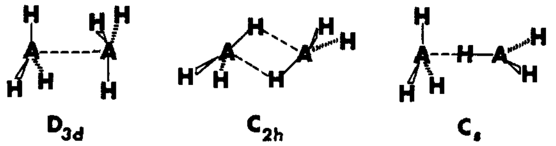

Figure 6. Three possible geometries for the approach of two AH_3 molecules during dimerization.

symmetries showed little change with angle except the $1b_{2g}$–$3a_{1g}$. This is the highest occupied orbital in ethane and forms a p–σ bond between the carbons, but it is empty in diborane. They identified it as the principal feature characterizing the difference between these two species.

Lorquet made the first attempt to construct a qualitative MO diagram correlating D_{3d} and D_{2h} geometries of A_2H_6 molecules.[14] His arguments are somewhat different from those given here and he offers no MO pictures. His diagram places $3a_{1g}$ above $1e_g$ for the D_{3d} structure and therefore requires orbital mixing. His arguments put $1b_{3u}$ rather far below $1b_{2u}$ for D_{2h} geometry and make $3a_g(D_{2h})$ higher than $1e_g(D_{3d})$. From his diagram one would conclude that diborane is bridged because of the stability of $1b_{3u}$, which is not in accord with this work or that of others.[5] Lorquet concluded that $C_2H_6^+$ should be bridged in disagreement with these qualitative results and with those of rigorous calculations.[11]

In a paper discussing, among other things, the excited states of ethane, Hoffmann includes a diagram similar to Figure 1 correlating the MO's of methyl radicals and ethane.[15] In another article Hoffmann and Williams present pictures of some of the valence MO's for D_{3d} and D_{2h} geometries of A_2H_6 molecules.[16] Hoffmann and Williams point out the steeply rising $1e_g$–$1b_{2g}$ molecular orbital, show pictorially the reasons for it (same as those given above), and specifically state that the high energy of $1b_{2g}$ is responsible for the instability of bridged ethane and $C_2H_6^+$. They do not, however, include a complete valence MO correlation diagram similar to Figure 2 or rationalize the behavior of other occupied orbitals. In particular, they do not mention the pronounced stability conferred on the bridged structure by the favorable overlap arrangement in $3a_g$.

Pearson[17] has studied the D_{3d} and D_{2h} shapes of ethane and diborane using the second-order Jahn–Teller effect as a criterion.

Methyl Radical and Borane Dimerization Processes

Both methyl radical and borane dimerize readily through exothermic reactions with zero or negligible activation energies.[18–21] The energy change for $2CH_3 \rightarrow C_2H_6$ is the carbon–carbon bond energy, $D(H_3C{-}CH_3)$ which is in the range 80 to 90 kcal/mol. The symmetrical diborane bridge bond energy $D(H_3B{-}BH_3)$ has been estimated indirectly in various ways. These estimates differ widely but likely assumptions lead to values around 22 and 35 kcal/mol.[18,19] An *ab initio* SCF-MO calculation plus an estimate of the error due to electron correlation gives 36 kcal/mol.[22] Despite a rather large uncertainty, all estimates agree that $D(H_3B{-}BH_3)$ is considerably less than $D(H_3C{-}CH_3)$.

Figure 6 shows three possible transition states through which two AH_3 groups might approach each other. The first two processes (D_{3d} and C_{2h}) lead directly to ethane and diborane geometries. The third transition state could, through simple rearrangement, lead to the bridged structure or even to the staggered form. Figure 1 is a correlation diagram for the D_{3d} process. Seven electrons in each of two methyl radicals can flow smoothly and directly from reactant energy levels to the lowest available energy levels of ethane. This picture shows that the total energy should steadily decrease (zero activation energy) as electrons in singly occupied $1a_2''$ orbitals on the methyl radicals fall in energy to become an electron pair in $3a_{1g}$ of ethane. It is conceivable that two borane molecules might approach each other in the staggered orientation but then rearrange to form the bridged structure. However, the D_{3d} approach is not favorable for two BH_3 molecules with six electrons each. An electron configuration $(2a_1')^2(2a_1')^2(1e')^4(1e')^4$ for 2 BH_3 would lead to $(2a_{1g})^2(2a_{2u})^2(1e_u)^4(1e_g)^4$ for staggered B_2H_6 with $3a_{1g}$ empty. For normal or greater B–B separations $3a_{1g}$ is above $1e_g$ anyway, so no violation of orbital symmetry conservation should occur.[23] Still this process would be uphill in energy all the way as the two borane molecules came together. For each occupied B–B bonding orbital there is a corresponding occupied antibonding orbital of similar composition and the energy lowering due to the bonding orbitals could be more than offset by the increase in energy resulting from the antibonding orbitals. Hence the D_{3d} transition state can be ruled out for the borane dimerization.

Figure 7 is a correlation diagram for the C_{2h} dimerization process. For convenience in drawing the MO pictures I have used an alternative basis set of AO's in which two of the Cartesian reference axes for the p orbitals are tilted by 45° relative to those in Figure 1. Figure 8 shows the A_2H_6 (D_{2h}) MO's as formed from this alternative basis set. Dashed lines in Figure 7 show the considerable mixing of $1e'$ and $1a_2''$ orbitals from isolated AH_3 fragments to make $1b_{3u}$, $3a_g$, and $1b_{2g}$ MO's for A_2H_6 in D_{2h} geometry. This mixing allows six electrons from each of two BH_3 molecules to flow smoothly into the lowest available energy levels for bridged B_2H_6. The total energy should decrease steadily as the two BH_3 molecules approach; *i.e.*, activation energy should be zero. Now the $3a_g$ energy of B_2H_6 is comparable with that of the $1e'$ molecular orbitals of BH_3. The stabilization of B_2H_6 offered by $1b_{2u}$ is at least cancelled by $1b_{3g}$. Therefore, the net energy lowering, $D(H_3B{-}BH_3)$, comes mainly from the formation of $1b_{3u}$. This is a π-type MO and it should provide less stabilization of B_2H_6 compared with $2BH_3$ than would the σ-type orbital $3a_{1g}$ for C_2H_6 relative to

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(14) J. C. Lorquet, *Discuss. Faraday Soc.*, **35**, 83 (1963).

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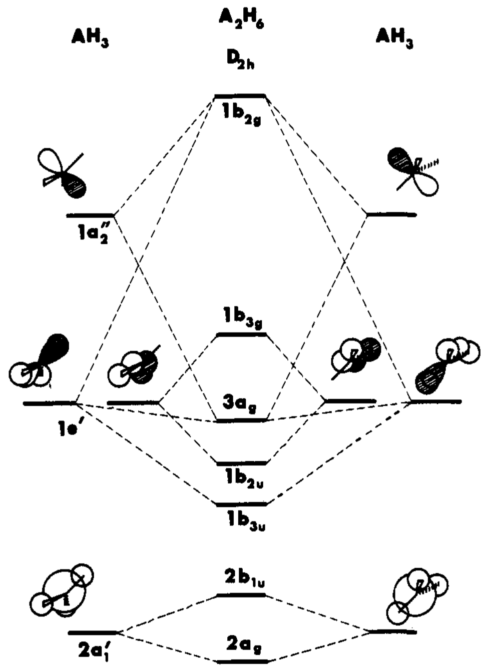
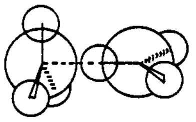
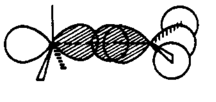


Figure 7. Qualitative correlation diagram for the association of two AH_3 molecules through the C_{2h} approach.

$2CH_3$, or $D(H_3B\text{-}BH_3) < D(H_3C\text{-}CH_3)$. There is experimental evidence to indicate that $D(H_3B^+\text{-}BH_3) > D(H_3B\text{-}BH_3)$.[18] This is in accord with the qualitative MO model (Figures 4 and 7); the electron lost to make $B_2H_6^+$ comes from the B–B antibonding MO $1b_{3g}$ which is clearly higher in energy than the highest occupied MO's (1e') of the BH_3 fragments.

To account for the high collisional efficiency of the reaction $2BH_3 \rightarrow B_2H_6$ Fehlner and coworkers have suggested that in the course of the reaction a complex something like the C_s structure in Figure 6 is formed.[20] Intramolecular rearrangement through this structure has been proposed to explain the magnetic equivalence of all hydrogens in the nmr spectrum of diborane dissolved in some solvents.[24] A comparison of qualitative molecular orbitals for C_s and C_{2h} structures fails to reveal anything conclusive about their relative energies or interconvertibility. No large energy changes are evident and no problems arise due to energy level crossings. At the B–B separations for which the C_s structure could be practical (>2.0 Å), most MO's are very nearly B–B nonbonding. Only two C_s orbitals might be expected to be bonding because the 1s orbital on the hydrogen on the B–B axis can overlap simultaneously with orbitals on both B atoms. Neither of these orbitals seem to be particularly lower in energy than the corresponding orbitals for the C_{2h} system.





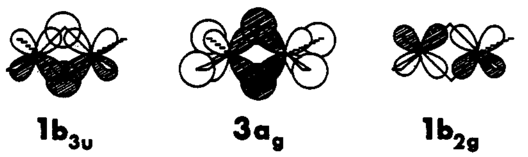


Figure 8. Pictures of molecular orbitals (D_{2h}) which appear to be different in the alternative AO basis set. Pictures of $1b_{2u}$ and $1b_{3g}$ are not included because they are exactly the same as those shown in Figure 2.

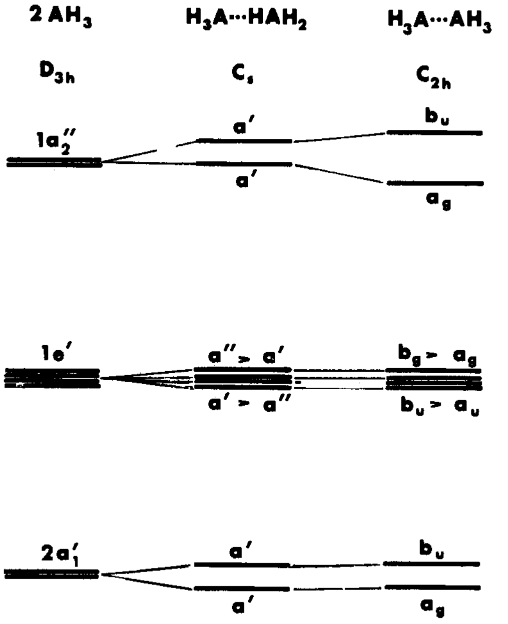
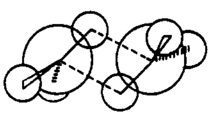


Figure 9. Extended Hückel correlation diagram for the process $2AH_3 \rightarrow H_3A\text{-}HAH_2\ (C_s) \rightarrow H_3A\text{-}AH_3\ (C_{2h})$. Calculations assume the same A–A separation for C_s and C_{2h} geometries.



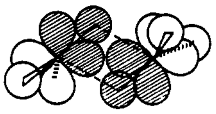


Figure 9, based on extended Hückel MO calculations, correlates MO energies of isolated planar AH_3 fragments with those of loosely associated A_2H_6 in C_s and C_{2h} structures for the same A–A separations. Although my geometry search was not extensive, calculated total energies for these two transition states were comparable for the 12 electron system for A–A distances up to 2.5 Å. For closer approaches the total energy of the C_{2h} transition state fell considerably lower. Qualitative arguments and related semiquantitative calculations have their limitations. It is impossible to deny or to affirm the existence of an intermediate of C_s symmetry for the reaction $2BH_3 \rightarrow B_2H_6$ using qualitative molecular orbital theory, and it seems unlikely that additional extended Hückel calculations would provide satisfying conclusions.

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