and triple bonds. The corresponding theoretical numbers are +9.1 (STO-3G), −11.3 (4-31G using STO-3G geometry), and −10.7 kcal/mol (full 4-31G geometry). Thus the correct sign is not given for this comparison unless the extended basis set is used.

Next consider the reaction

$$C_2H_5 + CH_4 \longrightarrow CH_3 + C_2H_6$$

Experimentally the energy of this process is +6 kcal/mol (ΔH at 298°K from Table III). The positive sign indicates that methyl substitution of a methyl radical (to give ethyl) leads to a stabilization of 6 kcal/mol (relative to methyl substitution of methane to give ethane). This is a quantitative measure of hyperconjugation in the ethyl radical. The corresponding theoretical quantities are +4.2 (STO-3G) and +3.3 kcal/mol (4-31G using STO-3G geometry).

A similar reaction for carbonium ions is

$$C_2H_5^+ + CH_4 \longrightarrow CH_3^+ + C_2H_6$$

The experimental energy here is +39 kcal/mol (ΔH at 298°K from Table III), reflecting strong hyperconjugation in the ethyl cation. The corresponding theoretical results are +30.9 (STO-3G) and +29.9 kcal/mol (4-31G using STO-3G geometry).

Conclusions

On the basis of the studies reported in this paper, the following general conclusions may be drawn.

1. The geometries of hydrocarbons are well described by a minimal Slater-type basis set in those cases for which experimental data are available. This lends credence to predictions for other systems. Some further improvement is achieved with the extended 4-31G basis for those molecules for which a geometry search has been carried out. The most notable difference is that the extended basis leads to a planar methyl radical, whereas STO-3G gives a slightly pyramidal form.

2. Relative energies of these hydrocarbons and cations are given more satisfactorily by the extended-basis set. In particular, the correct relative energies of single, double, and triple carbon–carbon bonds are only obtained at the extended level.

3. The combination of a geometry search using the simple STO-3G basis, followed by a single calculation with the extended 4-31G set (level B), appears to be a reasonable approach when a full treatment (level C) is not practical.

Acknowledgment. This research was supported in part by National Science Foundation Grant No. GP-9338.

The Shapes of Simple Polyatomic Molecules and Ions. III.
The Series HAB, H_2AB, and H_2ABH

B. M. Gimarc

Contribution from the Department of Chemistry,
University of South Carolina, Columbia, South Carolina 29208.

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Abstract: The rough features of the shapes of molecules with the general formulas HAB, H_2AB, and H_2ABH are discussed in terms of simple molecular orbital pictures and qualitative correlation diagrams deduced from the rule of maximization of overlap and orbital symmetry considerations. Extended-Hückel correlation diagrams are presented in support of the qualitative ones. Why ions such as FHF^- have the hydrogen between the two halogens rather than at an end position as in HCN or HOCl is easily explained. This explanation is then extended to describe hydrogen-bonded dimers such as $(HF)_2$. The qualitative molecular orbital model also gives a simple picture of the difference between planar inversion processes, such as those involved in isomerizations of $>C{=}N{-}R$, and rotations about single bonds such as $>N{-}O{-}R$.

A qualitative molecular orbital (MO) model of molecular shapes was formulated by Mulliken[1] and Walsh.[2] The model has recently been modified and extended in a more practical form. The model rather easily correlates large quantities of structural information and other data of chemical interest. It has great educational potential and it can be used to suggest the direction for new experiments or detailed quantum mechanical calculations. Paper I in this series deals with the shapes of molecules with the general formulas HAAH and BAAB, where A and B are nonhydrogen atoms.[3] Paper II treats AH_2, AH_3, and AH_4 molecules.[4] A related article discusses the shapes of the H_3 and H_4 transition states in hydrogen exchange reactions.[5] The present paper (part III) surveys the shapes of HAB, H_2AB, and H_2ABH molecules. Because of the particularly high symmetry of its members, the A_2H_4 series will be the subject of another study. Walsh has already discussed the shapes of the ordinary HAB and H_2AB molecules in terms of simple MO theory.[2] Justifications for reviewing them in this paper are the somewhat different arguments and the simpler approach used here.

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[1] R. S. Mulliken, *Rev. Mod. Phys.*, **14**, 204 (1942).

[2] A. D. Walsh, *J. Chem. Soc.*, 2260 (1953).

[3] B. M. Gimarc, *J. Amer. Chem. Soc.*, **92**, 266 (1970).

[4] B. M. Gimarc, *ibid.*, **93**, 593 (1971).

[5] B. M. Gimarc, *J. Chem. Phys.*, **53**, 1623 (1970).

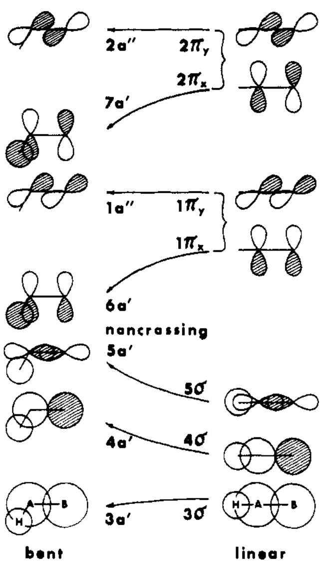

Figure 1. Molecular orbital pictures and qualitative correlation diagram for bent and linear HAB molecules. Open and cross-hatched areas represent orbitals or parts of orbitals of different phase. Changes in shape which increase in-phase overlaps between atomic orbitals lower the molecular orbital energy. Brackets indicate degeneracies.

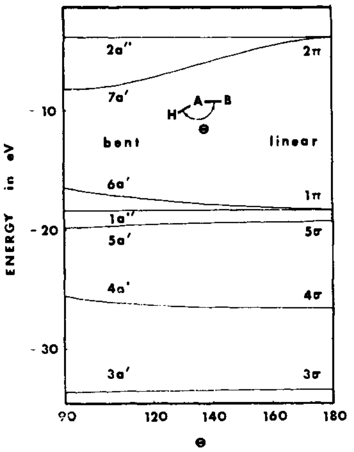

Figure 2. Extended-Hückel correlation diagram for an HAB molecule.

Two rules form the basis of the qualitative MO model. The first is that molecules of the same general formula have qualitatively similar molecular orbitals and, therefore, the molecular shape depends only on the number of valence electrons occupying the MO system. The other rule is the rule of maximization of atomic orbital overlap: if changing geometry increases the in-phase overlap of two atomic orbitals (AO's) in an MO then the energy of that MO is lowered. Some simple symmetry arguments are also useful, including a special case of the noncrossing rule: orbitals of the same symmetry cannot cross.

From qualitatively deduced MO pictures, MO correlation diagrams can be constructed which show how MO energies change with bond angles. The qualitative correlation diagrams are supported by similar diagrams obtained from extended-Hückel calculations.[6] Since only the qualitative results are of interest here, the numerical details of the extended-Hückel calculations have been omitted; limited discussions can be found elsewhere.[3,4]

The HAB Series

Some typical HAB molecules of known geometry are listed in Table I. With only three atoms these molecules are either linear or bent in shape. Still other HAB molecules are known. The ions FHF$^-$, ClHCl$^-$, and BrHBr$^-$ (16 valence electrons) are linear and symmetric, with the hydrogen between the two halogens.[7] The qualitative MO model gives a rather simple explanation of why these ions have the structure XHX$^-$ rather than HXX$^-$. At high temperatures LiOH (eight electrons) is present in the gas phase as diamond-shaped dimers.[8] Since simple MO models such as the extended-Hückel method are known to fail to describe adequately the electronic structure of highly ionic molecules,[9] the alkali hydroxides will not be considered here. The occupied valence MO's for the linear HAB molecule are very easy to write down. To a zeroth approximation they are just diatomic A_2 or AB molecular orbitals, shown in most introductory chemistry textbooks, but with the hydrogen 1s orbital combining in phase at one end. The hydrogen 1s mixes only with the σ MO's; the nodal planes in the π orbitals prevent any 1s contribution to these MO's. Figure 1 shows schematic pictures of the MO's for linear and bent HAB. These diagrams are easier to interpret if, as is done in Figure 1, the A–B atoms and AO's are held fixed and only the hydrogen changes position between the linear and bent shapes.

Table I. Shapes of the HAB Series

HAB	No. of valence electrons	Shape
HCN, HCP	10	Linear ground state, bent excited state
HCO	11	Bent ground state, linear excited state
HNO, HPO, HCF	12	Bent
HO$_2$,[a] HNF[b]	13	Bent
HOCl,[c,d] HOBr[d]	14	Bent

[a] D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **38**, 2627 (1963). [b] M. E. Jacox and D. E. Milligan, *ibid.*, **46**, 184 (1967). [c] K. Hedberg and R. M. Badger, *ibid.*, **19**, 508 (1951); R. A. Ashby, *J. Mol. Spectrosc.*, **23**, 439 (1967). [d] I. Schwager and A. Arkell, *J. Amer. Chem. Soc.*, **89**, 6006 (1967). For all others see ref 11.

The orbitals 5σ and 1π should be rather close together in energy. The relative position or order of these two orbitals, and those related to them in the following series, is difficult to assign on the basis of the qualitative arguments used here. In HAB molecules, the hydrogen 1s overlap with the A atom p_z orbital probably pulls 5σ below 1π. This ordering makes the interpretation of the relative energies of the bent HAB MO's a bit more difficult, but in fact, it has little direct effect on the shapes of HAB molecules. The MO ordering in the qualitative correlation diagram of Figure 1 is the same as that in the extended-Hückel diagram of Figure 2,

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(6) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

(7) J. A. Ibers, *ibid.*, 40, 402 (1964); J. C. Evans and G. Y.-S. Lo, *J. Phys. Chem.*, 70, 11 (1966); 71, 3697 (1967); 73, 448 (1969).

(8) O. Glemser and H. G. Wendlandt, *Advan. Inorg. Chem. Radiochem.*, **5**, 215 (1963).

(9) R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **45**, 3682 (1966); L. C. Allen and J. D. Russell, *ibid.*, 46, 1029 (1967).

which in turn resembles the diagram for HCN, based on *ab initio* SCF-MO calculations, given by Pan and Allen.[10]

The changes in energy of the HAB orbitals on bending follow from the rule of maximization of overlap and some simple symmetry considerations. The only symmetry element of the bent HAB molecule is the molecular plane (plane of page in Figure 1). Molecular orbitals must be either symmetric (designated a′) or antisymmetric (a″) with respect to reflection in this plane. There is a rather sizable energy gap between the bonding 1π and antibonding 2π degenerate pairs. Individual members of those pairs are denoted by a subscript x or y to indicate that they are made up of p_x (x axis vertical, in plane of page) or p_y (y axis perpendicular to page) AO's only. Related to each linear π_y MO is an a″ MO of bent geometry. The energy of these a″–π_y levels is independent of HAB angle because on bending, the hydrogen moves on the nodal plane of the p_y orbitals, and, therefore, the hydrogen 1s orbital cannot contribute to a″ in bent geometry. The hydrogen orbital can contribute to the a′ orbital related to each π_x. In a′–π_x, bending moves the hydrogen away from the nodal surface of the p_x AO's, allowing the hydrogen 1s to mix in phase with a lobe of the p_x on atom A.

The lowest energy valence orbital is 3a′–3σ. The energy of 3a′ should be lower than that of 3σ because bending increases the in-phase overlap between the hydrogen 1s and the B-atom s orbitals. Quite generally, the energy changes for these nodeless orbitals of lowest energy are very small and the lowering of 3a′ on bending has no effect on the shapes of HAB molecules if the higher energy orbitals are occupied.

Next higher in energy is the 4a′–4σ level. Bending raises the energy of 4a′ relative to 4σ because of increased out-of-phase overlap between the hydrogen 1s and B-atom s orbitals. The 3a′ and 4a′ orbitals constitute a bonding–antibonding pair. The increase in the energy of 4a′ due to increased out-of-phase overlap is much larger than the decrease in the energy of 3a′ due to increased in-phase overlap. This rule also applies to similar bonding–antibonding pairs.

The energy of 5a′ should be higher than that of 5σ because bending pulls the hydrogen 1s orbital out of maximum possible overlap with the A-atom p_z orbital. When HAB is bent the hydrogen moves off the nodal plane in $1\pi_x$ and the 1s orbital can overlap with a lobe of p_x on the neighboring A atom. Thus, on bending, the energy of 6a′ should decrease relative to $1\pi_x$. Overlap considerations, therefore, predict that the MO's 5a′ and 6a′, stemming from 5σ and $1\pi_x$ which are already close in energy, should converge on one another. That two levels of the same symmetry (a′ in this case) should cross is prohibited by the noncrossing rule. Instead, they mix and diverge as, in fact, they do in the extended-Hückel diagram of Figure 2, and in the *ab initio* MO diagram.[10] Because of the energy gap between 1π and 2π, mixing of 6a′ and 7a′ is negligible for moderate HAB angles.

For ten-electron HAB molecules such as HCN, the electrons occupy levels which, on the whole, tend to keep the molecule linear. On excitation, an electron moves from an orbital (6a′–$1\pi_x$) that actually helps hold the molecule linear to one (7a′–$2\pi_x$) that shifts to significantly lower energy in the bent shape. Thus, ten-electron molecules have linear ground states and bent excited states.[11] The 11-electron radical HCO should be bent in the ground state. Excitation takes an electron from an orbital (7a′–$2\pi_x$) that holds the molecule bent and adds it to an orbital (2a″–$2\pi_y$) with no geometry preference. The lower energy orbitals occupied with 10 valence electrons (like HCN) then make HCO linear in the excited state. Molecules with 12 or more valence electrons will be bent in both ground and excited states because at least one electron will be in 7a′–$2\pi_x$.

XHX^-

Unlike the more common HAB molecules, the ions FHF^-, $ClHCl^-$, and $BrHBr^-$ have the hydrogen located between the two halogens These ions are linear and symmetrical. Pimentel[12] and Linnett[13] have given simple MO and double quartet models to explain the stability provided by this arrangement. The following is a different, perhaps more generally useful explanation.

It is easy to think of the ordinary HAB species as an AB^- ion with a proton stuck on one end. In fact, HCN (10 electrons), HNO (12 electrons), and HOCl (14 electrons) are all weak acids and the corresponding AB^- ions are known. One would not expect the ion F_2^{2-} (16 electrons, isoelectronic with Ne_2) to be bound because the stabilization resulting from four occupied bonding valence MO's is more than cancelled by the effect of an equal number of filled antibonding orbitals. Coulson[14] has shown that complete shells of molecular orbitals give negative bond order unless overlap is neglected. An ion such as HFF^- would, therefore, be unlikely. For the XHX^- system, the insertion of a proton between two halogen atoms stabilizes the antibonding σ_u and π_g orbitals (particularly the highest occupied $3\sigma_u$ which has p_z orbitals pointing directly at each other out of phase) by separating the antibonding fragments, thereby decreasing their out-of-phase overlaps and making them nonbonding. At the same time, the central hydrogen 1s orbital provides in-phase overlap to stabilize somewhat the bonding σ_g MO's. The out-of-phase overlaps are minimized in the linear arrangement. Only the bonding π_u orbitals are raised in energy (to become nonbonding) by the separation resulting from the inserted hydrogen. Schematically, Figure 3 shows what happens.

Pimentel and Spratley[15] have predicted the existence of FHeF, reasoning from analogy with the isoelectronic ion FHF^- and XeF_2. On the basis of *ab initio* valence-bond and SCF-MO calculations, Allen and coworkers[16] and Noble and Kortzeborn[17] conclude that FHeF should be unstable. The calculations should be reliable on this point; they also show that FHF^- is stable. It is necessary to rationalize the difference in stability of

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[10] D. C. Pan and L. C. Allen, *J. Chem. Phys.*, **46**, 1797 (1967).

[11] G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. III. "Electronic Spectra and Electronic Structure of Polyatomic Molecules," D. Van Nostrand, Princeton, N. J., 1965, p 583; L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 11** (1958); **No. 18** (1965).

[12] G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).

[13] J. W. Linnett, *Science*, **167**, 1719 (1970).

[14] C. A. Coulson, *Mol. Phys.*, **15**, 317 (1968).

[15] G. C. Pimentel and R. D. Spratley, *J. Amer. Chem. Soc.*, **85**, 826 (1963).

[16] L. C. Allen, R. M. Erdahl, and J. L. Whitten, *ibid.*, **87**, 3769 (1965).

[17] P. N. Noble and R. N. Kortzeborn, *J. Chem. Phys.*, **52**, 5375 (1970).

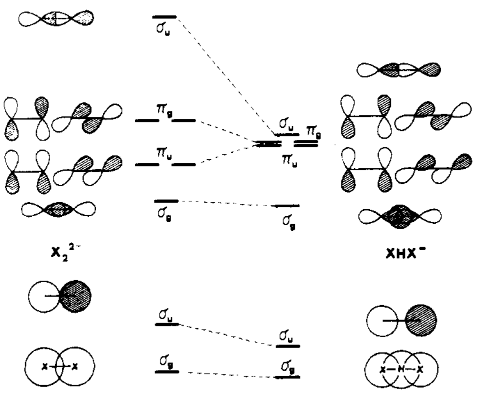

Figure 3. Energy levels and orbital pictures for X_2^{2-} and XHX^-. The energy levels shown are those calculated by the extended-Hückel method for F_2 and FHF^- at experimental bond distances.

these two apparently similar, isoelectronic species. Now the stability of XZX systems, where Z is an atom such as H, He, or perhaps Li that does not contribute p AO's to the MO system, must be strongly dependent on the X---X distance. The 1s AO of a hydrogen atom or a hydride ion has a much smaller orbital exponent or effective nuclear charge than the 1s orbital of a helium atom. Therefore, the helium atom is smaller and does not force sufficient separation of the halogen atoms to lower the energy of the antibonding σ_u MO's (particularly the highest occupied) and stabilize FHeF. Of course, none of the arguments presented can conclusively prove that FHF^- is stable while FHeF is not, but they do point out a strong stabilizing effect for FHF^- which would be much smaller for FHeF.

Other Possible $AHA^\pm$ Systems

Dierksen and Preuss[18] and Ray[19] have performed *ab initio* calculations which indicate that the two-valence-electron ion Li_2H^+ is stable and has the linear symmetric structure $LiHLi^+$. The qualitative molecular orbital model would predict this ion to be bent or triangular like the isoelectronic species LiH_2^+ or H_3^+.[4,5] An explanation of this structure must rest on the peculiar properties of the Li–Li and Li–H bonds. The Li_2 bond is the longest (2.67 Å) and weakest (26 kcal/mol) of all the first-row homonuclear diatomic molecules. The Li–Li bond is almost twice as long as the bond in Li–H, the ratio R_{Li-H}/R_{Li-Li} being around 0.6. With very little difficulty a proton could slip between two lithium atoms in Li_2. Because of its small effective nuclear charge, the lithium 2s orbital is quite large. The hydrogen 1s orbital can overlap effectively with both Li atom 2s orbitals and hardly disturb the 2s,2s overlap. In this way the proton can form two Li–H bonds and still maintain the Li–Li bond. The *ab initio* results predict that Li_2H^+ is more stable that LiH and Li^+ by 60–63 kcal/mol, an amount slightly larger than the energy of the LiH bond (58 kcal/mol).

Preuss and coworkers[18,20] also predict the four-electron ions Li_2H^- and Be_2H^+ to be stable by about 7 kcal/mol relative to LiH + Li^- and BeH^+ + Be, respectively. Again, the ions should have the linear, symmetric structure $AHA^\pm$. The story here must be similar to the one for FHF^-. Simple MO theory would predict that Li_2^{2-} and Be_2 would not be bound. Once more, see Figure 3. Insertion of a proton between the two Li or Be atoms would stabilize the antibonding $2\sigma_u$ MO by separating two out-of-phase 2s AO's and at the same time provide some measure of in-phase overlap among Li- or Be-atom 2s and hydrogen 1s AO's in $2\sigma_g$ to hold together the ions $LiHLi^-$ and $BeHBe^+$.

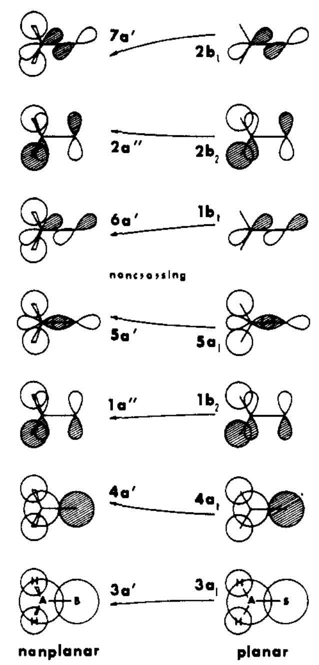

Figure 4. Molecular orbital pictures and qualitative correlation diagram for H_2AB molecules in planar and nonplanar shapes. In the pictures for the nonplanar structure, the hydrogens are sticking up and out of the page.

Extending these arguments one would expect $AHA^\pm$ ions with six valence electrons or less to be stable with respect to H^+ and A_2 or A_2^{2-}. Any electrons more than six would occupy the destabilized π_u MO in $AHA^\pm$. The only information available for comparison is the calculation by Preuss and coworkers[20] for $BeHBe^-$ which they find has a higher energy than BeH + Be. Unfortunately these are not convenient dissociation products for comparison for the simple MO model. $BeHBe^-$ might still be metastable, a possibility noted by Preuss.

Hydrogen-Bonded Dimers

Kollman and Allen[21] conclude on the basis of semiempirical CNDO/2 and *ab initio* SCF–MO calculations that the dimers HFHF and H_2OHOH as well as the mixed species H_2OHF are bound by several kilocalories per mole. All three are 16-electron systems. Simple MO considerations of the type already presented for FHF^- say that no 16-electron ions such as HFF^-, H_2OF^-, or H_2OOH^- would be possible because there would be net nonbonding or worse between the F–F, O–F, or O–O atoms. Insertion of a hydrogen bond between members of these pairs would stabilize the strongly antibonding highest occupied MO related to the highest energy σ_u orbital in Figure 3. Maximum stabilization would occur in each case for the linear ar-

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(18) G. Dierksen and H. Preuss, *Int. J. Quantum Chem.*, **1**, 637, 641 (1967).

(19) N. K. Ray, *J. Chem. Phys.*, **52**, 463 (1970).

(20) R. Janoschek, G. Dierksen, and H. Preuss, *Int. J. Quantum Chem.*, **2**, 159 (1968).

(21) P. A. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 753 (1970); *J. Chem. Phys.*, **51**, 3286 (1969); **52**, 5085 (1970).

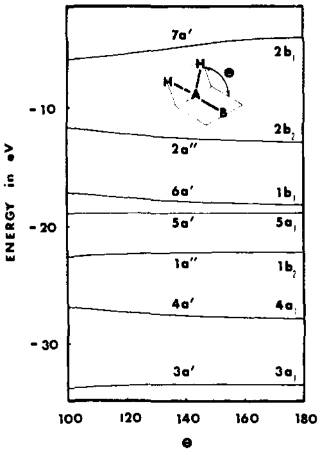

Figure 5. Extended-Hückel correlation diagram for an H_2AB molecule.

rangement, with the hydrogen inserted on the F---F, O---F, or O---O axis. These are the arrangements Kollman and Allen found through their calculations.

The H_2AB Series

Molecules with the general formula H_2AB, where both hydrogens are bound to A, are either planar or nonplanar. Some examples of known geometry are listed in Table II. Esr data indicate that the methylamino radical H_2CN (11 valence electrons) is planar.[22] Formaldehyde, H_2CO (12 electrons), is planar in its ground state but has nonplanar excited states.[11] The radical H_2CF (13 electrons) is nonplanar, but not strongly so.[23] Chloramine, H_2NCl (14 electrons), is nonplanar.[11]

Table II. Shapes of the H_2AB Series

H_2AB	No. of valence electrons	Shape
H_2CN^a	11	Planar
H_2CO^b	12	Planar ground state; nonplanar excited state
H_2CF^c	13	Nonplanar
H_2NCl^b	14	Nonplanar

[a] Reference 22. [b] Reference 11. [c] Reference 23.

The occupied MO's for H_2AB are easily formed from the A_2 or AB diatomic MO's by adding the two hydrogen 1s orbitals in phase with the AO's on the A atom. Figure 4 contains schematic diagrams of the MO's for H_2AB in planar and nonplanar shapes. Figure 5 is the correlation diagram as calculated by the extended-Hückel method. It may be of some help to relate the diatomic MO's to those for planar H_2AB. The hydrogen 1s orbitals mix in phase with the σ diatomic MO's to form $3a_1$, $4a_1$, and $5a_1$ in Figure 4. The hydrogen 1s orbitals can mix with π_x orbitals to form MO's of symmetry b_2, but not with π_y. The π_y diatomic MO's become, unchanged, the b_1 MO's of planar H_2AB. Thus, the degeneracies of both the bonding and the antibonding π levels are removed. There is also some rearrangement in the energy order of the MO's, but this can be understood in terms of overlap and has no bearing on molecular shapes. In the linear HAB case, 5σ was slightly lower in energy than the 1π pair, but in H_2AB the related $5a_1$ orbital, as shown in Figure 4, lies between $1b_1$ and $1b_2$ which are related to 1π. Assuming that the HAH angle in H_2AB is around 120°, then each hydrogen 1s in $5a_1$ is in about 50% of maximum possible overlap with the p_z orbital on A.[24] This is roughly comparable with the amount of overlap between the p_z and the single hydrogen 1s orbitals in the related 5σ MO of linear HAB. Therefore, if 5σ is below 1π for linear HAB, then $5a_1$ should be below $1b_1$ for planar H_2AB. In $1b_2$ each hydrogen 1s is in 87% of the maximum possible overlap with the p_x orbital of A. The considerable 1s,p_x overlap here is apparently enough to place $1b_2$ below $5a_1$ in energy as it is in Figures 4 and 5. The relationships among AB, HAB, H_2AB, and H_2ABH MO's are summarized in Figure 6. Schwartz and Allen[25] report *ab initio* orbital energies for planar H_2BF. Their ordering of energy levels is the same as that in Figures 4 and 5 except that they show $5a_1$ above $1b_1$. This difference has no effect on the shapes of H_2AB molecules.

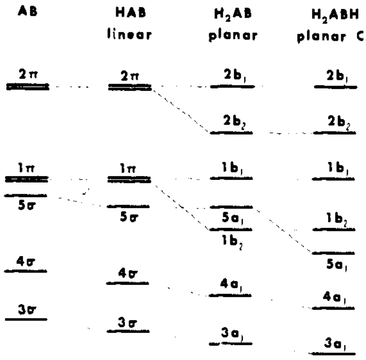

Figure 6. Relationship between molecular orbital energy levels for AB, HAB, H_2AB, and H_2ABH molecules.

Now, consider bending the molecule from planar to nonplanar shape, holding A and B fixed in the plane of the page and pulling the hydrogens up above the page as is done in Figure 4. The MO's for nonplanar H_2AB are either symmetric (a′) or antisymmetric (a″) with respect to the plane perependicular to the plane of the page and passing through A and B. The energy changes of the calculated levels in Figure 5 can be explained by applying the rule of maximization of overlap to the MO pictures in Figure 4. The $1b_1$ and $5a_1$ MO's of planar geometry are relatively close together in energy. On folding to nonplanar geometry, they both become MO's of a′ symmetry and, according to the rule of maximization of overlap and the pictures in Figure 4, should converge on each other and possibly intersect. The noncrossing rule prevents this, however; 5a′ and 6a′ actually mix and diverge as shown in the calculated correlation diagram in Figure 5. Notice the changes in overlap between the hydrogen 1s and B-atom s AO's in 3a′–$3a_1$ and 4a′–$4a_1$. In general, an out-of-phase overlap change has a larger effect on the energy than a similar in-phase change. Two more MO's with comparable in-phase and out-of-phase overlap changes are

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(22) E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, **36**, 1938 (1962).

(23) R. W. Fessenden and R. H. Shuler, *ibid.*, **43**, 2704 (1965); D. L. Beveridge, P. A. Dobosh, and J. A. Pople, *ibid.*, **48**, 4802 (1968).

(24) For an explanation of these overlap arguments, see ref 4.

(25) M. E. Schwartz and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 1466 (1970).

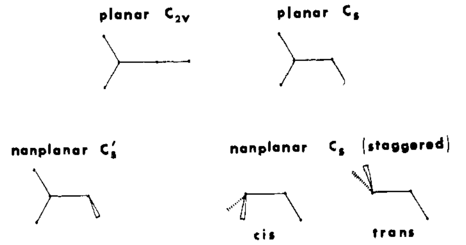


Figure 7. Some possible shapes for H_2ABH molecules.

1a''-$1b_2$ and 2a''-$2b_2$. Here the AO's involved are the hydrogen 1s and the B atom p_x.

In the formaldehyde molecule (12 electrons) the orbitals 4a', 6a', and 2a'' hold the molecule planar, outweighing the folding effect of 5a' and 1a''. The radical H_2CN, with only 11 electrons, is also planar.[22] In formaldehyde, electronic excitation removes an electron from an orbital (2a''-$2b_2$) that helps hold H_2CO planar and adds it to an orbital (7a'-$2b_1$) that favors the nonplanar structure. Therefore, the excited states of H_2CO should be nonplanar. With 2a''-$2b_2$ doubly occupied and one electron in 7a'-$2b_1$, the 13-electron radical H_2CF is nonplanar. Chloramine, H_2NCl, is nonplanar with 7a'-$2b_1$ doubly occupied. Walsh's rule for the H_2AB series states that molecules with 12 electrons or fewer should be planar, but those with 13 or more electrons should be nonplanar.

The H_2ABH Series

Figure 7 shows several possible shapes for molecules with the general formula H_2ABH. The known molecules, listed in Table III, exhibit only two of these shapes: planar C_s and nonplanar C_s (trans, staggered). This series turns out to be a fortunate combination of the series H_2AB and HAB just discussed, giving a hint of the way that simple MO arguments for simple molecules could be extended to even more complex systems. For molecules with 11 electrons or more, the ABH part of H_2ABH is bent just like those HAB molecules with 11 or more electrons. The H_2AB part of H_2ABH is planar for molecules with 12 electrons or fewer but nonplanar for molecules with 13 or 14 electrons, following the rule for an isolated H_2AB system.

Table III. The Shapes of the H_2ABH Series

H_2ABH	No. of valence electrons	Shape
H_2CCH[a]	11	Planar, C_s
H_2COH^+,[b] H_2CNH[c]	12	Planar, C_s
H_2COH[d]	13	Nonplanar, C_s ?
H_2NOH[e]	14	Nonplanar, C_s (trans-staggered)

[a] References 27 and 28. [b] Reference 29. [c] Reference 29; D. E. Milligan, *J. Chem. Phys.*, **35**, 1491 (1961); C. B. Moore, G. C. Pimentel, and T. D. Goldfarb, *ibid.*, **43**, 63 (1965). [d] W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 3119 (1963). [e] References 11 and 31.

Figure 8 contains simple MO pictures for H_2ABH in the planar C_{2v} shape. Figure 6 relates these MO's to those for H_2AB and HAB. For H_2ABH in the planar C_{2v} shape, imagine bending the lone hydrogen on B in the plane to form the planar C_s arrangement.

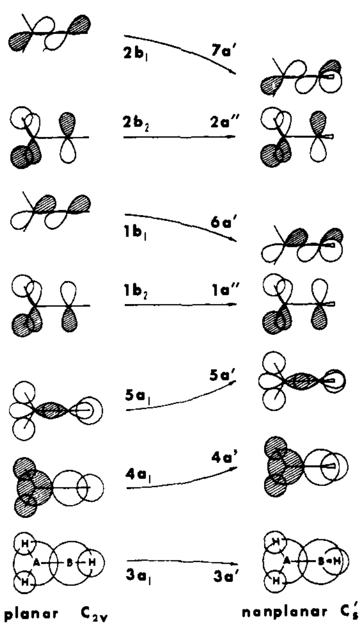
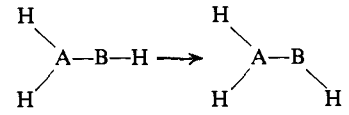


Figure 8. Molecular orbital pictures and qualitative correlation diagram for H_2ABH molecules in planar C_{2v} and nonplanar C_s' shapes.



No new correlation diagram is necessary for this process because it is very similar to the one shown in Figure 1 for an isolated HAB molecule. A comparison of MO pictures for planar C_{2v} H_2ABH (Figure 8) and for linear HAB (Figure 1) would be helpful here. From these two diagrams one can see that a ten-electron species such as the vinyl carbonium ion H_2CCH^+ should be planar C_{2v}. This is consistent with chemical information about substituted carbonium ions.[26] It is also apparent that 11- and 12-electron molecules have lower energy in the planar C_{2v} shape (linear ABH). Esr data indicate that the 11-electron vinyl radical H_2CCH is planar C_s.[27] Extended-Hückel and other semiempirical calculations indicate that the angle ABH in the vinyl radical is rather large: around 150°.[28]

Figure 8 also contains MO pictures for the other ABH bending possibility: pulling the lone hydrogen on B out of the plane to make the nonplanar C_s' shape.

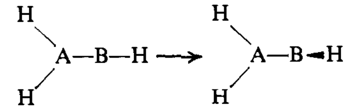


Figure 8 shows that molecules with 11 or 12 electrons have even higher energy in the nonplanar C_s' structure than they do in the planar C_{2v} shape. While neither the planar C_{2v} nor the nonplanar C_s' is the shape of 11- or

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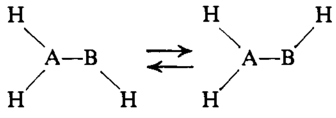
(26) D. R. Kelsey and R. G. Bergman, *J. Amer. Chem. Soc.*, **92**, 228 (1970).

(27) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); E. L. Cochran, F. J. Adrian, and V. A. Bowers, *ibid.*, 40, 213 (1964).

(28) F. J. Adrian and M. Karplus, *ibid.*, 41, 56 (1964); G. A. Petersson and A. D. McLachlan, *ibid.*, 45, 628 (1966); T. Yonezawa, H. Nakatsuji, T. Kawamura, and H. Kato, *Bull. Chem. Soc. Jap.*, 40, 2211 (1967).

12-electron H_2ABH molecules, they are possible transition states for conversion of one planar C_s structure into the other



an isomerization process which is believed to take place in the vinyl radical, H_2CCH; methylenimine, H_2CNH; and protonated formaldehyde, H_2COH^+. Isomerization could occur by a lateral shift or planar inversion around the B atom, through a planar C_{2v} transition state, or by way of a rotation around the A–B bond, through the nonplanar C_s' structure. The arguments above, based on simple MO pictures, suggest that the transition state for planar inversion has lower energy than the rotational transition state. Semiempirical and *ab initio* calculations also favor the inversion mechanism.[29] It is fairly easy to extend the qualitative MO pictures to study the isomerization with a carbon substituent on the B atom and in this case, too, the planar inversion mechanism is favored. Experimental data support a planar inversion mechanism for isomerization of imines.[30]

Now compare the MO pictures for the planar C_{2v} structure of H_2ABH in Figure 8 with those for H_2AB in Figure 4. Applying the same arguments to similar orbital pictures leads to similar conclusions. For H_2ABH molecules with 11 or 12 electrons the H_2AB section is planar, but for molecules with 13 or 14 electrons the H_2AB part is nonplanar. Now for 13- and 14-electron molecules the ABH portion is also bent. Only one question remains. What conformation of 13- and 14-electron molecules such as H_2COH and H_2NOH is most stable? For hydroxylamine experiment[11] and *ab initio* calculations[31] agree that the trans-staggered (C_s) conformation is the most stable. Extended-Hückel calculations and therefore the qualitative MO model favor the cis-staggered conformation. The extended-Hückel method does give the proper conformation (staggered) for ethane. Lowe,[32] using arguments based on MO nodal properties and MO pictures similar to those in this paper, has recently given a qualitative explanation of the barriers to internal rotation in ethane and methanol. Now ethane, methanol, and hydroxylamine are isoelectronic, though not isoatomic, and the hydrogens in cis-staggered H_2NOH occupy the same relative positions as those in the minimum-energy conformations of ethane and methanol. The simple MO model favors the *cis*-staggered conformer for H_2NOH for the same reasons that Lowe gives for the conformations of ethane and methanol and no new arguments or pictures are necessary here.

The failures of simple molecular orbital theory are at least as important as the successes. There is a simple MO preference for the wrong conformation (cis-staggered) for hydroxylamine. Other effects, not explicitly included in simple MO theory, must be responsible for the fact that the minimum energy conformer of H_2NOH is trans-staggered. The most obvious of these effects would be internuclear repulsions, although there are electronic effects as well. Simple MO theory may be ambiguous about how internuclear repulsions enter extended-Hückel calculations and the qualitative MO pictures, but surely *differences* in repulsions between different conformations are neglected completely. Repulsions between hydrogens on opposite ends of ethane favor the staggered conformation, supplementing the MO preference for that arrangement. Repulsions between hydrogens on hydroxylamine favor the trans-staggered conformation, opposing the MO preference. Difference in repulsions between the cis- and trans-staggered conformations are large compared to those for ethane (staggered *vs.* eclipsed) and they must outweigh the MO effects.

Conclusions

It is easy to draw simple molecular orbital diagrams and to use them to explain or rationalize the rough features of molecular shapes. Failures may occur for cases in which energy differences between conformations are smaller than those arising from effects neglected in simple MO theory, but these are also the failures of extended-Hückel calculations. The qualitative MO model also provides a simple picture of isomerization processes and hydrogen bonding. There is hope that the MO arguments about molecular shapes and hydrogen bonding can be extended to larger systems without much difficulty.

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