role of the HOMO in chemical reactivity,[13b,14b] the present work on the role of HOMO in governing molecular geometry suggests that the behavior of the HOMO may provide a simple unifying principle in chemistry for understanding the structure and reactivity of molecules.

and overlap forces whereas Nakatsuji, by adopting certain approximations for the two- and three-center force integrals, splits the atomic plus nuclear repulsion force into atomic dipole (AD) and gross charge (GC) forces, while the overlap force is expresed as an exchange (EC) force. Nakatsuji's model predicts the shapes of a number of molecule classes including AH_2, AH_3, HAB, H_2AB, AB_2, ABC, and X_mABY_n molecules. The following remarks may be made regarding this model. (1) The planar shapes of 7 valence electron AH_3 molecules like CH_3, NH_3^+ etc., have been accepted rather than predicted. (2) The use of Mulliken approximation, which is rather inaccurate[78] in calculating force integrals, may be open to question. (3) For AH_3 and H_2AB molecules the vanishing of the net force (along the pyramidal axis) on A in the planar configuration does not necessarily mean that the molecule considered is planar; this out-of-plane force will always vanish in the planar configuration for symmetry reasons. Actually, for predicting the equilibrium shapes of such planar molecules one should choose a force in a HAH or HAB plane. (4) The fairly good numerical estimates of the pyramidal angles in CH_3^- and H_2CO (excited), based on force computations using INDO charge densities, are quite interesting in view of the well-known failure of such attempts on other molecules using *ab initio* densities.[9,10a] Since a major source of trouble in *ab initio* force computations is inner-shell polarization, the neglect of core polarization in CNDO/2 and INDO densities could mean that such densities may be more useful for force computations on molecules than the corresponding *ab initio* densities, as far as equilibrium shape predictions are concerned.

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(77) H. Nakatsuji, *J. Amer. Chem. Soc.*, **95**, 345, 354, 2084 (1973).
(78) B. M. Deb, *Proc. Indian Nat. Sci. Acad., Sect. A*, **37**, 349 (1971).

A Simple Mechanical Model for Molecular Geometry Based on the Hellmann–Feynman Theorem. II. HAAH, BAAB, AB_3, H_2AB, and B_2AC Molecules

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Abstract: The simple model for molecular geometry proposed in an earlier paper (part I) has been applied to five more molecule classes. The postulate that *the gross equilibrium molecular shapes are determined primarily by the behavior of the highest occupied molecular orbital* (HOMO) is successful in making geometry predictions for the above five molecule classes. These Walsh-type predictions seem to work well even if one replaces the nonhydrogenic atoms by groups of atoms. The change of shape of one molecule on being added to another molecule, *e.g.*, in $BF_3 \leftarrow NH$, can also be predicted.

In part I (hereafter referred to as I)[2] a simple mechanical model for molecular geometry, based on qualitative interpretations drawn from the Hellmann–Feynman (H–F) theorem, was proposed. The general principles of the method were illustrated with six molecule classes: AH_2, AH_3, AH_4, AB_2, HAB, and ABC. In this paper we examine five more molecule classes and show that the model is successful in predicting the gross shapes and certain bond angle and bond length variations in these molecules also (see ref 76 in I).

The Shapes of Molecules

1. HAAH Molecules (Linear–Bent and Planar–Nonplanar Correlations). Planar bent HAAH molecules may assume two forms, cis and trans. In order to decide whether a planar HAAH molecule will adopt a linear or a nonlinear form, it will be sufficient to consider correlations between the cis form and the linear form. This refers to a change in the angular variable θ (Figure 1a) with nuclear motions. Correlations involving a change in the dihedral angle will be considered later. The bending of the molecule is achieved by symmetric motions of the hydrogen atoms in the molecular plane, keeping the two A atoms and the A–H length fixed.

By using the rules given in I the ten valence MO's of a cis (C_{2v}) HAAH molecule ($\angle H_1AZ_1 = 30°$, say) may be constructed from appropriate s and p group AO's (see Table I) as follows: (i) $1a_1$, an MO that is A–A and A–H bonding; (ii) $2a_1$, an MO that is A–A bonding and feeble A–H bonding; (iii) $3a_1$, an MO which is feeble A–A bonding and feeble A–H antibonding (this may also be taken as a "lone pair" combination of AO's on the heavier atoms); (iv) $4a_1$, an MO that is mild A–A bonding and A–H antiboding; (v) $1b_1$, a π MO which is A–A bonding; (vi) $1a_2$, another π MO which is A–A antibonding; (vii) $1b_2$, an MO that is A–H bonding and feeble A–A antibonding; (viii) $2b_2$, an MO which is feeble A–H bonding and feeble A–A antibonding; (ix) $3b_2$, an MO which is feeble A–H and feeble A–A antibonding (this may also be taken as a "lone pair" combination of AO's on the heavier atoms); (x) $4b_2$,

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(2) B. M. Deb, *J. Amer. Chem. Soc.*, **96**, 2030 (1974).

an MO that is A–H antibonding and feeble A–A antibonding.[3] The MO's are represented schematically in Figures 2–4. They are not identical with calculated MO's.[4] However, the qualitative bonding features of our MO's are essentially the same as the *ab initio* MO's.[4] Using the rules in I and considering the MO energy order for AH_2 molecules, the above constructed MO's may be arranged in the sequence $1a_1 < 1b_2 < 2a_1 < 1b_1 < 3a_1 < 2b_2 < 1a_2 < 3b_2 < 4a_1 < 4b_2$. This order matches with the calculated energy order of Fink and Allen[5a] and Gimarc[4a] but is not identical with that of Kaldor and Shavitt[4b] as well as of Palke and Pitzer.[5b]

The $1a_1$ MO concentrates more charge inside the molecular trapezium than outside it and so this MO will not favor a linear molecule. The $2a_1$ orbital will also favor a nonlinear molecule. By looking at the balance of atomic and overlap forces generated by the $3a_1$ MO it is reasonable to expect that this orbital will result in a negative transverse force on the protons (see I) and will, therefore, favor a linear molecule. Because the orbitals $1b_1$ and $1a_2$ are perpendicular to the plane of the molecule and are concerned with only the A–A bond, they are expected to exert very little transverse force on the terminal protons. The $1b_2$ MO will clearly favor a linear form since it throws more charge outside than inside the molecular trapezium. However, an examination of the overlap and atomic forces indicates that the $2b_2$ MO will exert a net positive charge on the terminal protons and will therefore favor a bent form. The mildly antibonding $3b_2$ MO will obviously favor a linear configuration. These expectations are in agreement with the signs of the gradients of the MO energy curves obtained in *ab initio* and extended Hückel calculations,[5] as well as previous force calculations.[6] The various predictions about molecular shapes, made on the basis of the shape diagram (Figures 5–8) for HAAH molecules, are summarized in Table II. Such predictions seem to parallel those for HAB molecules (see I) so that the HAAH molecules may be regarded as a special class of HAB molecules as far as molecular shapes are concerned. *Ab initio* calculations on two- and five–eight-electron HAAH molecules would help to decide whether the present shape predictions for these molecules are correct.[7]

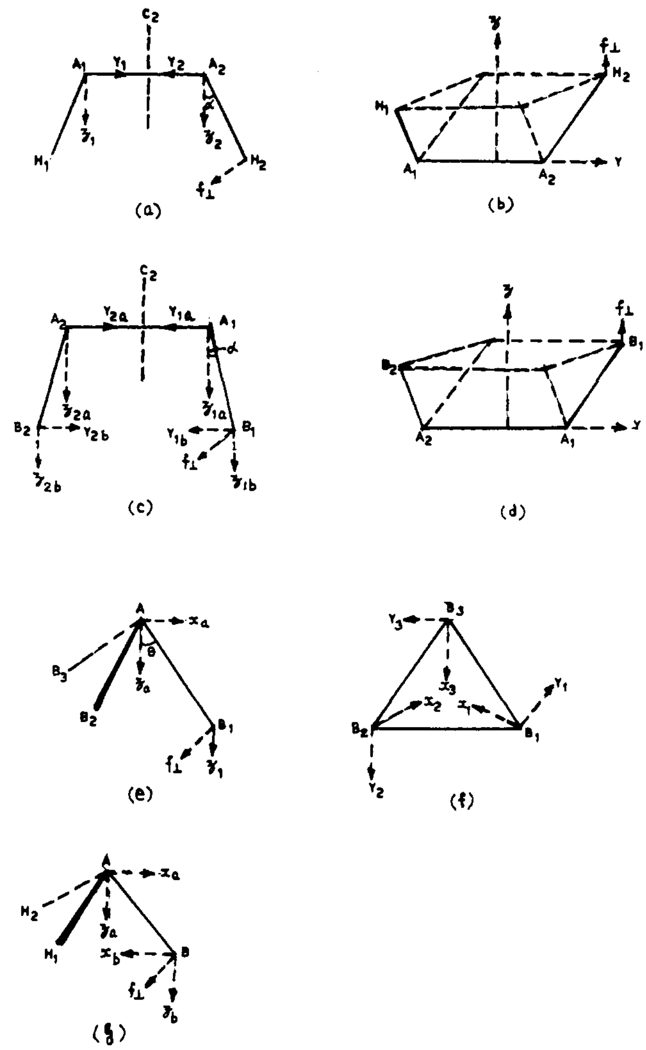

Figure 1. Coordinate systems and transverse forces ($f_\perp$) for five molecule classes: (a) C_{2v} HAAH molecule, (b) C_2 HAAH molecule, (c) C_{2v} BAAB molecule, (d) C_2 BAAB molecule, (e) C_{3v} AB_3 molecule, (f) basal plane of 3 B atoms in an AB_3 moledule, (g) pyramidal H_2AB molecules. Pyramidal B_2AC molecules have similar coordinate systems as in e and f. In e and g a thick line indicates that the terminal atom is *above* the plane of the paper whereas a dotted line indicates that the terminal atom is below the plane of the paper.

The occupancy of the $2b_2$ orbital is seen to be essential for the bent shapes of certain common HAAH molecules. As in I, one can explain bond length changes from molecule to molecule within a class. In the horizontally homologous series C_2H_2, N_2H_2, and H_2O_2, increased occupancy of the $2b_2$ orbital should lead to

(3) In constructing the b_2 MO's we have kept A–A antibonding as small as possible.

(4) (a) B. M. Gimarc, *J. Amer. Chem. Soc.*, **92**, 266 (1970); see also G. W. Schnuelle and R. G. Parr, *ibid.*, **94**, 8974 (1972); (b) U. Kaldor and I. Shavitt, *J. Chem. Phys.*, **44**, 1823 (1966).

(5) (a) W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2261 (1967); (b) W. E. Palke and R. M. Pitzer, *ibid.*, **46**, 3948 (1967).

(6) C. A. Coulson and B. M. Deb, *Int. J. Quantum Chem.*, **5**, 411 (1971).

(7) In the preliminary classification of planar HAAH molecules into bent and linear ones, one may start from the trans configuration, instead of the cis, and arrive at similar conclusions, although the situation here is less straightforward. As an illustration, consider the seven low-lying valence MO's of trans HAAH molecules, as depicted in Figure 9. These may be arranged in the energy order $1a_g < 1b_u < 2b_u$, $2a_g < 1a_u < 3a_g < 1b_g$. However, the MO's $2b_u$ and $2a_g$ cross each other in the Walsh–Allen diagram,[4a] making the choice of HOMO difficult for five–ten valence electron molecules. The $2b_u$ and $1a_u$ orbitals correlate with the $1\pi_u$ orbitals of the linear molecule which, in turn, correlate with the $1b_1$ and $3a_1$ orbitals of the cis molecule. The $2a_g$ orbital correlates with the $2\sigma_g$ orbital of the linear molecule and the $2a_1$ orbital of the cis molecule. The $3a_g$ and $1b_g$ MO's correlate with the $1\pi_g$ MO's of the linear molecule. From Figure 9 it is clear that the $1a_g$, $2b_u$, and $3a_g$ orbitals will favor a bent molecule while the $1b_u$ and $2a_g$ orbitals will favor a linear molecule. The $1a_u$ and $1b_g$ orbitals, being perpendicular to the molecular plane, will have little influence on the bond angle. While the resulting shape predictions for 1–4 and 11–14 valence electron molecules agree with those made on the basis of the cis configuration (Table II), the shapes of five–ten valence electron molecules are difficult to decide, since these depend on a balance between the effects of the $2b_u$ and $2a_g$ MO's (see HOMO postulate in part I). The difficulty is that we cannot assume this balance to be of the same type for all five–ten-electron molecules. For instance, since C_2H_2 is linear it seems that, for nine–ten-electron molecules, the effect of the $2b_u$ MO predominates over that of the $2a_g$ MO. But, for five–eight-electron molecules, which are bent, the $2a_g$ MO predominates over the $2b_u$ MO. Thus, we see that although, in principle, we should obtain the same geometry predictions based on the trans configuration as those based on the cis configuration, the crossing of MO's in the trans configuration precludes straightforward geometry predictions. Therefore, for predictive purposes it is much easier to fall back upon the cis configuration where, fortunately, no such crossing of MO's occurs in the Walsh–Allen diagram. Such crossings are also encountered with certain other molecules (see sections 1 and 2).

Table I. Valence s and p Group Orbitals for Five Molecule Classes (see Figure 1)

Molecule class and point group	Irreducible representation	A group AO's	H group AO's	B group AO's	C AO's
HAAH (C_{2v})	A_1	$s_1 + s_2, py_1 + py_2, pz_1 + pz_2$	$h_1 + h_2$		
	B_1	$px_1 - px_2$			
	A_2	$px_1 + px_2$			
	B_2	$s_1 - s_2, py_1 - py_2, pz_1 - pz_2$	$h_1 - h_2$		
HAAH (C_2)	A	$s_1 + s_2, px_1 - px_2, py_1 - py_2, pz_1 + pz_2$	$h_1 + h_2$		
	B	$s_1 - s_2, px_1 + px_2, py_1 + py_2, pz_1 - pz_2$	$h_1 - h_2$		
BAAB (C_{2v})	A_1	$s_{1a} + s_{2a}, py_{1a} + py_{2a}, pz_{1a} + pz_{2a}$		$s_{1b} + s_{2b}, py_{1b} + py_{2b}, pz_{1b} + pz_{2b}$	
	B_1	$px_{1a} - px_{2a}$		$px_{1b} - px_{2b}$	
	A_2	$px_{1a} + px_{2a}$		$px_{1b} + px_{2b}$	
	B_2	$s_{1a} - s_{2a}, py_{1a} - py_{2a}, pz_{1a} - pz_{2a}$		$s_{1b} - s_{2b}, py_{1b} - py_{2b}, pz_{1b} - pz_{2b}$	
BAAB (C_2)	A	$s_{1a} + s_{2a}, px_{1a} - px_{2a}, py_{1a} - py_{2a}, pz_{1a} + pz_{2b}$		$s_{1b} + s_{2b}, px_{1b} - px_{2b}, py_{1b} - py_{2b}, pz_{1b} + pz_{2b}$	
	B	$s_{1a} - s_{2a}, px_{1a} + px_{2a}, py_{1a} + py_{2a}, pz_{1a} - pz_{2a}$		$s_{1b} - s_{2b}, px_{1b} + px_{2b}, py_{1b} + py_{2b}, pz_{1b} - pz_{2b}$	
AB$_3$ (C_{3v})	A_1	s_a, pz_a		$s_1 + s_2 + s_3, px_1 + px_2 + px_3, pz_1 + pz_2 + pz_3$	
	A_2			$py_1 + py_2 + py_3$	
	E	px_a		$2s_1 - s_2 - s_3, 2px_1 - px_2 - px_3, 2py_1 - py_2 - py_3, 2pz_1 - pz_2 - pz_3$	
		py_a		$s_2 - s_3, px_2 - px_3, py_2 - py_3, pz_2 - pz_3$	
H$_2$AB (C_s)	A′	s_a, px_a, pz_a	$h_1 + h_2$	s_b, px_b, pz_b	
	A′′	py_a	$h_1 - h_2$	py_b	
B$_2$AC (C_s)	A′	s_a, px_a, pz_a		$s_1 + s_2, px_1 + px_2, py_1 - py_2, pz_1 + pz_2$	s_c, px_c, pz_c
	A′′	py_a		$s_1 - s_2, px_1 - px_2, py_1 + py_2, pz_1 - pz_2$	py_c

an increase in A–A bond length[8a] (1.21, 1.22 calcd,[8b] 1.48 Å, respectively) and a decrease in A–H length (1.06, 1.08 calcd,[8b] 0.97 Å, respectively). Between the vertically homologous molecules H_2O_2 (0.97 Å) and H_2S_2 (1.33 Å) the latter should have a greater A–H bond length since the valence AO's of the S atoms have greater $\langle r \rangle$ values than those of the O atom and hence there will be less charge concentration in the H–S binding region (see I). Further, the ∠HSS (95°) will be smaller than the ∠HOO (105°) because the sulfur s and p AO's have greater $\langle r \rangle$ values than the corresponding values for the oxygen atom.

Once we have decided which HAAH molecules should be linear and which should be nonlinear it now remains to find out which of the nonlinear molecules should be planar (cis/trans) and which should be nonplanar. Consider the coordinate system and transverse forces for nonplanar HAAH molecules (C_2 symmetry) as depicted in Figure 1b. A planar molecule is achieved by symmetric transverse motions of the two protons with respect to their respective HA_1A_2 planes, keeping the two A atoms and the A–H length fixed. The following considerations are not applicable to linear molecules.

The eight low-lying MO's of a C_2 HAAH molecule can readily be arranged in the energy sequence 1a < 1b < 2a < 2b < 3a < 3b < 4a < 4b, using the rules in I. Figures 2–4 depict these MO's schematically and in simplified forms. These orbitals change over to the appropriate a_1, b_2, b_1, and a_2 orbitals in the cis configuration. In particular, the 2b and 4a orbitals in the C_2 configuration correlate with the $1b_1$ and $1a_2$ orbitals, respectively, in the cis configuration.

From Figure 1b we notice that any MO which concentrates more charge outside the molecular prism than inside it will favor a trans configuration. Orbitals which throw more charge inside the prism will favor a nonplanar (C_2) or a cis (C_{2v}) form. It is not possible to decide which of C_2 and C_{2v} would be more favored. From Figures 2–4 it appears that of the eight MO's only three, namely 2b, 3a, and 4a, will favor a trans configuration; the rest will favor a C_2/C_{2v} form. Therefore, we conclude that HAAH molecules with one, two, five, and six valence electrons will be either cis or nonplanar. Bent molecules with seven or eight electrons will prefer a trans form. However, a complication arises due to the crossing (at dihedral angle ≃90°) of the 3b and 4a curves in the Walsh–Allen diagram.[4–5] Since 3b and 4a orbitals favor C_2/C_{2v} and C_{2h} (trans) forms, respectively, this crossing means that 11–12-electron molecules are likely to have both cis and trans isomers (see also ref 4a). The shapes of 13–14-electron molecules depend on the balance between the influences of the 3b and 4a orbitals. The fact that 14-electron molecules like H_2O_2 and H_2S_2 are nonplanar shows that in such cases the 3b orbital predominates over the 4a MO in governing the molecular shape. The same is likely to be true for 13-electron molecules as well. One would obviously expect the barrier to internal rotation to be rather low in such nonplanar molecules. With electronic excitation to the 4b level the dihedral angle in 13–14-electron molecules is expected to decrease.

(8) (a) Unless otherwise mentioned, data for bond angles and lengths are taken from L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 11** (1958); *Chem. Soc., Spec. Publ., Suppl.*, **No. 18** (1965); (b) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., Chapter 4.

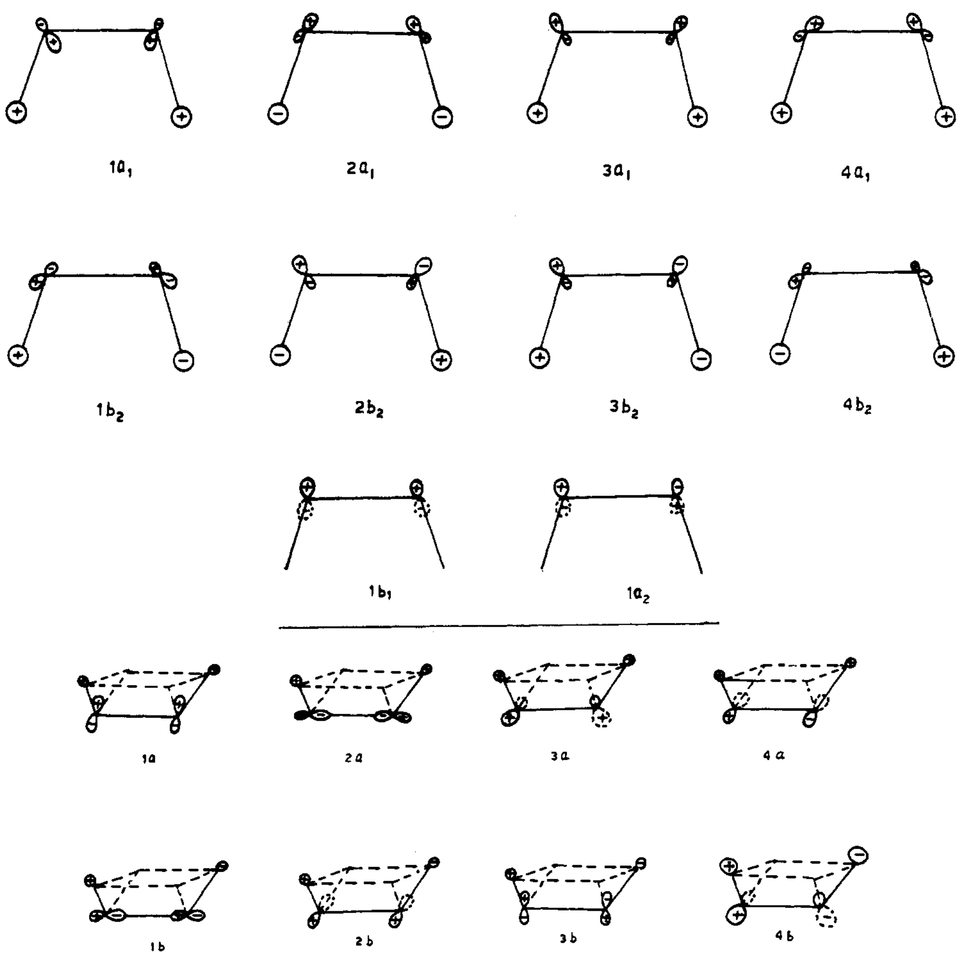

Figure 2. Schematic valence MO's for C_{2v} HAAH (top) and C_2 HAAH (bottom) molecules.

The angular behavior of the MO forces for C_2 molecules agrees with the force calculations of Coulson and Deb[6] and parallels the behavior of the corresponding MO energy gradients.

2. BAAB Molecules (Linear–Bent and Planar–Nonplanar Correlations). As with HAAH molecules, our approach will be to first consider which BAAB molecules are likely to be nonlinear and then to find out which of these nonlinear molecules would tend to assume a trans configuration. As depicted in Figure 1c, a linear configuration is achieved by symmetric transverse motions of the B atoms in the molecular plane, keeping the A atoms and the A–B length fixed.

The 16 valence MO's for a cis molecule (C_{2v}) may be constructed from valence s and p group AO's (see Table I) as follows: (i) $1a_1$, an orbital which is A–A and A–B bonding; (ii) $2a_1$, an MO which is primarily a "lone pair" combination of the terminal atom orbitals; (iii) $3a_1$, an MO which is feeble A–B and feebler A–A bonding (this may also be regarded as a "lone pair" combination of AO's on the A atoms); (iv) $4a_1$, an MO which is feeble A–A and feeble A–B bonding; (v) $5a_1$, an MO that is A–A bonding and feeble A–B antibonding; (vi) $6a_1$, an MO which is A–A bonding and A–B antibonding; (vii) $1a_2$, a π MO which is A–B bonding and A–A antibonding; (viii) $2a_2$, a π MO which is A–A and A–B antibonding; (ix) $1b_1$, a π MO that is A–A and A–B bonding; (x) $2b_1$, another π MO that is A–A bonding and A–B antibonding; (xi) $1b_2$, an MO which is A–B bonding; (xii) $2b_2$, an MO which is mainly a "lone pair" combination of the terminal atom orbitals; (xiii) $3b_2$, an MO which is feeble A–B bonding (this MO may be looked upon as a "lone pair" combination of AO's on the A atoms); (xiv) $4b_2$, an MO which is feeble A–B bonding and A–A antibonding; (xv) $5b_2$, an MO that is A–A antibonding and mild A–B antibonding; (xvi) $6b_2$, an MO which is A–B antibonding and mild A–A antibonding. Owing to the unavailability of relevant data it is not possible to compare these MO's with corresponding *ab initio* or extended Hückel MO's. Following the rules in I and using the MO energy order for AB_2 molecules, the above MO's may be arranged in the energy sequence $1a_1 < 1b_2 < 2a_1 < 1b_1 < 3a_1 < 2b_2 < 1a_2 < 3b_2 < 4a_1 < 2b_1 < 5a_1 < 4b_2 < 2a_2 < 5b_2 < 6a_1 < 5b_2$. Up to the $2a_2$ orbital this order agrees more or less with the extended Hückel energy order calculated by Gimarc[4a] which shows the orbitals from $1b_1$ to $4a_1$ lying very close to one another and sometimes crossing one another.

The schematic AO's for cis BAAB molecules are depicted in Figures 2–4. Arguments similar to the ones used previously show that the orbitals $1a_1$, $2a_1$, and $3a_1$ all favor a bent configuration while the $5a_1$ MO favors a linear configuration. In the case of the $4a_1$ orbital, the atomic and overlap forces would nearly balance each other and so this orbital is unlikely to have much influence on the bond angle. Of the MO's belonging to the B_2 representation only $4b_2$ favors a bent form, the other b_2 MO's favoring a linear form.

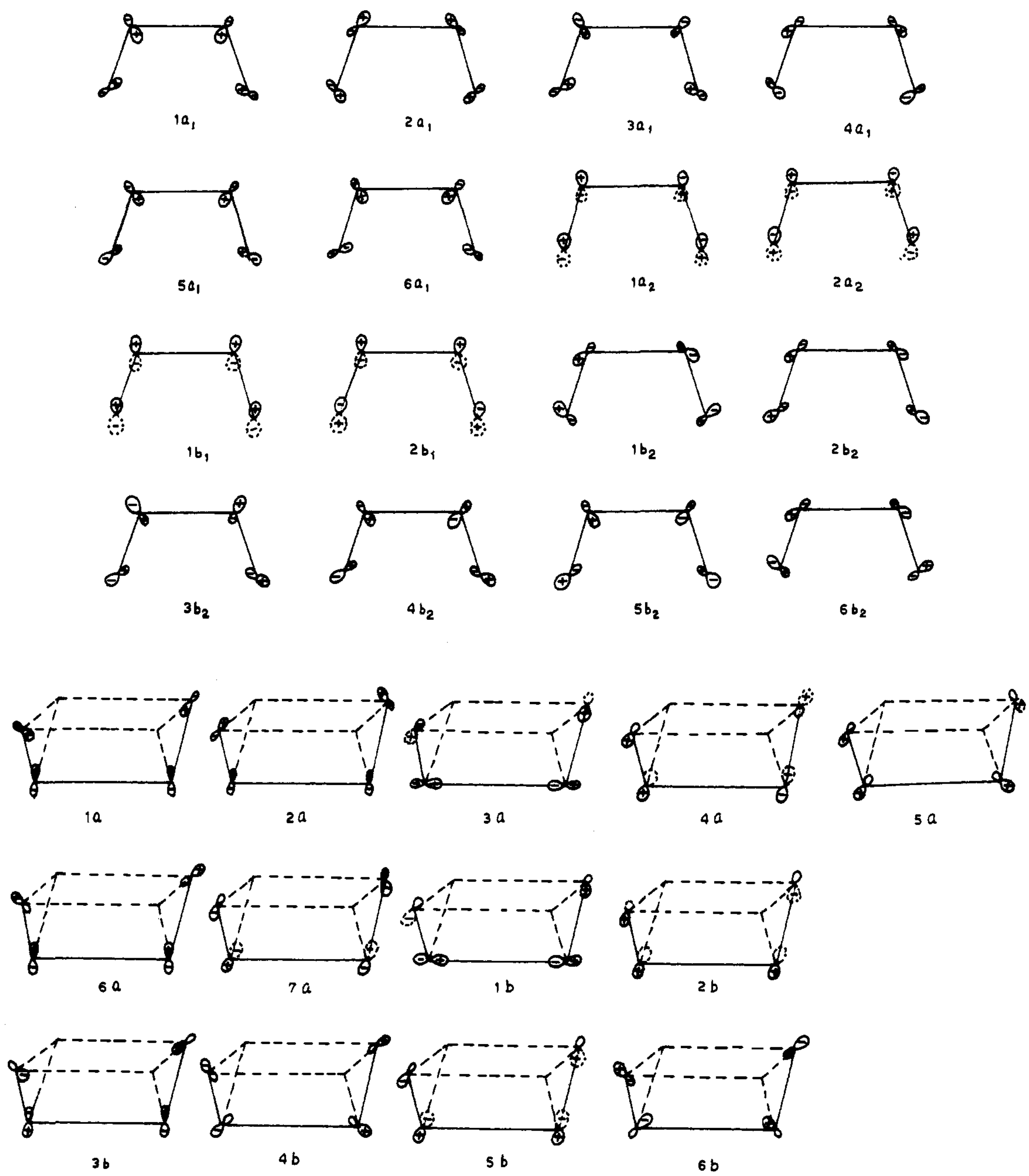

Figure 3. Schematic valence MO's for C_{2v} BAAB (top) and C_2 BAAB (bottom) molecules.

If we imagine that in the A–A and B–B antibonding orbital $1a_2$ both halves of the p lobe on an A or a B atom are directed away from the corresponding half-lobes on the neighboring A and B atoms, respectively, then it is easy to see that the $1a_2$ orbital would favor a linear form. Parallel considerations show that the $1b_1$ orbital would favor a bent form. Because of near cancellation between atomic and overlap forces, the $2a_2$ and $2b_1$ orbitals are expected to have little effect on the bond angle. The nature of these MO forces is in reasonable agreement with the extended Hückel orbital energy gradients.[4a] Allen and Russell[9] have previously demonstrated that the angular behavior of extended Hückel orbital energies parallels that of the corresponding *ab initio* orbital energies.

Table II summarizes the conclusions about the linearity or nonlinearity of BAAB molecules, based on the above considerations. Similar conclusions have also been reached by Gimarc[4a] as well as Pearson.[10] It is seen that the common nonlinear BAAB molecules must have the $4b_2$ orbital filled (the $2a_2$ orbital is not sensitive to bending of the molecular skeleton) and have 23–26 valence electrons. It is difficult to check the predictions regarding the shapes of molecules having <18 electrons since neither theoretical nor experimental data are available for these molecules.

An apparent exception to the present Walsh type rules is the 22-electron molecule N_2O_2 which is predicted to be linear. Experimental data[11] indicate a skew or cis from whereas *ab initio* calculations[12] favor a

(9) L. C. Allen and J. D. Russell, *J. Chem. Phys.*, **46**, 1029 (1967).

(10) R. G. Pearson, *J. Chem. Phys.*, **52**, 2167 (1970); *J. Amer. Chem. Soc.*, **91**, 4947 (1969).

(11) W. A. Guillory and C. E. Hunter, *J. Chem. Phys.*, **50**, 3516 (1969).

(12) J. N. Murrell and J. E. Williams, *J. Amer. Chem. Soc.*, **93**, 7149 (1971); T. Vladimiroff, *ibid.*, **94**, 8250 (1972).

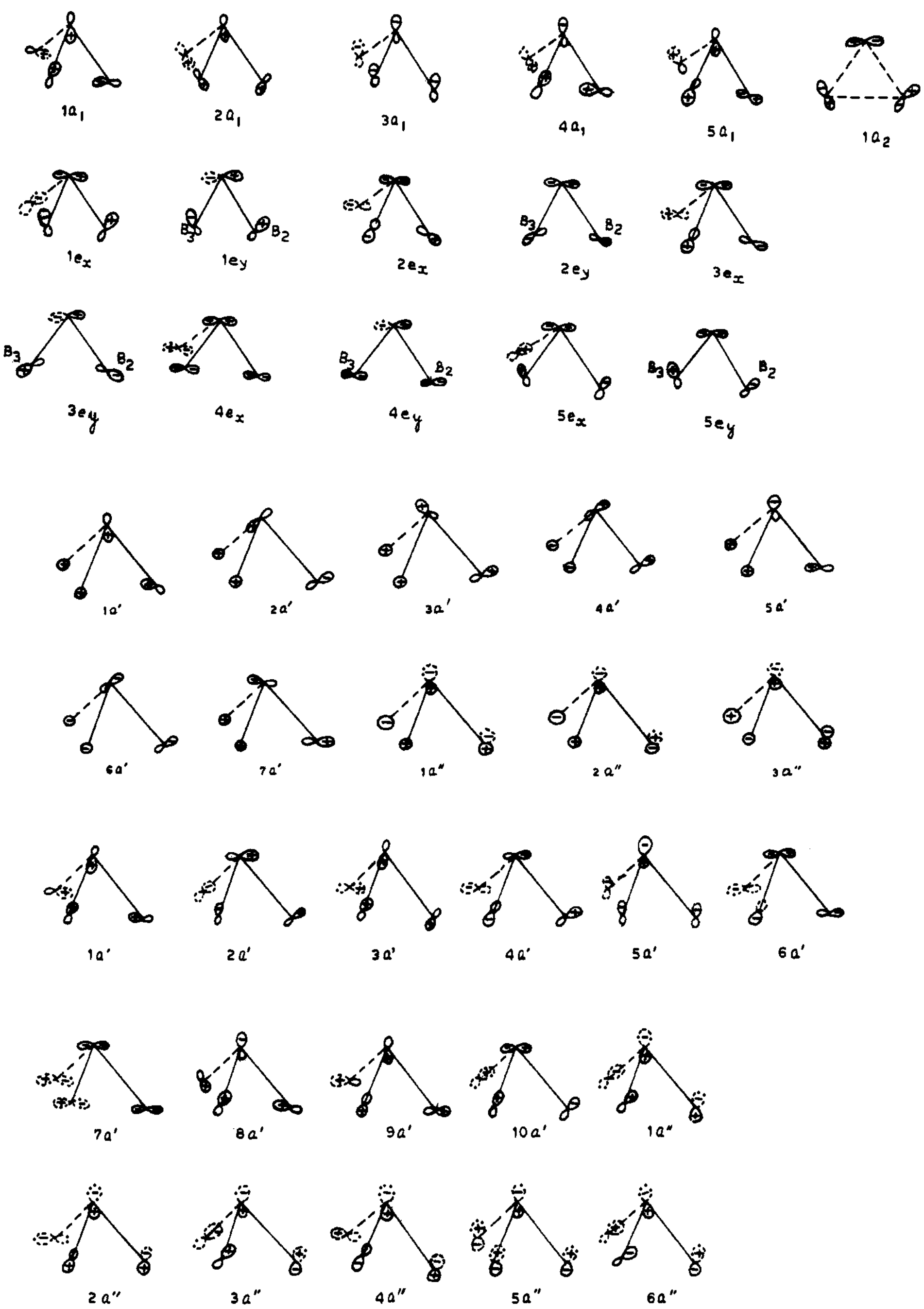

Figure 4. Schematic valence MO's for C_{3v} AB_3 (top), pyramidal H_2AB (middle), and pyramidal B_2AC (bottom) molecules.

cyclic or a trans form. Such a situation may arise when the $5a_1$ and $4b_2$ orbitals are either reversed in energy order or they cross each other in the Walsh–Allen diagram so that either (a) the $4b_2$ orbital is now the HOMO or (b) there is no unique choice for the HOMO. In case a the molecule will be bent whereas in case b the molecular shape will depend on the net effect of the $5a_1$ and $4b_2$ orbitals, the former favoring a linear and the latter favoring a bent form. Because of progressive filling of antibonding orbitals the A–F bond length in F_2O_2 (1.58 Å) is greater than that in F_2N_2 (1.38 Å).[8b]

Once we have decided which BAAB molecules should be linear or nonlinear it now remains to decide which of the nonlinear molecules should be planar or nonplanar. Just as with HAAH molecules, we have to choose between a C_{2h} (trans) and a C_2/C_{2v} configuration.

The 13 low-lying MO's of a C_2 molecule may be arranged in the energy order $1a < 1b < 2a < 2b < 3a < 3b < 4a < 4b < 5a < 5b < 6a < 6b < 7a$. For predicting planarity or nonplanarity our concern will be only with the 1-, 2-, 5–10-, and 23–26-electron molecules. The bonding characteristics of these MO's are evident from their schematic representation in Figures 2–4, which depicts the 1a, 2a, 2b, 3a, 6b, and 7a MO's constructed by using the rules in I and by comparing these with the corresponding MO's of a C_{2v} BAAB molecule. It is clear that these five MO's in the C_2 configuration correlate with the $1a_1$, $2a_1$, $1b_1$, $3a_1$, $4b_2$, and $2a_2$ MO's, respectively, in the C_{2v} configuration. From Figures 2–4 it is also clear that the 1a, 2a, and 3a orbitals favor a C_2/C_{2v} configuration, whereas the MO's 2b and 7a favor a trans (C_{2h}) configuration. By looking at the atomic and overlap forces arising from

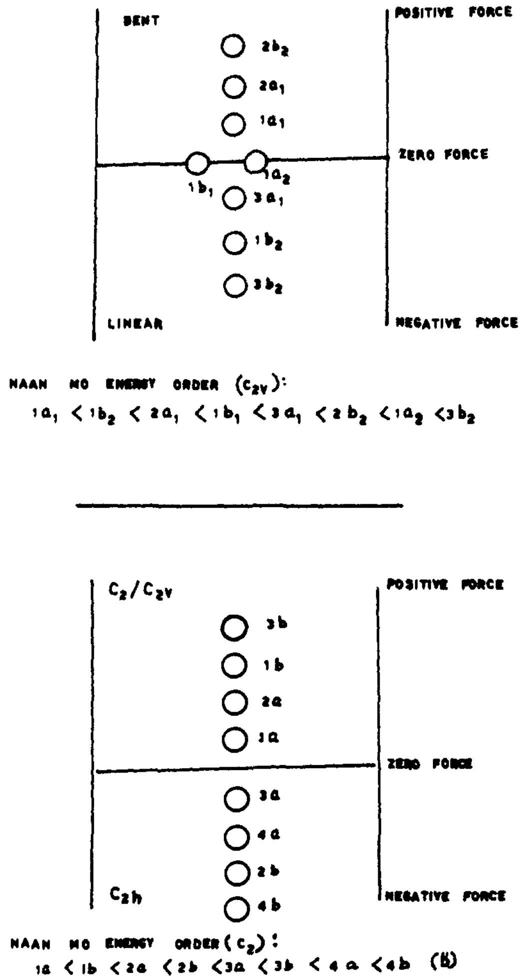

Figure 5. Shape diagrams for planar HAAH (top) and nonplanar HAAH (bottom) molecules.

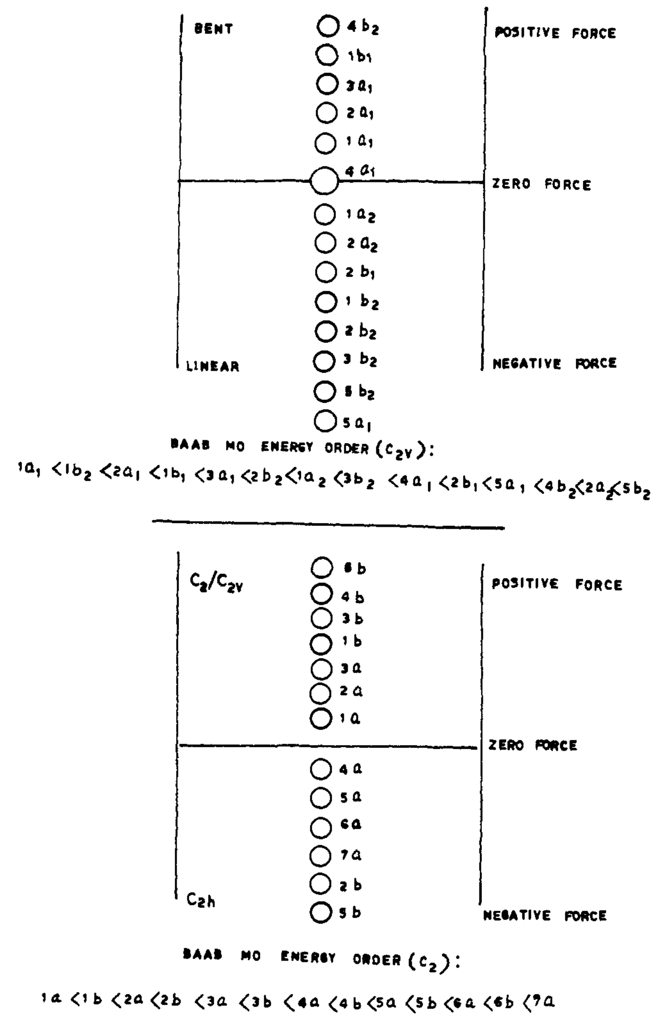

Figure 6. Shape diagrams for planar BAAB (top) and nonplanar BAAB (bottom) molecules.

the 6b MO it would not be unreasonable to expect the balance of the two to be somewhat on the positive side. This orbital would, therefore, favor a C_2/C_{2v} configuration. Therefore, BAAB molecules with one, two, five, and six valence electrons will be either cis or nonplanar, whereas those with seven–eight electrons will be trans. Nine–ten-electron molecules would again prefer a C_2/C_{2v} configuration. Owing to the unavailability of relevant experimental and theoretical data, it is not possible to check these predictions. The predictions for 23–26-electron molecules, however, are not straightforward because the orbital energy curves for the 6b and 7a MO's cross each other in the Walsh–Allen diagram.[4a] As with HAAH molecules, such energy crossing precludes the choice of a unique HOMO. Therefore, we are led to expect that 23–24-electron molecules will have both cis and trans isomers. The shapes of 25- and 26-electron molecules depend on the net effect of 6b and 7a orbitals favoring respectively C_2/C_{2v} and C_{2h} configurations. Since 26-electron molecules like O_2F_2, S_2Cl_2, etc., are nonplanar, it is expected that 25-electron molecules will also have a C_2 symmetry since the effect of the 6b MO predominates over that of the 7a MO.

3. **AB_3 Molecules (Pyramidal–Planar Correlation).** As a result of symmetric motions of the B nuclei, keeping the atom A and the A–B length fixed, the pyramidal form of an AB_3 molecule goes over into the planar form and *vice versa* (Figure 1). The 14 valence MO's of a C_{3v} AB_3 molecule ($\theta = 45°$, say) may be constructed from valence s and p group AO's (Table I) as follows: (i) $1a_1$, an MO having maximum bonding between A and the B atoms; (ii) $2a_1$, an MO which is a "lone pair" combination of AO's on the terminal atoms; (iii) $3a_1$, an MO which is feebly bonding between the central and terminal atoms; (iv) $4a_1$, an MO which is predominantly localized ("lone pair") on the central atom; (v) $5a_1$, an MO that is feebly antibonding between A and the terminal atoms; (vi) $1a_2$, an MO which is B–B antibonding and lies in the basal plane of the pyramid; (vii) $1e_x$ and $1e_y$, two orbitals which are A–B bonding; (viii) $2e_x$ and $2e_y$, two orbitals which are primarily "lone pair" combinations on the terminal atoms; (ix) $3e_x$ and $3e_y$, two orbitals which are mild A–B antibonding; (x) $4e_x$ and $4e_y$, two orbitals which are A–B π antibonding; (xi) $5e_x$ and $5e_y$, two orbitals which are A–B full antibonding. In the absence of calculated data on AB_3 MO's our constructed orbitals cannot be compared with *ab initio* MO's. Using the rules in I the constructed MO's may be arranged in the energy order $1a_1 < 1e < 2a_1 < 3a_1 < 2e < 3e < 1a_2 < 4e < 4a_1 < 5a_1 < 5e$ (see also AB_2 energy order in I). This order matches with extended Hückel calculations of Gimarc and Chou,[13] whose MO energy order for

(13) B. M. Gimarc and T. S. Chou, *J. Chem. Phys.*, 49, 4043 (1968).

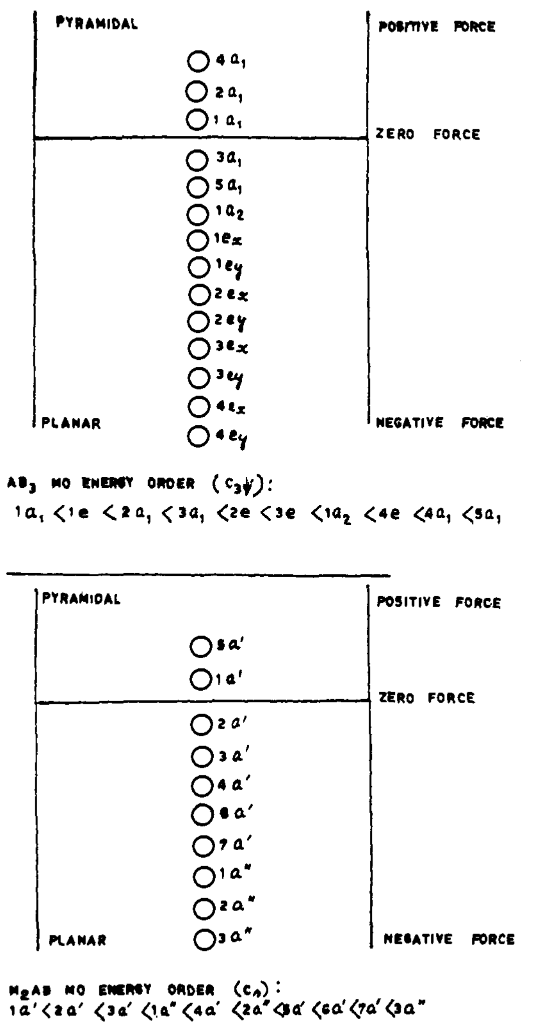

Figure 7. Shape diagrams for AB_3 (top) and H_2AB (bottom) molecules.

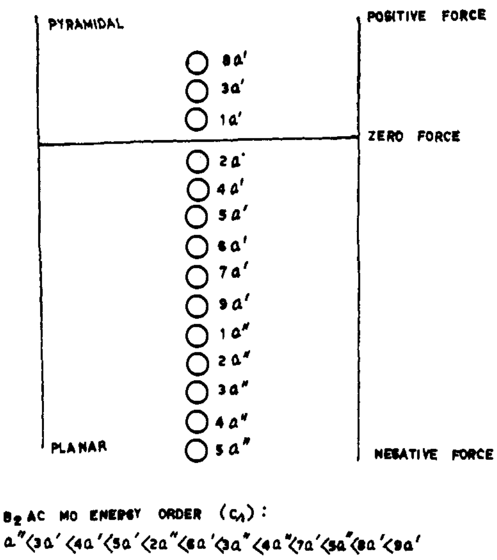

Figure 8. Shape diagram for the B_2AC molecule.

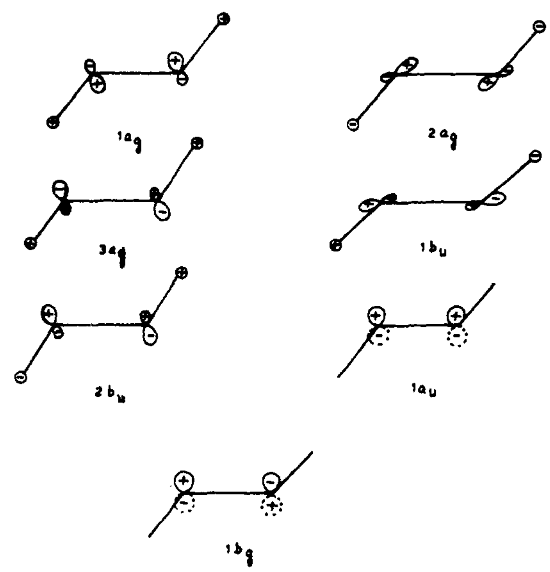

Figure 9. Schematic valence MO's for trans HAAH molecules (see ref 7).

planar CO_3 molecule, however, is not identical with the *ab initio* MO energy order[14] for BF_3, a planar molecule.[15]

From Figures 2–4 it is clear that of the five a_1 MO's for AB_3 molecules $1a_1$, $2a_1$, and $4a_1$ will all favor a pyramidal molecule whereas the remaining two a_1 orbitals will favor a planar molecule. The $1a_2$ orbital will clearly throw charge outside the molecular pyramid and thus favor the planar configuration. The e orbitals will all favor a planar molecule. The shape diagram for these molecules is given in Figures 5–8 and the resultant geometrical predictions are summarized in Table II. The occupancy of the $4a_1$ "lone pair" MO by the outermost electron seems to be essential for the pyramidal shape of common AB_3 molecules. It is easy to understand why in a complex like $NH_3 \rightarrow BF_3$ the BF_3 fragment is pyramidal since this can be looked upon as a 25-electron fragment. The radical trimethylmethyl, $(CH_3)_3C$, obtained in the pyrolysis of isobutane, or neopentane, should be pyramidal since this is a 25-electron molecule. Similarly, on further ionization NO_3^- changes its shape from planar to pyramidal. However, 20-electron tetrahedral molecules such as P_4, As_4, etc., are apparent exceptions to our predictions. This may be due to our neglect of d orbitals[16] which may participate significantly in the bonding of such molecules (*cf.* BaX_2 molecules in I). In the horizontally homologous series BF_3, CF_3, and NF_3 the pyramidal angle θ is expected to decrease due to the progressive occupancy of the $4a_1$ orbital (see also ref 17).

It is worthwhile to examine the effect of ligand substitution on the shapes of AB_3 molecules. In the series PF_3 (1.535 Å), PCl_3 (2.043 Å), PBr_3 (2.18 Å), and PI_3 (2.43 Å) the P–X bond length is expected to increase because the heavier halogens have increasing $\langle r \rangle_s$ and $\langle r \rangle_p$ values for their valence AO's. The greater diffuseness of the valence AO's of the heavier halogens means that the terminal nuclei "see" less charge concentration between them in the $4a_1$ MO which is bonding between the terminal atoms. This means that the

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

(15) There may be minor variations in the above energy order for certain molecules; for example, R. M. Golding and M. Henchman, *J. Chem. Phys.*, **40**, 1554 (1964), argue that the unpaired electron in NO_3 should be in the $1a_2$ orbital rather than in the 4e MO. The $1a_2$ orbital also favors a planar molecule.

(16) R. G. A. R. Maclagan, *J. Chem. Soc. A*, 2992 (1970); 222 (1971).

(17) W. F. Luder, "The Electron-Repulsion Theory of the Chemical Bond," Reinhold, New York, N. Y., 1967.

Table II. Geometry Predictions for Five Molecule Classes (The Known Molecular Shapes Are Either Empirical or Theoretical)[8,10,19 a]

Molecule class	No. of valence electrons	Ground state geometry	Examples	Excited state geometry	Examples	Apparent exceptions, if any
HAAH	1, 2	Bent (C_{2v}/C_2)				
	3, 4	Linear				
	5, 6	Bent (C_{2v}/C_2)				
	7, 8	Bent (C_{2h})				
	9, 10	Linear	C_2H_2, $N_2H_2^{2+}$	Bent (HOMO $2b_2$)		
	11, 12	Bent (C_{2v}/C_{2h})	N_2H_2, $(CH)_2H_2$[b]			
	13, 14	Bent (C_2)	H_2O_2	Linear (HOMO $3b_2$)		
	15, 16	Linear				
BAAB	1, 2	Bent (C_{2v}/C_2)				
	3, 4	Linear				
	5, 6	Bent (C_{2v}/C_2)				
	7, 8	Bent (C_{2h})				
	9, 10	Bent (C_{2v}/C_2)				
	11–22	Linear	Hg_2Cl_2, B_2O_2, C_2N_2, C_2F_2, $C_2O_2^{2-}$	Bent (HOMO $4b_2$)		N_2O_2 (see text)
	23, 24	Bent (C_{2v}/C_{2h})	N_2F_2, $N_2O_2^{2-}$, $(CH_3)_2N_2$, $(CH)_2I_2$			
	25, 26	Bent (C_2)	S_4^{2-}, S_2F_2, Cl_2O_2, $(CH_3)_2S_2$, $(CH_2)_2Cl_2$	Linear (HOMO $5b_2$)		
	27, 28	Linear				
AB_3	1, 2	Pyramidal				
	3–6	Planar				
	7, 8	Pyramidal				
	9–24	Planar	SO_3, NO_3^-, CO_3, CO_3^{2-}, BO_3^{3-}, BF_3, N_3F, NO_3, $GaCl_3$, $B(OH)_3$, CF_3^+	Pyramidal (HOMO $4a_1$)		P_4, As_4 (see text)
	25–26	Pyramidal	IO_3^-, $BiCl_3$, NF_3, CF_3, PCl_3, NO_3^{2-}, ClO_3, SO_3^{2-}, XeO_3, BrO_3^-, $(CH_3)_3C$	Planar (HOMO $5a_1$)		
	27, 28	Planar	ClF_3			
H_2AB	1, 2	Pyramidal				
	3–12	Planar	H_2CO, H_2BF, $H_2C(CH)$, $H_2C(CH)^+$, H_2CN, $H_2C(NH)$, $H_2C(CH)_2)$,[b] $H_2{}^+CF$	Pyramidal (HOMO $5a'$)	H_2CO	
	13, 14	Pyramidal	H_2CF, H_2NF, $H_2C(OH)$, $H_2N(OH)$, $H_2N(NH_2)$, $H_2N(CH_3)$[c]	Planar (HOMO $6a'$)		
	15–20	Planar				
B_2AC	1, 2	Pyramidal				
	3–6	Planar				
	7, 8	Pyramidal				
	9–24	Planar	$COCl_2$, $(CH_3)BF_2$, $NClO_2$, F_2BO, $(CH_3)_2CO$	Pyramidal (HOMO $8a'$)	$(CH_3)_2CO$	
	25, 26	Pyramidal	$F_2C(OF)$, $F_2N(OF)$, $F_2N(NF_2)$, $(CH_3)_2SO$, $SOCl_2$, Cl_2PF	Planar (HOMO $9a'$)		
	27, 28	Planar				

[a] M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 4046 (1970); L. D. Kispert, C. U. Pittman, D. L. Allison, T. B. Patterson, C. W. Gilbert, C. F. Hains, and J. Prather, *J. Amer. Chem. Soc.*, **94**, 5979 (1972). [b] This implies that the molecule is planar. [c] In formamide the $H_2NC\equiv$ fragment will be pyramidal since this can be looked upon as a 14-electron fragment, taking three electrons from the remaining three bonds to carbon.

bending force constant should increase in the series $PF_3 > PCl_3 > PBr_3$.[18] Similarly, one can predict that the bending force constant would increase in the series $PCl_3 > AsCl_3 > BiCl_3$.[18]

Once we have decided which AB_3 molecules are pyramidal and which are planar it now remains to find out which planar molecules will have an approximate T shape. For this one need not construct a separate shape diagram since such predictions can be made from the shape diagram for AB_2 molecules. An example, ClF_3, has been discussed in I (see also Table II).

From the present order of energy levels one would expect 21-electron molecules to undergo the static Jahn–Teller effect. If the $4e_x$ orbital is occupied by the unpaired electron then we may expect the $A-B_1$ bond to be longer than the other two. On the other hand, if the $4e_y$ orbital is occupied then the $A-B_2$ and $A-B_3$ bonds are expected to be longer than the remaining one (see Figures 2–4).

(18) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1964, p 177.

4. H_2AB Molecules (Pyramidal–Planar Correlation). Although pyramidal H_2AB molecules have no axis of symmetry we shall continue to define the pyramidal angle θ as the angle between a bond and an imaginary threefold axis. This, in fact, presumes that $\angle HAH = \angle HAB$, and, although it is generally not true, it simplifies our discussion and does not invalidate any of the following conclusions. The transverse forces and the coordinate system for H_2AB molecules are depicted in Figure 1.

The ten valence MO's of a pyramidal (C_s) H_2AB molecule ($\theta = 45°$, say) may be constructed as follows (see Table I): (i) 1a′, an orbital that is primarily A–B bonding; (ii) 2a′, an orbital that is primarily A–H bonding; (iii) 3a′, a "lone pair" orbital on the B atom; (iv) 4a′, an orbital which is feeble A–H and feeble A–B bonding; (v) 5a′, a "lone pair" orbital on the central atom; (vi) 6a′, an MO that is feeble A–B bonding and A–H mild antibonding; (vii) 7a′, an MO that is A–H feeble bonding and A–B mild antibonding; (viii) 1a″, an MO which is A–H bonding and A–B π bonding; (ix) 2a″, an MO which is A–H bonding and A–B π antibonding. In the absence of calculated data on nonplanar H_2AB molecules, the above MO's could not be compared with the *ab initio* ones. Using the rules in I, the above MO's may be arranged in the energy order 1a′ < 2a′ < 3a′ < 1a″ < 4a′ < 2a″ < 5a′ < 6a′ < 7a′ < 3a″. Although *ab initio* calculations exist on planar H_2AB molecules, computed data on the energy order of nonplanar molecules are lacking.

From the schematic MO's in Figures 2–4 one can readily see that of the ten MO's only two, *viz.*, 1a′ and 5a′, favor a pyramidal molecule, whereas the other eight MO's favor a planar molecule. The shape diagram for H_2AB molecules is indicated in Figures 5–8 and the resultant geometry predictions are listed in Table II. H_2AB molecules which are pyramidal should have either the 1a′ MO or the 5a′ "lone pair" orbital occupied by the outermost electron. Because of progressive filling of the "lone pair" orbital 5a′, the pyramidal angle in the 13-electron molecule H_2CF is expected to be larger than that in the 14-electron molecule H_2NF. Approximate MO calculations[8b,19] agree with this expectation.

After we have concluded which H_2AB molecules are likely to be planar we must find out which of these planar molecules are likely to be T shaped. This can be easily done by looking at the shape diagram for AH_2 molecules (see I) and then deciding which of the planar H_2AB molecules will have a linear AH_2 fragment (see Table II). For example, a molecule like H_2LiBe is expected to be T shaped since the four-electron (H_2Li–) fragment will be linear (see also I).

5. B_2AC Molecules (Pyramidal–Planar Correlation). We shall adopt the view that AB_3 molecules are special cases of the less symmetric B_2AC molecules in which we shall assume that $\angle BAB = \angle BAC$. As with H_2AB molecules, this simplifying assumption will not affect the validity of our conclusions. We also assume that the B atoms are heavier than C.

The low-lying valence MO's of a pyramidal B_2AC molecule may be constructed (see valence s and p group AO's for the C_s molecule) by enlisting help from the AB_3 MO's. Each doubly degenerate E level of AB_3 molecules now splits into an A′ and an A″ level.

(19) M. S. Gordon and J. A. Pople, *J. Chem. Phys.*, **49**, 4643 (1968).

The various MO's may be written as: (i) 1a′, an orbital that is primarily A–B bonding; (ii) 2a′, an orbital that is primarily A–C bonding; (iii) 3a′, an orbital which is predominantly localized on the C atom; (iv) 4a′, an orbital which is predominantly localized on the B atoms; (v) 5a′, an orbital which is mild A–B and A–C bonding; (vi) 6a′, an orbital which is mild A–B bonding and feeble A–C antibonding; (vii) 7a′, an orbital which is mild A–C bonding and mild A–B antibonding; (viii) 8a′, a "lone pair" orbital on the A atom; (ix) 9a′, an orbital that is mild A–B and A–C antibonding; (x) 10a′, an orbital that is A–B and A–C antibonding; (xi) 1a″, an orbital which is A–B bonding and A–C π bonding; (xii) 2a″, a "lone pair" orbital on the B atoms; (xiii) 3a″, an orbital that is A–C π antibonding and A–B bonding; (xiv) 4a″, an orbital which is A–C π bonding and A–B mild antibonding; (xv) 5a″, an MO which is mild A–B and A–C antibonding; (xvi) 6a″, an MO which is A–C π antibonding and A–B antibonding. In the absence of calculated data on B_2AC MO's our constructed MO's which are represented schematically in Figures 2–4 could not be compared with *ab initio* MO's. Using the rules in I the above MO's may be arranged in the energy order 1a′ < 2a′ < 1a″ < 3a′ < 4a′ < 5a′ < 2a″ < 6a′ < 3a″ < 4a″ < 7a′ < 5a″ < 8a′ < 9a′ < 10a′ < 6a″. From overlap considerations the MO 7a′ should have lower energy than the "lone pair" MO 8a′.

The schematic MO's in Figures 2–4 indicate that of all the a′ MO's only 1a′, 3a′, and 8a′ favor a pyramidal molecule while all the other a′ MO's as well as all the a″ MO's favor a planar configuration. Therefore, we conclude that, like AB_3 molecules, B_2AC molecules with 1, 2, 7, 8, 25, and 26 valence electrons will be pyramidal whereas all the other B_2AC molecules will be planar. This is indicated in the appropriate shape diagram in Figures 5–8. Molecules in the B_2ACD class also fit in this scheme. Table II summarizes the various geometric predictions made for B_2AC molecules. It is seen that for common pyramidal molecules occupancy of the central atom "lone pair" orbital 8a′ by the outermost electron is the crucial factor in determining their shapes.

In the pyramidal series F_2SO, Cl_2SO, and Br_2SO the S–X bond length (1.59, 2.07, and 2.27 Å) is expected to increase because of the increasing $\langle r \rangle$ values of the terminal halogen atoms. Likewise, one may predict that in $SOCl_2$ replacement of S by Se will result in a decrease in the pyramidal angle.