

Predictions of Molecular Geometry from Structural Fragments¹

Joel F. Liebman

*Contribution from the Department of Chemistry, University of Maryland
Baltimore County, Baltimore, Maryland 21228. Received October 3, 1973*

Abstract: A simple, noncalculational, nonempirical method is suggested as a predictor of molecular geometry. It is applied to triatomic molecules and various subclasses of tetraatomic molecules. The process uses as input parameters only the number of electrons in the constituent fragments. To apply this method to triatomic molecules, the molecule is dissected into atomic and closed shell diatomic fragments. Atoms having a closed shell or being one electron short are designated "blocked." All other atomic electron configurations are designated "porous." The closed shell diatomics are divided into essentially two classes: σ -rich, isoelectronic with BH or CO, and π -rich, isoelectronic with HF or F₂. General rules are suggested as follows: blocked + σ -rich = bent, porous + σ -rich = linear, blocked + π -rich = linear, porous + π -rich = bent. Analogous dissections and definitions are introduced for tetraatomic molecules. The procedure has been applied to numerous molecules and ions; only two exceptions or ambiguities have been found. One may be correlated with an anomalously low bending force constant and the other is also unsatisfactorily described by most other geometry predictors. Justifications for the general validity of the suggested approach to molecular geometry are also given.

Previously, the geometry^{2,3} of molecules has been described in terms of the orbitals of the entire molecule⁴⁻⁶ and in terms of those of the component atoms.^{7,8} This paper attempts to gain an understanding of the molecular geometry by conceptually decomposing or dissecting molecules into simple structural fragments. For example, triatomic molecules are studied in terms of diatomic molecules and atoms. (In using the words "molecule" and "atom," we do not intend to preclude ions.) This dissection of the molecule allows consideration of smaller and consequently presumably better understood units than would the observation and study of the total species. Conversely, we are not belabored by the excessive number of states that may be formed by atomic partitioning of the molecule and putting it "back together again." For example, the Wigner-Wittmer Rules⁹ show that one may only form the ¹ Σ and ³ Σ states of HCN from ²S H + ² Σ CN, whereas a ⁷ π state is also in principle possible from ²S H + ³P C + ⁴S N. However, one does not have to worry about these rules or even spin conservation to get results.

We begin with triatomic molecules and with what may appear to be chemical taxonomy. Atoms and molecules may be classified as being either open or closed shelled. All closed shell atoms and diatomic molecules have zero orbital angular momentum¹⁰ and zero spin and are designated ¹S and ¹ Σ , respectively. At this stage, we will define two new terms: "blocked"

and its opposite "porous." A blocked atom is an atom that has either a closed valence shell or is only one electron short of being closed. A porous atom is an atom with more than one vacancy in the valence shell. It is initially ambiguous how to define a blocked or porous molecule, since the eight-valence electron ¹ Σ LiF is porous relative to the ten-valence electron ¹ Σ CO. For triatomic molecules, it is unnecessary to consider blocked or porous molecules and thus we are temporarily absolved from the problem.

However, we need not consider all closed shell¹¹ diatomics in one category. These species may be divided into several classes. The first class consists of the four-valence electron BH and the ten-valence electron CO and their isoelectronic analogs. These may be referred to as σ -rich species since there are more σ valence shell electrons than π valence shell electron in these compounds. BH has a σ^4 configuration and CO has a $\sigma^6 \pi^4$ configuration. Not surprisingly, the "cations"¹² derived by loss of an electron from a molecule of this class have a ² Σ configuration arising from loss of a σ electron. By analogy to the isoelectronic CH and NO, BH⁻ and CO⁻ most likely have a ² π configuration. (BH⁻, CH, CO⁻, and NO all belong to the group of "anions" derived from this class of diatomics.)

The second class of diatomics consists of the eight-valence electron HF and the 14-valence electron F₂ and their isoelectronic analogs.¹³ These species may be referred to as π -rich; since there are at least as many π electrons as σ electrons, LiF has a $\sigma^4 \pi^4$ configuration and F₂ has a $\sigma^6 \pi^8$ configuration. The ground state

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(2) Most of the results of this paper and of those of ref 3 through 8 are identical with those predicted by valence shell electron pair repulsion theory: R. J. Gillespie, *J. Chem. Educ.*, **40**, 295 (1963).

(3) H. Nakatsuji, *J. Amer. Chem. Soc.*, **95**, 345, 354 (1973).

(4) A. D. Walsh, *J. Chem. Soc.*, 2266 (1953), and the following papers.

(5) B. M. Gimarc, *J. Amer. Chem. Soc.*, **93**, 815 (1971).

(6) S. D. Peyerimhoff and R. J. Buenker, *J. Chem. Phys.*, **49**, 2473 (1968).

(7) Y. Takahata, G. W. Schnuelle, and R. G. Parr, *J. Amer. Chem. Soc.*, **93**, 785 (1971).

(8) H. B. Thompson, *J. Amer. Chem. Soc.*, **93**, 4609 (1971).

(9) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. 1, Van Nostrand, Princeton, N. J., 1950, pp 315-322 and 446-447; Vol. 3, 1966, pp 281-296.

(10) The converse is not true. ¹S and ¹ Σ species may be open shell such as ¹S O and ¹ Σ O₂.

(11) Low-lying empty orbitals produce complications in the definition of closed shell. For the first three rows (H through Ar) this is probably irrelevant for our problem. A consequence of our approximation is that we do not treat d atomic orbitals and δ molecular orbitals. It will be noted that these orbitals cause complications in more established theories. For example, standard application presented in ref 2 and ref 4 through 8 to the alkaline earth dihalides suggests that these triatomics should all be linear. However, the more polar species are all bent in agreement with an *a posteriori* inclusion of d orbitals into the Walsh (ref 4) diagram: E. F. Hayes, *J. Phys. Chem.*, **70**, 3740 (1966).

(12) All data on diatomic molecules and ions were taken from ref 9, Vol. 1, unless a citation is given to the contrary.

(13) In this definition of the second class of diatomic molecules, it is assumed that hydrogen and the alkali metals are isoelectronic although this is customarily not done (see ref 14 and 15).

(14) H. A. Bent, *J. Chem. Educ.*, **43**, 170 (1966).

(15) J. F. Liebman, *J. Chem. Educ.*, **48**, 188 (1971).

for both LiF^{+16} and F_2^+ is most probably 2π . LiF^- most likely has a 2Σ ground state by analogy to BeF . It will also be noted that LiF^- and CO^+ are also isoelectronic. The ground state of F_2^- has been calculated to be 2Σ and the higher lying 2π states are unbound.¹⁷

The third class of diatomics consists of H_2 and its isoelectronic analogs, the alkali metal hydrides and the alkali metal dimers.¹⁸ Both the cations and anions¹⁹ have 2Σ ground states. We may disregard this class of diatomics, since there are essentially no orbitals available for covalent bonding.²⁰

The fourth and final class of diatomics consists of He_2 and Ne_2 and their isoelectronic analogs. These species are almost exclusively unbound.^{21,22} As such, they may be disregarded by our study, since we are interested in a bound triatomic molecule.²³

We are now ready to attempt to predict the geometry of triatomic molecules from attributes of the diatomic and atomic fragments. We first divide the ABC molecule (or ion) into $\text{AB}^{q+} \text{C}^{r-}$, where q and r are positive or negative integers or zero. The AB^{q+} is so chosen as to be either of the first or second class, *i.e.*, σ - or π -rich. It is then ascertained whether C^{r-} is blocked or porous. The geometry prediction is then made using Table I.

Table I^a

AB^{q+}	σ -rich π -rich	C^{r-}	
		Blocked	Porous
		Bent	Linear
		Linear	Bent

^a Predictor for ABC geometry on the basis of the classifications of AB^{q+} and C^{r-} .

The number of valence electrons in bound triatomic molecules ranges from 3 (*e.g.*, BeH_2^+) to 22 (*e.g.*, XeF_2). The number of valence electrons, v , in an atomic fragment ranges from 0 (*e.g.*, H^+) to 8 (*e.g.*, F^-). We recall that the closed shell diatomic molecules of interest have 4, 8, 10 or 14 valence electrons. With the excep-

(16) M. Krauss, *Nat. Bur. Stand. (U.S.), Tech. Note, No. 438* (1967), cites unpublished calculations from the Laboratory of Molecular Structure and Spectra. Using the same basis set at the same internuclear distance of $2.955a_0 = 1.56 \text{ \AA}$, the 2π state was computed to be more stable than the 2Σ by $0.019 \text{ au} = 11.9 \text{ kcal/mol}$.

(17) T. L. Gilbert and A. C. Wahl, *J. Chem. Phys.*, **55**, 5247 (1971).

(18) P. J. Dagdigian and L. Wharton, *J. Chem. Phys.*, **57**, 1487 (1972).

(19) See, for example, H. S. Taylor and F. E. Harris, *J. Chem. Phys.*, **39**, 1012 (1963), for a quantum chemical calculation on H_2^- .

(20) This is *not strictly true*, since there are cationic complexes such as the well-known H_3^+ in the gas phase. There have also been calculations of the relatively weak anionic complexes $(\text{X}-\text{H}_2)^-$ where $\text{X} = \text{CH}_3, \text{NH}_2, \text{OH}$, and F (H. F. King and C. D. Ritchie, *J. Amer. Chem. Soc.*, **90**, 825, 833, 838 (1968) and lithium "salts" of $(\text{F}-\text{H}_2)^-$ and $(\text{F}-\text{Li}_2)^-$ (P. A. Kollman, J. F. Liebman, and L. C. Allen, *J. Amer. Chem. Soc.*, **92**, 1142 (1970)). The latter authors suggested that $\text{LiF}-\text{H}_2$ and $\text{LiF}-\text{Li}_2$ are more properly described as LiFX^+X^- , where $\text{X} = \text{H}$ and Li , respectively.

(21) More properly, the dimers of the noble gases are very slightly bound by van der Waals forces. This bonding is too small to be significant for our problem.

(22) In the mass spectrum of XeOF_4 , a small amount of the ion XeF^- was observed: M. H. Studier and E. N. Sloth in "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, 1963, pp 42-50. This ion is indubitably bound by ion-induced dipole forces which, although stronger than the van der Waals forces for the neutral noble gas dimers, are also probably too small to be significant here.

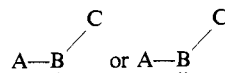
(23) The converse is not true. The 1Σ state of ArF^+ is strongly bound: J. F. Liebman and L. C. Allen, *Chem. Commun.*, 1355 (1969); J. Berkowitz and W. A. Chupka, *Chem. Phys. Lett.*, **7**, 447 (1970). However, ArF_2 formed by the conceptual combination of $1\Sigma \text{ ArF}^+ + 1\Sigma \text{ F}^-$ has evaded all synthetic attempts and thus appears to be unbound.

tion of 3, all numbers from 3 to 22 inclusive can be expressed as $4 + v, 8 + v, 10 + v$, or $14 + v$. It should also be noted that the seven-valence electron dihydrides can also not be treated here. Accordingly, all triatomic molecules with the exception of those isoelectronic to BeH_2^+ and NH_2 may be studied here. Our predictions are tested for a sample of triatomic molecules in Table II.

Having noted that this fragment procedure is highly accurate as a geometry predictor, we must try to explain its success. The archetypal blocked group is the electron. We recall that σ -rich diatomics react with electrons to form π , *i.e.*, 2π , anions. (For example, $\text{NO}^+ + e^- \rightarrow (\text{NO}^+)^- \equiv \text{NO}$.) We expect if a group were attached to the electron the orientation of the electron relative to the diatomic would not change. Since the electron was concentrated in the direction perpendicular to the diatomic axis, we anticipate this new bond will also be perpendicular to the axis. Equivalently, the molecule will be bent. The σ , *i.e.*, 2Σ , anion formation from π -rich diatomics is likewise associated with the formation of a σ -oriented bond and thus the triatomic will be linear.

The analogous archetypal porous group is a "hole" or positive charge and we now speak of σ and π cations. Corresponding bonding and bending rules apply to this case. The requirement that a porous group be missing at least two electrons from a complete shell arises from the nature of the covalent bond. In this paper, all bonds between diatomics and atoms contain at least two electrons.²⁴ Let us assume that only one electron was transferred from the closed shell diatomic molecule to the atom. If the atom was just one electron short of the closed shell, it would have a closed shell subsequent to this electron transfer. The bond between the erstwhile closed shell diatomic and just-filled closed shell atom would contain only one electron. This bond violates our earlier statement on the nature of bonds in compounds discussed here. In order to form a two-electron bond between the diatomic molecule and the atom, the atom must have been at least two electrons short of a closed shell. Accordingly, one electron short of a closed shell is equivalent to closed for our procedure and the new terms "blocked" and "porous" are not superfluous. We may also explain the current method in terms of some of the literature methods of predicting molecular geometry.

We will initially analyze the current method in terms of valence shell electron pair repulsion theory (VSEPR, ref 2). Our archetypal σ -rich diatomic molecules, BH and CO, may be written H-B: and $:\text{O}-\text{C}^+$, respectively. If either of these is combined with a porous atom, the lone pair is "replaced" by a bond pair. There are two groups around the central atom, the new atom and the H or O⁻ in the current cases. In VSEPR, two groups suggests linearity, and accordingly we confirm σ -rich + porous \rightarrow linear. If the σ -rich diatomic molecule is combined with a blocked atom, we form either



(24) The Pauli principle strictly prevents any bond from containing more than two electrons. However, we may still say that the new C-O bond formed by combining CO and O to get CO_2 contains four electrons, two σ and two π .

Table II

Triatomic	Diatomic AB ^{α+}	-Rich	Atom C ^{α-}	Blocked or porous	Predicted geometry ^a	Exptl angle, deg
BeH ₂	HBe ⁻	σ	H ⁺	Porous	Linear	180
BH ₂	BH	σ	H	Blocked	Bent	131
CH ₂ (¹ A ₁)	CH ⁺	σ	H ⁻	Blocked	Bent	102
H ₂ O ^b	OH ⁻	π	H ⁺	Porous	Bent	105
HCN ^c	CH ⁺	σ	N ⁻	Porous	Linear	180
	CN ⁻	σ	H ⁺	Porous	Linear	
HCO	CH ⁺	σ	O ⁻	Blocked	Bent	120
	CO	σ	H	Blocked	Bent	
HCF	CH ⁺	σ	F ⁻	Blocked	Bent	111
	CF ⁺	σ	H ⁻	Blocked	Bent	
NO ₂ ^{+d}	NO ⁺	σ	O	Porous	Linear	180
NO ₂ ^d	NO ⁺	σ	O ⁻	Blocked	Bent	134
NO ₂ ^{-d}	NO ⁺	σ	O ²⁻	Blocked	Bent	115
BO ₂	BO ⁻	σ	O ⁺	Porous	Linear	180
	BO ⁺	π	O ⁻	Blocked	Linear	
CO ₂	CO	σ	O	Porous	Linear	180
	CO ²⁺	π	O ²⁻	Blocked	Linear	
NO ₂	NO ⁺	σ	O ⁻	Blocked	Bent	134
	NO ³⁻	π	O ³⁺	Porous	Bent	
SO ₂	SO ²⁻	π	O ²⁺	Porous	Bent	120
ClO ₂ (OCIO)	ClO ⁻	π	O ⁺	Porous	Bent	118
XeF ₂	XeF ⁺	π	F ⁻	Blocked	Linear	180
I ₃ ⁻	I ₂	π	I ⁻	Blocked	Linear	180
C ₃	C ₂ ²⁻	σ	C ²⁺	Porous	Linear	180 ^e ,
	C ₂	π	C	Porous	Bent	
N ₃	N ₂	σ	N	Porous	Linear	180
	N ₂ ²⁺	π	N ²⁻	Blocked	Linear	
O ₃	O ₂	σ	O ²⁻	Blocked	Bent	117
	O ₂ ²⁻	π	O ²⁺	Porous	Bent	

^a All data in this table, unless noted otherwise, were taken from ref 2 through 9. ^b It will be noted that NH₂ has not been included. As noted before, there is no way within the framework of the current approach to do NH₂. One may decompose NH₂ into the σ-rich diatomic NH²⁺ and a "super-blocked" H²⁻, but although this correctly predicts NH₂ is bent, the logic appears artificial. ^c The geometry of HCN can be predicted by dissecting HCN into HC⁺ + N⁻ or into H⁺ + CN⁻. Most species can be dissected in more than one way, and in almost all cases the results agree. We may anticipate that disagreement in prediction between two different but reasonable dissections corresponds to a low-bending force constant. In most cases, we may tacitly assume that isoelectronic molecules (ref 14 and 15) have the same geometry. ^d A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, London, 1962, p 625. ^e In accord with the ambiguity in the predictions for the geometry of C₃, experimentally the molecule is known to be linear but has a bending frequency of 69 cm⁻¹ = 0.2 kcal/mol: D. R. Stull and H. Prophet, Ed., *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand., No. 37* (1971). From the same reference, data are presented that strongly suggest that the isoelectronic Al₂O is bent.

In both cases, the molecule is bent since there are three groups around the central atom, one of which is the stereochemically active single electron or lone pair. Likewise, our archetypal π-rich diatomic molecules, HF and F₂, may be written H-F: and F-F:. If either of these is combined with a porous atom, one of the lone pairs is replaced by a bond pair. However, there are still four groups around the central atom: the new atom, two stereochemically active lone pairs, and the H or F in the current cases. In VSEPR, four groups suggest a tetrahedral arrangement and accordingly the atoms form a bent arrangement. If the π-rich diatomic molecule is combined with a blocked atom, we now have five groups around the central atom forming a trigonal bipyramid. Since either three of these groups are lone pairs, or just two and a single electron, our noncentral atoms are placed on the axial positions of the bipyramid. This corresponds to a linear atomic array and accordingly π-rich + blocked → linear.

Alternatively, we may explain our rules in terms of Takahata, Schnuelle, and Parr's all-atom fragment logic (TSP, ref 7.). The archetypal σ-rich diatomic molecules, BH and CO, may be reformulated H⁻ B⁺ and O²⁻ C²⁺. If BH is combined with a porous atom, then we may express the resultant triatomic molecule as H⁻ B³⁺ A²⁻, since porous means at least two electrons short of a complete shell. By the TSP procedure, this species is linear. In contrast, if BH is com-

bined with a blocked atom, then the resultant triatomic molecule is either H⁻ B²⁺ A⁻ or H⁻ B⁺ A. In both cases, these new species are predicted to be bent by TSP. Analogous structures may be written for CO and other σ-rich diatomic molecules, from which we may reduce σ-rich + porous → linear and σ-rich + blocked → bent. The archetypal π-rich diatomic molecules, HF and F₂, may be reformulated H⁻ F⁺ and F⁻ F⁺. If HF is combined with a porous atom, we have H⁻ F²⁺ C^{α-}, which is almost never observed to have F⁷⁺ because A is rarely sufficiently electron deficient. Accordingly, π-rich + porous almost always gives bent. (We may *a posteriori* explain the linear structure of LiOH^{25,26} (and other alkali metal hydroxides²⁷) in terms of H⁻ O⁶⁺ Li⁵⁻ but this reasoning seems rather rigged. Admittedly, the author's method would have initially said bent although the current intermethod comparison does suggest the correct answer.) If HF is combined with a blocked atom, we form a linear triatomic molecule if blocked and closed shell are equated. These triatomic molecules have 16 valence electrons and are linear by symmetry constraints described by TSP. The 15-electron triatomic molecule case yields a contradiction; the author's

(25) D. R. Stull and H. Prophet, Ed., *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand., No. 37* (1971).

(26) G. W. Schnuelle and R. G. Parr, *J. Amer. Chem. Soc.*, **94**, 8974 (1972).

(27) N. Acquista and S. Abramowitz, *J. Chem. Phys.*, **51**, 2911 (1970).

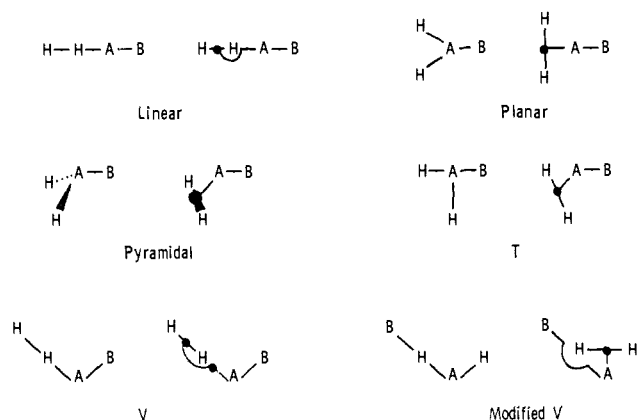


Figure 1. Generic structures for H_2AB species where \bullet is the $H \cdots H$ midpoint. Linear and planar are described as straight in the current method, while pyramidal, T, V, and modified V are all described as angled.

method suggests linear and TSP suggests bent. No data exist to resolve this question. Analogous comparisons exist for F_2 suggesting, in general, π -rich + porous \rightarrow bent and π -rich + blocked \rightarrow linear.

Let us now compare the present method with that of Walsh and Gimarc (ref 4 and 5). In principle, we could form three-dimensional diagrams plotting orbital energy and interfragment distance. (We must consider this distance since the fragments are initially at infinite separation and at only approximately 1–2 Å in the triatomic molecule of interest.) Several problems arise in this analysis despite the essentially universal success of Walsh's and Gimarc's analyses. First of all, orbital energies vary for isoelectronic species. For example, both authors show that the highest occupied orbital in linear HCN is of π symmetry. Accordingly, by Koopmans' theorem,²⁸ HCN⁺ is predicted to be ${}^2\pi$. This prediction is indeed correct, but there is nothing to suggest why the isomeric and isoelectronic HNC⁺ is ${}^2\Sigma$.²⁹ It is highly unlikely that this difference is due to the difference in C–N bond lengths: $r_{CN}(\text{HCN}) = 1.153 \text{ \AA}$, $r_{CN}(\text{HNC}) = 1.168 \text{ \AA}$.²⁹ The second problem with Walsh–Gimarc orbital analyses is that quantitative, *i.e.*, *ab initio*, studies do not always reproduce the qualitative features. In the case of HCN, one π orbital increases in energy and the other decreases as the molecule is bent,³⁰ while Walsh and Gimarc predict one orbital (the one perpendicular to the plane) is unchanged in energy. More importantly, summing the valence electron orbital energies gives a lower energy at 140° than at 180°, thereby *a posteriori* and incorrectly predicting that HCN is bent.³⁰ We may thus conclude that the earlier desired three-dimensional diagram would be harder to construct than might be initially apparent and that its reliability would be somewhat suspect.

Let us assume interfragment distance does not affect relative orbital energy orderings and that the qualitative analyses are sufficient for our purpose. As done earlier in this paper, if we neglect inner shell electrons, the σ -rich diatomic molecules HB and CO can be written $\sigma^2\sigma^2$ and $\sigma^2\sigma^2\pi^4$, respectively. Blocked atoms characterized by seven or eight valence electrons

may be written $\sigma^2\sigma^1\pi^4$ or $\sigma^2\sigma^2\pi^4$ as molecule formation lifts the degeneracy of the atomic p orbitals. Assuming separation is maintained as the *linear* triatomic molecule is formed, $HB + \text{blocked} \rightarrow \sigma^2\sigma^2\sigma^2$ (σ^1 or σ^2) π^4 . However, the ground state of this molecule has a $\sigma^2\sigma^2\sigma^2\pi^4$ (π^1 or π^2) configuration. If we assert that ground state reactants ought to yield ground state products, we are forced to conclude the reaction is "forbidden."³¹ However, if we consider *bent* triatomic molecule formation, the resulting lifting of p and π orbital degeneracies allows the ground state triatomic molecule to be formed. In the absence of the electrons of the second σ orbital of the atomic fragment, *i.e.*, we now have a porous atom, we form $\sigma^2\sigma^2\sigma^2\pi^4$ which is indeed the ground state of the ten-valence electron triatomic molecule. We thus conclude $HB + \text{porous} \rightarrow \text{linear}$, $HB + \text{blocked} \rightarrow \text{bent}$, in agreement with our previous conclusions. Analogous phenomena exist for CO. CO and blocked atoms give $\sigma^2\sigma^2\sigma^2\sigma^2$ (σ^1 or σ^2) $\pi^4\pi^4$, while the ground state for the linear triatomic molecule is $\sigma^2\sigma^2\sigma^2\sigma^2\pi^4\pi^4$ (π^1 or π^2). Again ground state products are formed by constructing bent triatomic molecules or by removing the second σ orbital electrons from the atom making it porous. No constraints appear to be operative for the π -rich $\sigma^2\sigma^2\pi^4\pi^4$ HF and $\sigma^2\sigma^2\sigma^2\pi^4\pi^4$ F₂. That is, the angle in the triatomic molecule cannot be determined solely by orbital symmetry. One must take into account the orbital energies and their angle dependence directly and then the analysis then proceeds as given by Walsh and Gimarc.

As may be expected, the proposed method needs modification for describing tetraatomic molecules. We will currently limit our investigation to H_2AB and its isomers. As we had conceptually fragmented 3 into 2 and 1, we may conceptually fragment 4 into 2 and 2. We will commence our geometry predictions with H_2AB itself. (It should be noted that hydrogen is in general replaceable by simple univalent radicals such as alkyl and aryl groups and halogens, without affecting our predictions.) The most symmetric, and accordingly the most reasonable, dissection of H_2AB is into the diatomic fragment AB^{q+} and the associated dihydrogen species H_2^{r-} . The AB fragment is then labeled σ or π -rich as in our previous triatomic molecule discussion. We note that H_2 has two electrons out of a maximum possible of four; that is, H_2 has a σ^2 configuration, while $\sigma^2\sigma^{*2}$ is allowed without "molecular valence shell expansion." ("Molecular valence shell expansion" is defined by analogy to atomic valence shell expansion, use of orbitals of higher n and/or l than in the free atom.) Accordingly, H_2 may be said to be a porous diatomic molecule as are H_2^+ and H_2^{2+} , whereas H_2^- and H_2^{2-} may be said to be blocked.

For tetraatomic molecules, linear must be redefined, since H–H–A–B usually makes little chemical sense.³² Linear is, however, simply translated into meaning that A, B, and the midpoint of $H \cdots H$ are linear. We will use the adjective, or descriptor "straight," in this case, although straight H_2AB is more conventionally referred to as planar. (Symmetry suggests that both

(31) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1969.

(32) Quantum mechanical calculations have been performed on LiFH₂ and a binding energy of 2 kcal/mol was found for the linear complex LiFHH: Kollman, Liebman, Allen, ref 20.

(28) T. A. Koopmans, *Physica*, **1**, 104 (1933).

(29) D. Booth and J. N. Murrell, *Mol. Phys.*, **24**, 1117 (1972).

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

Table III

H ₃ A	Diatomic	-Rich	Associated dihydrogen species	Blocked or porous	Predicted geometry	Literature geometry
BH ₃	BH	σ	H ₂	Porous	Straight	Planar ^{a-d}
CH ₃	CH ⁺	σ	H ₂ ⁻	Blocked	Angled	Planar ^{b, c, e, f}
NH ₃	NH ²⁺	σ	H ₂ ²⁻	Blocked	Angled	Pyramidal ^{a-d, g}
	NH ₂ ⁻	π	H ₂ ²⁺	Porous	Angled	
H ₂ O	OH ⁻	π	H ₂ ⁺	Porous	Angled	V ^h
H ₃ F	HF	π	H ₂	Porous	Angled	T ⁱ

^a See references 2-4, 7, 8, and 26. ^b See B. M. Gimarc, *J. Amer. Chem. Soc.*, **93**, 593 (1971). ^c See W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *ibid.*, **93**, 6377 (1971). ^d See R. G. Pearson, *ibid.*, **91**, 4947 (1969). ^e See references 2, 4, 7, and 8. ^f Many non-rigorous molecular geometry methods (*b* and *e* above) predict the seven-valence electron CH₃ to be pyramidal, although the author of ref 3 provides an experimental explanation for the discrepancy. It should be noted that the isoelectronic SiH₃, GeH₃, and SnH₃ are all pyramidal: G. S. Jachel and W. Gordy, *Phys. Rev.*, **176**, 443 (1968). This discrepancy with the planarity of CH₃ has been reconciled (Jachel and Gordy, above, and L. Pauling, *J. Chem. Phys.*, **51**, 2767 (1970)). Quantum mechanical calculations have been performed on BH₃⁻, CH₃, and NH₃⁺; CH₃ and NH₃⁺ are planar, while BH₃⁻ is pyramidal with a very low barrier to inversion: T. A. Claxton and N. A. Smith, *J. Chem. Phys.*, **52**, 4317 (1970), and T. A. Claxton, M. J. Godfrey, and N. A. Smith, *J. Chem. Soc., Faraday Trans. 2*, 181 (1972). In general, phosphine radical cations appear to be pyramidal (A. Begum and M. C. R. Symons, *ibid.*, 43 (1973)), although PF₃⁺ is planar (J. P. Maier and D. W. Turner, *ibid.*, 711 (1972)), with a markedly lower barrier to inversion than silyl radicals (Begum and Symons, above). ^g Highly accurate quantum mechanical calculations have shown that nitrogen 3d orbitals must be utilized to explain the existence, as well as magnitude, of the NH₃ inversion barrier: A. Rauk, L. C. Allen, and E. Clementi, *J. Chem. Phys.*, **55**, 3780 (1971). ^h In *c* above, H₂O was described as a weakly bound, hydrogen-bonded "complex between H₂O and H."⁸ ⁱ H₃F is unknown, but the analogous Ar₃I and ClF₃ are T shaped (ref 33). Second-order Jahn-Teller reasoning (in *d* above) suggests that the unknown but isoelectronically related ClH₃ also has this shape.

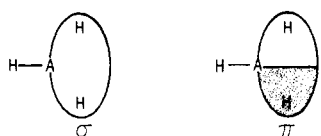


Figure 2. Local symmetry of H₂ and H₂²⁻. The shaded region of the orbital is the negative lobe. This convention will be used throughout this paper.

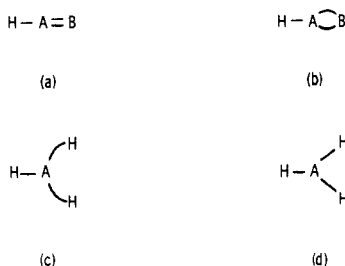


Figure 3. The transformation of a double bond into two single bonds.

HAB angles are equal.) In those rare cases where all four atoms are colinear, we will use the term "linear." Likewise, bent would be expected to be translated into nonplanar or pyramidal, although we note that the geometry of monomeric (C₆H₅)₂ICl³³ also qualifies as bent. We will use the adjective or descriptor "angled" in these nonstraight cases. (See Figure 1.)

Let us commence with B = H. Table III presents our predictions for these H₃A molecules, where the literature geometry is noted and described in terms of the structures in Figure 1. With the exception of the not uncommonly misassigned structure of CH₃, all of our predictions are correct.

We may explain the success of the predictions for the H₃A molecular geometry by redescribing these molecules as H₂AH. In the "porous-blocked" description of H₂ and the other associated dihydrogen species, we considered these diatomic fragments as though they were a single atom. Accordingly, our

(33) J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969).

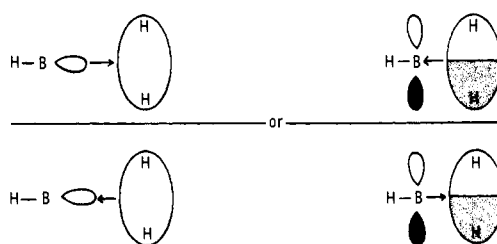


Figure 4. Orbital symmetry, electron donation, and the geometry of BH₃. The direction of the arrow shows the direction of electron donation.

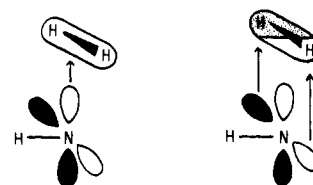


Figure 5. Orbital symmetry, electron donation, and the geometry of NH₃. NH₃ is shown as being synthesized from the fragments NH₂⁻ and H₂²⁺.

treatment of the tetraatomic molecules of interest was transformed into one of triatomic molecules. In terms of local symmetry, H₂ has a σ^2 configuration, while H₂²⁻ is $\sigma^2\pi^2$ (see Figure 2). Accordingly, we may use the orbital symmetry logic earlier used for triatomic molecules. (In this treatment, we are merely expressing the equivalence of double bonds,^{34,35} banana bonds,³⁴ and indeed two single bonds.³⁵ See Figure 3.) The planar structure of BH₃ and nonplanar structure of NH₃ correspond to the linear HBO³⁶ and the bent HNO.³⁷ (See Figures 4 and 5.) Symmetry suggests correctly that all hydrogens are equivalent, but there are admitted complications with and belated

(34) L. Pauling in "Theoretical Organic Chemistry; The Kekulé Symposium," Butterworths, London, 1959, pp 2-5.

(35) J. F. Liebman, *J. Fluorine Chem.*, **3**, 27 (1973/4).

(36) E. R. Lory and R. F. Porter, *J. Amer. Chem. Soc.*, **93**, 634 (1971).

(37) J. Peslak, Jr., D. S. Klett, and C. W. David, *J. Amer. Chem. Soc.*, **93**, 5000 (1971).

Table IV

H ₂ AB	Diatomic	-Rich	Associated dihydrogen species	Blocked or porous	Predicted geometry	Lit. geometry
H ₂ CC	C ₂ ²⁻	σ	H ₂ ²⁺	Porous	Straight	Planar ^a
H ₂ LiF	LiF ²⁻	σ	H ₂ ²⁺	Porous	Linear	Linear ^b
H ₂ CN	CN ⁻	σ	H ₂ ⁺	Porous	Straight	Planar ^c
H ₂ CO	CO	σ	H ₂	Porous	Straight	Planar ^c
H ₂ CF	CF ⁺	σ	H ₂ ⁻	Blocked	Angled	Pyramidal ^d
H ₂ NO	NO ⁺	σ	H ₂ ⁻	Blocked	Angled	Pyramidal ^{d,e}
H ₂ NF	NF ²⁻	π	H ₂ ²⁺	Porous	Angled	Pyramidal ^{d,f}
H ₂ OF	OF ⁻	π	H ₂ ⁺	Porous	Angled	No data
H ₂ SO ⁻	SO ²⁻	π	H ₂ ⁺	Porous	Angled	No data ^g
H ₂ F ₂	F ₂	π	H ₂	Porous	Angled	Modified V and T ^h

^a See A. C. Hopkinson, K. Yates, and I. G. Czismadia, *J. Chem. Phys.*, **55**, 3780 (1971), and N. Bodor, M. J. S. Dewar, and J. S. Wasson, *J. Amer. Chem. Soc.*, **94**, 9095 (1972). ^b See ref 20 and 32. ^c See ref 4, 5, and 17. ^d See ref 3, 4, and 7. Also see B. M. Gimarc, *J. Amer. Chem. Soc.*, **93**, 815 (1971). ^e Experimental data on compounds with the general structure R₂NO; the so-called nitroxides or nitroxyl radicals are ambiguous. For example, apparently contradictory results are reported by G. J. Kruger and J. C. A. Bolyens, *Proc. Nat. Acad. Sci. U. S.*, **61**, 422 (1968), and J. Lajzerowicz-Bonneteau, *Acta Crystallogr., Sect. B*, **24**, 196 (1968). Quantum chemical calculations on H₂NO itself (A. W. Salotto and L. Burnelle, *J. Chem. Phys.*, **53**, 333 (1970)) suggest a marked nonplanar structure with an extremely small inversion barrier. A recent critical analysis: A. Rossit and P. Rey, *Tetrahedron*, **29**, 1599 (1973). ^f Strictly speaking, Nakatsuji (ref 3) discusses the geometry of H₂NCl. We may partition this species into the π-rich NCl²⁻ and the porous associated dihydrogen species H₂²⁺. Accordingly, H₂NCl is predicted to be bent as is H₂NF. ^g Radical anions of several aromatic sulfoxides have been reported, but insufficient evidence was presented to ascertain the geometry of the C₂SO⁻ fragment. Furthermore, in these cases, considerable charge and spin density was delocalized onto the rings: M. Murbery and E. T. Kaiser in "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Wiley, New York, N. Y., 1968, Chapter 8. As such, it is highly probable the electronic environment of this fragment is only slightly different from the unreduced sulfoxide. ^h The ground state structure of H₂F₂ is that of a normal hydrogen-bonded complex containing a bent HFH fragment and a linear FHF fragment: P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, **52**, 5085 (1970), and P. A. Kollman, *J. Amer. Chem. Soc.*, **94**, 1837 (1972). The alternative T shaped structure is found for the related diaryl iodonium chlorides (see ref 33).

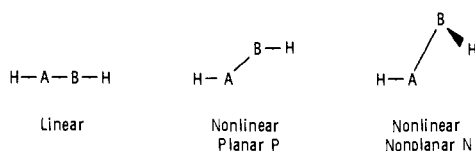


Figure 6. Generic structures for HABH species. Linear is clearly straight in the current method, while nonlinear planar (P) and nonlinear nonplanar (N) are described as angled.

explanations with the T shape of FH₃ and its isoelectronic analogs such as ClF₃.³³ For our comparison of triatomic and tetraatomic molecules, we have equated =B (in particular =O) and



In both HBO and HNO, there are double bonds between the heavy (*i.e.*, nonhydrogen) atoms. However, by isoelectronic comparison with HOF³⁸ or by application of Schnuelle-Parr²⁶ analysis, there is only a single bond between the O and the F in HFO. Accordingly, the geometry comparison cannot be made.

The analysis for H₂AB molecules proceeds analogously for those cases where B does not equal H. Our predictions are given in Table IV. It is accordingly seen that all of the predictions for the general H₂AB species are correct.

Let us now consider the HABH isomers of H₂AB wherein the logical dissection is into HA and BH. All of the diatomic hydrides have between zero and four π electrons and accordingly a π⁴ configuration corresponds to a closed shell. We may thus generalize our earlier definitions of blocked and porous and assert that π³ and π⁴ configurations are blocked, while π⁰, π¹, and π² configurations are porous. That is, diatomic hy-

drides isoelectronic with HF and OH are blocked and those isoelectronic with BH, CH, and NH are porous. We may additionally assert that if bonding between HA and BH occurs through an H, the diatomic molecule bearing the hydrogen bonding H may also be said to be porous. It is of course necessary to check the geometry at both the HA and BH sites; *i.e.*, we must know whether both the HAB and ABH molecular fragments are linear or bent. However, we need consider only those cases where A equals B and then apply symmetry reasoning provided we are willing to consider an apparent plethora of charged tetraatomic species. Figure 6 gives possible HABH geometries. Let us invoke and only later explain the somewhat arbitrary postulate that H₂AB and HABH are either both planar or both nonplanar. Our predictions are given in Table V. It will be noted that all of our predictions are in accord with experiment.

We may gain additional information by considering σ- and π-rich triatomic molecules, HAB, for later use in the formal fragmentation 4 = 3 + 1. Corresponding to the σ-rich CO is the isoelectronic HCN. HCN⁺ has a ²π electronic configuration,³⁹ but HCC⁴⁰ and HNC⁺²⁹ have ²Σ electronic configurations. Admittedly erroneously, we will consider HCN and all isoelectronic analogs as σ-rich. HCN⁻ and HCO⁴¹ have ²A' ground states which formally correspond to adding an additional π electron and then letting the molecules relax by a Jahn-Teller distortion into nonlinear structures. (HCN⁻ and HCO may thus be described as π radicals, since we are adding a π electron, although they normally would be described as σ radicals, since the unpaired electron is a symmetric orbital with respect

(39) J. M. Hollas and T. H. Sutherly, *Mol. Phys.*, **24**, 1123 (1972).

(40) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 808 (1971).

(41) F. J. Adrian, E. L. Cochran, and V. A. Bowers, *Phys. Rev.*, **177**, 129 (1969).

(38) E. H. Appelman, *Accounts Chem. Res.*, **6**, 113 (1973).

Table V

HABH	HA	-Rich	BH	Blocked or porous	Predicted geometry		Lit. geometry
					HAB part	Whole HABH	
HBBH	HB	σ	BH	Porous	Linear	Linear	Linear ^a
HCCH ⁺	HC ⁺	σ	CH	Porous	Linear	Linear	Linear ^b
CCCH	HC ⁺	σ	CH ⁻	Porous	Linear	Linear	Linear ^{b,c}
HCCCH ⁻	HC ⁺	σ	CH ²⁻	Blocked	Bent	P	P ^d
HNNH	HN ²⁺	σ	NH ²⁻	Blocked	Bent	P	P ^e
	HN ²⁻	π	NH ²⁺	Porous	Bent	P	
HNNH ⁻	HN ²⁻	π	NH ⁺	Porous	Bent	N	N ^d
HOOH	HO ⁻	π	OH ⁺	Porous	Bent	N	N ^c
HOOH ⁻	HO ⁻	π	OH	Blocked	Linear	Linear	No data ^e
HFFH	HF	π	FH	Blocked	Linear	Linear	No data
	HF	π	HF	Porous	Bent HFH		
	FH	π	FH	Blocked	Linear FHF	L	L ^f

^a R. G. Pearson, *J. Chem. Phys.*, **52**, 2167 (1970), predicts linearity for HBBH but invokes a triplet ground state. ^b See B. M. Gimarc, *J. Amer. Chem. Soc.*, **92**, 266 (1970). ^c See ref 4, 26, and Pearson (see *a* above). ^d While Schnuelle and Parr (ref 26) talk about HCNH and HNOH instead of (HCCH)⁻ and (HNNH)⁻, both their logic and the author's strongly suggest this difference is irrelevant. ^e No data exist on the geometry of HOOH⁻ or the radical anion of any peroxide. The radical anions of the isoelectronic disulfides have been observed in the 1,2-dithiolane, lipoic acid: R. L. Wilson, *Chem. Commun.*, 1425 (1970). No structural information can be obtained as to the most stable geometry as the five-membered ring system applied constraints to the possible structure. ^f See P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, **52**, 5085 (1970), and P. A. Kollman, *J. Amer. Chem. Soc.*, **94**, 1837 (1972).

to the molecular plane.) Corresponding to the π -rich F₂ is the isoelectronic HOF. In agreement with experiment,⁴² intuitively, we would suspect HOF⁺ is formed from HOF by removal of a π electron by analogy to F₂¹⁷ or ClF.⁴³ We now recall the parallelism of an electron and blocked groups and of a hole and porous groups. The results from Table I may be directly applied to the new ABH framework. Further geometry specifications may be derived from those in Figure 7. Predictions for the geometry of HABH molecules are made by adapting Table I. Assuming isoelectronic molecules have the same geometry shows all of our predictions are correct. Our earlier seemingly arbitrary postulate that H₂AB and HABH species are either both planar or nonplanar is thus explained.

Information about the trihydrides, H₃A, may be deduced by isoelectronic comparisons, if we assume⁴⁴ that halogens and hydrogen are essentially isoelectronic. For example, the pyramidal shape of H₂OF⁺ correctly suggests H₃O⁺ and NH₃ are pyramidal, and the T shape of H₂FF correctly suggests H₃F and H₃Cl are also T shaped. By sequentially comparing H₂C=N⁻, H₂CO, H₂CF⁺, H₂BF, and BH₃, we correctly deduce that BH₃ is planar.

As with HABH species, we may derive information about the tetraatomic molecules with three heavy atoms, HABC, by either of the formal fragmentations: 4 = 3 + 1 or 4 = 2 + 2. The results of Table I can be directly used to predict the geometry of these more general HABC species. The decision about nonlinear planar P and nonlinear nonplanar N for HABC molecules with bent ABC fragments is based on the decision in HABH. Table VI presents our predictions for the 3 + 1 fragmentation. It is thus seen that all of our predictions are in accord with the literature. The alternative fragmentation into 2 + 2 such as HCCF or FCCH into the σ -rich FC⁺ and porous CH⁻ is also in total accord with the literature.

We may correctly predict the HAB angles in the pre-

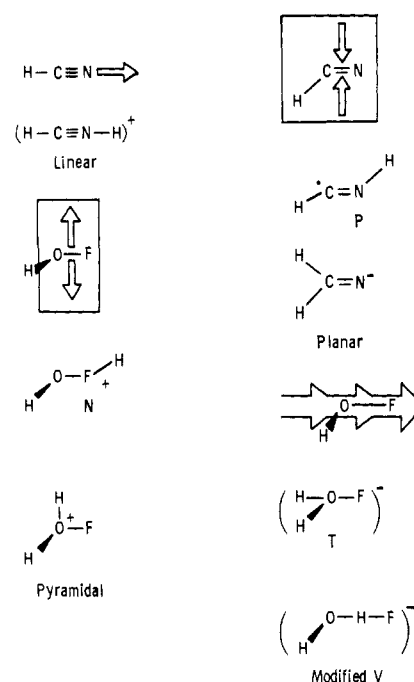


Figure 7. Geometry predictions based on σ - and π -rich triatomic molecules using the terminology of Figures 1 through 6. The arrows show the direction of the electron flow and equivalently the position of the attack of porous and blocked group.

viously mentioned HABC tetraatomic molecules if we hypothesize that CCF⁻, CCCI⁻, CCB_r⁻, and CNO⁻ are σ -rich while CCN³⁻, NCN²⁻, NCO⁻, N₃⁻, OBO⁻, and OOF⁻ are π -rich. All of these assignments are in accord with intuition, but there is no apparent way of interrelating these assignments to the σ - and π -rich diatomic and HAB triatomic molecular species. (We note NCO,⁴⁵ N₃,⁴⁵ OBO,⁴⁵ and OOF^{46,47} are π radicals, while by analogy to CCH,⁴⁰ CCF, CCCI, and CCB_r are probably σ radicals.) Let us consider the litera-

(42) J. Berkowitz, J. L. Dehmer, and E. H. Appelman, *Chem. Phys. Lett.*, **19**, 334 (1970).

(43) The comparison of ClF and HOF was made by J. Berkowitz, E. H. Appelman, and W. A. Chupka, *J. Chem. Phys.*, **58**, 1950 (1973).

(44) J. H. Walker, T. E. H. Walker, and H. P. Kelly, *J. Chem. Phys.*, **57**, 2094 (1972), and suggestion of the referee.

(45) G. Herzberg, "The Spectra and Structures of Simple Free Radicals," Cornell University Press, Ithaca, N. Y., 1971, p 117.

(46) P. H. Kasai and A. D. Kirschenbaum, *J. Amer. Chem. Soc.*, **87**, 3069 (1965).

(47) R. D. Spratley and G. C. Pimentel, *J. Amer. Chem. Soc.*, **93**, 7149 (1971).

Table VI

Tetraatomic HABC	Triatomic HAB ^{a+}	-Rich	Atom C ^{r-}	Blocked or porous	Predicted geometry of ABC	Lit. ABC angle, deg (or geometry)
HCCF	HCC ⁻	σ	F ⁺	Porous	Linear	180 ^a
HCCCl	HCC ⁻	σ	Cl ⁺	Porous	Linear	180 ^b
HCCBr	HCC ⁻	σ	Br ⁺	Porous	Linear	180 ^b
HCCN	HCC ⁻	σ	H ⁺	Porous	Linear	180 ^c
HCNO	HCN	σ	O	Porous	Linear	180 ^d
HNCN	HNC	σ	N	Porous	Linear	180 ^b
HNCO	HNC	σ	O	Porous	Linear	180 ^{a,b,e}
HNNN	HNN ⁺	σ	N ⁻	Porous	Linear	180 ^{a,e}
HNNF	HNN ⁺	σ	F ⁻	Blocked	Bent	Trans ^a
HOBO	HOB	σ	O	Porous	Linear	180 ^e
HOCN	HOC ⁺	σ	N ⁻	Porous	Linear	180 ^a
HOCO	HOC ⁺	σ	O ⁻	Blocked	Bent (P)	
HONO	HON ²⁺	σ	O ²⁻	Blocked	Bent (P)	116 ^{a,b,f}
	HON ²⁻	π	O ²⁺	Porous	Bent (N)	
HNSO	HNS ²⁺	σ	O ²⁻	Blocked	Bent (P)	116 ^{a,h}
	HNS ²⁻	π	O ²⁺	Porous	Bent (N)	
HOOF	HOO ⁻	π	F ⁺	Porous	Bent (N)	N ^{a,b}
HFLiF	HFLi ⁻	σ	F ⁺	Porous	Linear	180 ⁱ

^a See L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 289 (1971). ^b See H. Nakatsuji, *J. Amer. Chem. Soc.*, **95**, 2084 (1973). ^c There is no experimental data on the geometry of this species. However, the linear CCN geometry predicted is in accord with what is expected of cyanocarbene, $\text{H}\ddot{\text{C}}\text{C}\equiv\text{N}$, as well as ethynylnitrene, $\text{HC}\equiv\text{CN}\dot{\text{N}}$. ^d See W. D. Sheasley and C. W. Mathews, *J. Mol. Spectrosc.*, **43**, 467 (1972). ^e See ref 25. ^f The nitrogen in HONO is best described as having an oxidation state of +3. As such, the fragmentation $\text{HON}^{2+}\text{O}^{2-}$ is more "realistic" than $\text{HON}^{2-}\text{O}^{2+}$ and accordingly we may predict that the geometry of HONO is P. ^g See W. H. Kirchoff, *J. Amer. Chem. Soc.*, **91**, 2437 (1969). ^h The sulfur in HNSO is best described as having an oxidation state of +4. As such, the fragmentation, $\text{HNS}^{2+}\text{O}^{2-}$ is more "realistic" than $\text{HNS}^{2-}\text{O}^{2+}$ and accordingly we may predict that the geometry of HNSO is P. ⁱ See ref 32.

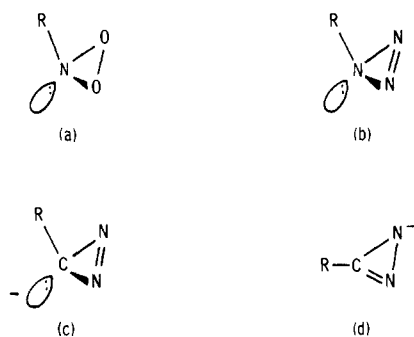


Figure 8. Probable structures for (a) 3*H*-dioxaziridine, (b) triazirine, and (c) diaziridinide. R, as always, may be any univalent radical, but rearrangement of c to the planar but unsymmetric d is probable, as this places the negative charge on the more electro-negative nitrogen.

ture methods with respect to this HAB angle. Valence shell electron pair repulsion theory makes correct predictions if we choose the appropriate resonance structure by the Schnuelle-Parr procedure.²⁶ For example, with respect to HNCO, we must know to consider $\text{HN}=\text{C}=\text{O}$ and not $\text{HN}^+\equiv\text{CO}^-$. However, do we choose $\text{HC}\equiv\text{CN}$, ethynylnitrene, or $\text{HCC}\equiv\text{N}$ for HCCN? To draw Walsh-Gimarc diagrams for the HABC case, it is *not* sufficient to fuse the HAB and ABC diagrams. For example, whereas both HCN and HNC are linear,²⁹ HNCO but not HCNO has a bent HAB fragment. cursory examination of the data shows that the HAB part of HABC has the same local geometry as in HAAH (see Tables V and VI) and the ABC part the same geometry as the triatomic ABC. However, the geometry of the ABC part occasionally differs from CBBC.⁴⁷ (For example, the CNO part of HCNO is linear whereas ONNO contains a bent NNO group.^{26, 48, 49, 50} Accordingly, one cannot simply fuse

(48) B. M. Gimarc, *J. Amer. Chem. Soc.*, **92**, 266 (1970).

the diagrams for HAAH and CBBC. The TSP rules⁷ note that HABC molecules are planar when there are 18 or less valence electrons. However, since only pyramidal and nonlinear nonplanar (N) qualify as nonplanar among all of the structures in Figures 1 and 6, these rules give inadequate geometry discriminatory power to the user when considering the H-A-B-C isomers. If we consider the Y shaped isomers, H-A(-B)-C, there are at least three probable exceptions to this TSP electron counting rule, although to date all three species are admittedly unknown. These three species are the cyclic isomers of nitrous acid, 3*H*-dioxaziridine; of hydrazoic acid, triazirine; and the anion of diazomethane, diaziridinide (see Figure 8). The first species is isoelectronic and isostructural to aziridine, a normal amine, and as such most probably contains a pyramidal nitrogen. Equivalently, the HNO_2 structure is nonplanar. No derivatives of this species are known, but the photochemistry of nitro compounds may be explained in terms of the associated biradical $\text{R}-\text{N}(\text{O}\cdot)_2$.⁵¹ The second species contains 4π electrons if the molecule is planar. This number of π electrons corresponds to an antiaromatic ring system,^{52, 53} but this destabilization can most likely be lessened by having a nonplanar structure. It has recently been noted that even in the 6π analog, pyrrole, there is insufficient evidence to prove the customarily asserted planar structure.⁵⁴ We note that this ring system which

(49) J. E. Williams and J. N. Murrell, *J. Amer. Chem. Soc.*, **93**, 7149 (1971).

(50) T. Vladimiroff, *J. Amer. Chem. Soc.*, **94**, 8250 (1972). Vladimiroff and Williams and Murrell present different structures for $(\text{NO})_2$ but in neither case is linear ONNO suggested.

(51) H. A. Morrison, "The Chemistry of the Nitro and Nitroso Groups," H. Feuer, Ed., Interscience, New York, N. Y., 1969, Part 2.

(52) M. J. S. Dewar, *Advan. Chem. Phys.*, **8**, 121 (1965).

(53) R. Breslow, J. Brown, and J. J. Gajewski, *J. Amer. Chem. Soc.*, **89**, 4383 (1967).

(54) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969, p 409.

used to be proposed for the structure of azides⁵⁵ indeed is an intermediate in a minor path in the synthesis of azide from nitrous acid and hydrazines.⁵⁶ Diazirines, the conjugate acids of the third class of compounds, do not react with concentrated NaOH.⁵⁷ This may be explained by the previously mentioned antiaromaticity but accordingly denies us any stereochemical information as to the structure of the anion.

The geometry of the ABC fragment of the H-A-B-C tetraatomic molecule can be predicted by using π -rich closed shell and thus blocked diatomic molecules along with closed shell atoms. For example, the linear fragment NCO in HNCO may be predicted from $\text{HN}^{2-}\text{C}^{4+}\text{O}^{2-}$, while the bent fragment NNF in HNNF may be predicted from $\text{HN}^{2-}\text{N}^{3+}\text{F}^-$. This appears to be a useful generalization for tetraatomics. Extension and verification for general polyatomic species is in progress, as well as trying to explain the geometry of the HAB fragment in tetraatomic and larger species.

Nakatsuji's method^{3,58} is highly accurate in pre-

(55) See, for example, E. S. Wallis, "Organic Chemistry, an Advanced Treatise," Vol. 1, 2nd ed, H. Gilman, Ed., Wiley, New York, N. Y., 1943.

(56) D. V. Banthorpe, "The Chemistry of the Azido Group," S. Patai, Ed., Interscience, New York, N. Y., 1971.

(57) E. Schmitz, *Advan. Heterocycl. Chem.*, **2**, 122 (1963).

(58) H. Nakatsuji, *J. Amer. Chem. Soc.*, **95**, 2084 (1973).

dicting molecular geometries, but like the VSEPR² and Schnuelle-Parr²⁶ principle, one has to make assumptions about the bonding in the molecule. For example, the distinction made in explaining the different structures of HCCl and HNCO cannot be directly applied to the isoelectronic¹⁴ HCNO. Even greater uncertainty in obtaining the reference calculation state arises in those cases where there are major resonance structures with marked bonding differences such as in HCCN.

In conclusion, it is seen that the current method, characterized by essentially no input parameters except, the number of electrons in the component fragments, is capable of predicting the geometry of triatomic molecules and large subclasses of tetraatomic molecules. Moreover, the deficiencies of the proposed method are shared by the other methods in the literature, most of which require more input information.

Acknowledgment. I wish to thank Deborah Van Vechten for her editorial comments and Drs. A. S. Hyman, R. G. Parr, J. J. Ritter, J. S. Taylor, and J. S. Vincent for many discussions on molecular geometry. I also gratefully acknowledge the prodding of the referees for me to find the interrelations of the current method and other methods already in the literature.

Neglect of Differential Overlap in Calculations of Barriers to Inversion and an Extension of INDO to Calculations Involving Second Row Atoms

Philip E. Stevenson* and David L. Burkey

Contribution from the Department of Chemistry, Worcester Polytechnic Institute, Worcester, Massachusetts 01609. Received November 28, 1973

Abstract: Several different versions of the CNDO and INDO molecular orbital methods are compared for their effectiveness in predicting inversion barriers primarily for alkylamines and chloroalkylamines. It is concluded that the INDO method is the most suitable of these methods for calculating such barriers in these compounds. Values of Slater-Condon parameters, F^2 and G^1 , are proposed for an extension of INDO to molecules containing second row atoms.

The feasibility of using molecular orbital theory to study the inversion barrier in NH_3 has been demonstrated by the self-consistent-field (SCF)¹ calculations of Stevens² and Rauk, *et al.*³ Stevens obtained a barrier of 5.9 kcal/mol using a large basis set of Slater type orbitals, and Rauk obtained a barrier of 5.08 kcal/mol using a large Gaussian basis set. Both values are in good agreement with the measured barrier of 5.8 kcal/mol.⁴

Freed⁵ and Allen and Arents⁶ have shown in general that the LCAO-MO-SCF method is capable of predicting barriers. Allen and Arents argue moreover that

- (1) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).
- (2) R. M. Stevens, *J. Chem. Phys.*, **55**, 1725 (1971).
- (3) A. Rauk, L. C. Allen, and E. Clementi, *J. Chem. Phys.*, **52**, 4133 (1970).
- (4) J. D. Swalen and J. D. Ibers, *J. Chem. Phys.*, **36**, 1914 (1962).
- (5) K. F. Freed, *Chem. Phys. Lett.*, **2**, 255 (1968).
- (6) L. C. Allen and J. Arents, *J. Chem. Phys.*, **57**, 1818 (1972).

carefully parametrized semiempirical adaptations of the SCF method should be useful in studies of barriers and conformational preferences in large molecules.

The most popular semiempirical methods in present use are the extended Hückel theory (EHT),⁷ complete neglect of differential overlap (CNDO),⁸⁻¹⁴ and intermediate neglect of differential overlap (INDO).^{14,15}

- (7) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).
- (8) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S129 (1965).
- (9) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, S136 (1965).
- (10) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).
- (11) D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967).
- (12) D. P. Santry, *J. Amer. Chem. Soc.*, **90**, 3309 (1968).
- (13) J. R. Sabin, D. P. Santry, and K. Weiss, *J. Amer. Chem. Soc.*, **94**, 6651 (1972).
- (14) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.
- (15) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).