

Effects of Filled π and Unfilled σ Molecular Orbital Interactions on Molecular Structure

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Although Walsh's rules for predicting the shapes of polyatomic molecules were formulated nearly a quarter of a century ago,¹ this subject has continued to interest theoreticians.² Pearson has developed symmetry rules for molecular distortions, based on the second-order Jahn-Teller effect.³ In this approach bending of an AH_2 molecule or pyramidalization of an AH_3 molecule is expected, if such a geometric change allows substantial mixing of the highest occupied MO (HOMO) with the lowest unoccupied MO (LUMO). More recently Gimarc, by considering mainly changes in overlap integrals on bending or pyramidalization, was able to rationalize how the energies of the valence MO's of AH_2 and AH_3 molecules varied as a function of geometry.⁴ The preferred geometries of these molecules could then be related to the electron occupation of the valence MO's. Finally, we⁵ and Levin⁶ have shown how differences in the geometries of tri- and tetraatomic molecules within an isoelectronic series can be related to the identity of the central atom and also how substituents affect the equilibrium geometries. This was accomplished by assuming that the key intramolecular interaction on distortion involves the HOMO and the LUMO. Then, using second-order perturbation theory, it was possible to determine how the magnitude of this interaction depends upon the identity of the central and substituent atoms.

In this Account we discuss how variations in the size of nascent HOMO-LUMO interactions can be utilized to explain differences in the structures of a wide range of molecules. Throughout, we emphasize the importance of the existence of a small HOMO-LUMO energy gap in predisposing a molecule toward geometric distortion.

Theoretical Background

Perturbation theory⁷ provides a convenient framework for discussing orbital interactions. If there is no degeneracy between the interacting MO's, as will be the case in the molecules of interest to us here, the change in the energy of ψ_m due to its interaction with orbital ψ_n is given by expression 1, where E_m and E_n are the

$$\Delta E_m = \frac{\langle \psi_m | H | \psi_n \rangle^2}{E_m - E_n} \quad (1)$$

unperturbed energies of ψ_m and ψ_n , respectively. It is clear that ΔE_m depends inversely on the energy difference $E_m - E_n$, so that when this quantity is small, ΔE_m is large, and vice versa. However, a large interaction between ψ_m and ψ_n does not necessarily have an appreciable effect on the total energy. When these two MO's interact, the energy of not only ψ_m but also that of ψ_n is affected; in fact, the change in energy of ψ_n is equal in magnitude and opposite in sign to that of ψ_m . Therefore, if ψ_m and ψ_n contain an equal number of electrons, the change in the total energy caused by mixing ψ_m and ψ_n is zero.⁸ However, if ψ_n does not contain electrons, an increase in its energy has no effect on the total energy. Thus, mixing between a filled and an unfilled MO has the greatest effect on lowering the total energy. By definition, the HOMO and LUMO are the filled and unfilled MO's that are closest in energy. Therefore, their intramolecular interaction, caused by some perturbation, can, in principle, provide substantial net energetic stabilization.

In this Account, we focus our attention on the HOMO-LUMO interaction, brought about by a molecular distortion, with the expectation that the smaller the energy gap between these MO's, the greater the energy lowering caused by their mixing.⁹ However, it should be recognized that on distortion many other changes occur in addition to the change in the HOMO-LUMO interaction.^{2,5b} Especially if the energetic effect of the HOMO-LUMO interaction is small, these other changes can greatly affect the equilibrium geometry. Nevertheless, in this Account we shall demonstrate the power of a theoretical analysis, based

(1) A. D. Walsh, *J. Chem. Soc.*, 2260 (1953), and papers thereafter.

(2) For a recent discussion, see R. J. Buenker and S. D. Peyerimhoff, *Chem. Rev.*, 74, 127 (1974).

(3) R. Pearson, *J. Am. Chem. Soc.*, 91, 4947 (1969).

(4) B. M. Gimarc, *J. Am. Chem. Soc.*, 93, 593 (1971); *Acc. Chem. Res.*, 7, 384 (1974).

(5) (a) W. R. Cherry and N. D. Epiotis, *J. Am. Chem. Soc.*, 98, 1135 (1976); (b) W. T. Borden, "Modern Molecular Orbital Theory for Organic Chemists", Prentice-Hall, Englewood Cliffs, N.J., (1975); see in particular pp 29-38 and 180-183.

(6) C. C. Levin, *J. Am. Chem. Soc.*, 97, 5649 (1975).

(7) For a concise presentation of perturbation theory, see ref 5b, and also M. J. S. Dewar, "Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969.

(8) This analysis neglects overlap. When it is included, a two-orbital, four-electron interaction is destabilizing. For discussions, see N. C. Baird and R. M. West, *J. Am. Chem. Soc.*, 93, 4427 (1971), and K. Müller, *Helv. Chim. Acta*, 53, 1112 (1970).

(9) It is assumed, in making comparisons, that the variation of $E_m - E_n$ dominates the variation of the interaction matrix element $\langle \psi_m | H | \psi_n \rangle$. For examples where the reverse situation obtains, see N. D. Epiotis, W. R. Cherry, R. L. Yates, S. Shaik, and F. Bernardi, *Top. Curr. Chem.*, in press.

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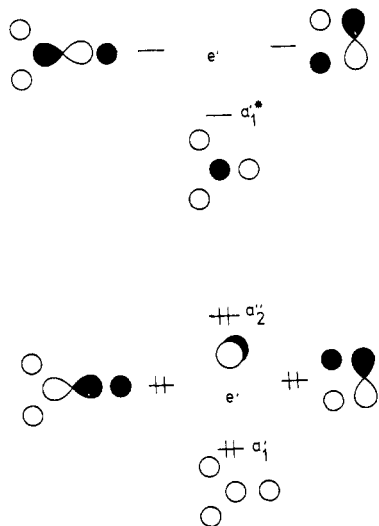


Figure 1. The valence MO's for a typical planar AH_3 molecule.

only on consideration of HOMO–LUMO interactions, in qualitatively explaining differences in molecular geometries and inversion barriers.

AB_3 and AB_2 Molecules

We now apply HOMO–LUMO analysis to the case of AH_3 molecules and inquire as to how their ground-state geometries and the magnitudes of their inversion barriers depend on the nature of A. Our approach is best illustrated by comparing NH_3 and PH_3 . In the planar geometry of these AH_3 molecules the HOMO, a doubly occupied $p\pi$ AO on the central atom, and the LUMO, an antibonding σ MO (see Figure 1), are orthogonal and cannot mix. However, as pyramidalization occurs, the two orbitals begin to interact. The resulting stabilization energy (SE), arising from the HOMO–LUMO interaction, is the decrease in energy of the HOMO times the number of electrons (n) it contains.

$$SE = n(\psi_{HOMO}|H|\psi_{LUMO})^2/(E_{HOMO} - E_{LUMO}) \quad (2)$$

The initial slope of a plot of SE vs. pyramidalization angle depends inversely on $E_{HOMO} - E_{LUMO}$. If this energy difference is smaller in planar PH_3 than in planar NH_3 , the rate of change of the stabilization energy upon pyramidalization will be larger for PH_3 than NH_3 . If this is the case, it may then be inferred that the net energy lowering upon pyramidalization of PH_3 will be larger than that in NH_3 and that PH_3 will have a smaller equilibrium bond angle than NH_3 . In drawing such inferences we are, of course, assuming that comparison of SE for two molecules at some small distortion angle not only reflects the behavior of their total energies at this angle but also that the total energy (E_T) curves do not subsequently cross. This type of "noncrossing rule" is tacitly assumed in the application of perturbation theory to problems of reactivity.¹⁰ Our basic premises regarding the behavior of SE and E_T are illustrated in Figure 2.

We have carried out CNDO/2¹¹ calculations on planar NH_3 and PH_3 molecules to determine the initial

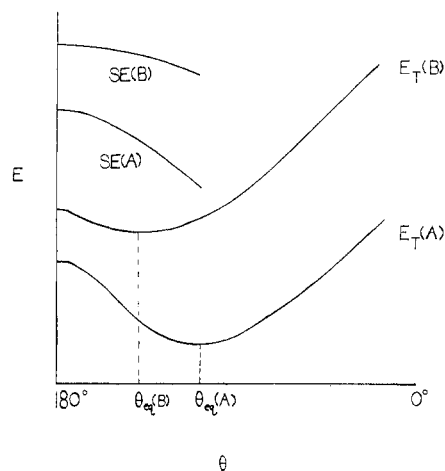


Figure 2. Plots of the stabilization energy (SE) and total energy (E_T) vs. the central HAH angle for two hypothetical molecules. The stabilization energy is greater for case A than for case B and results in a smaller equilibrium angle for case A.

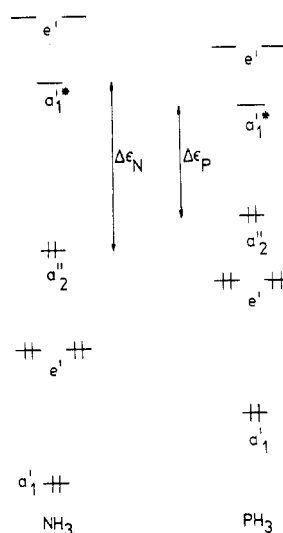


Figure 3. The relative energies of the valence MO's of planar NH_3 and PH_3 as obtained from CNDO/2 calculations.

HOMO–LUMO energy separation. The calculations reveal that the HOMO and LUMO in PH_3 are, indeed, much closer in energy than those in NH_3 . The orbital energies for both planar molecules are shown graphically in Figure 3. The actual HOMO–LUMO differences are 0.4143 and 0.8245 au in PH_3 and NH_3 , respectively. The smaller energy separation between the HOMO and LUMO in planar PH_3 leads us to expect this molecule to have a larger barrier to inversion and smaller equilibrium bond angles than NH_3 . Experimentally, the inversion barrier for ammonia is 5.78 kcal/mol.¹² The barrier for phosphine is so large that it has not been possible to measure it, although various SCF ab initio calculations indicate the value to be 34–38 kcal/mol.¹³ Inversion barriers in compounds of the general formula NR_3 and PR_3 have been measured, and, in all cases, the inversion barriers for the phosphorus compounds are substantially larger.¹⁴ Finally, the HAH bond angle has been experimentally determined

(10) J. D. Swaken and J. A. Ibers, *J. Chem. Phys.*, **36**, 1914 (1962).

(11) For a discussion of perturbation theory as applied to reactivity problems, see R. F. Hudson, *Angew. Chem., Int. Ed. Engl.*, **12**, 36 (1973).

(12) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970.

(13) (a) J. M. Lehn and B. Munsch, *Mol. Phys.*, **23**, 91 (1972); (b) R. Alrichs, F. Keil, H. Lischka, W. Kutzelnigg, and V. Staemmler, *J. Chem. Phys.*, **63**, 455 (1975).

(14) J. Lambert, *Top. Stereochem.*, **6**, 19 (1971).

Table I
Stabilization Energies, HAH Angles, and Inversion Barriers for Some AH₃ Molecules

	SE ^a	HAH angle, deg		Inversion barrier, kcal/mol	
		Exptl	Calcd	Exptl	Calcd
CH ₃ ⁻	0.1238		105, ^e 110.4 ^f		5.2, ^h 2.1 ^f
SiH ₃ ⁻	0.2982			>24 ⁿ	39.6 ⁱ
NH ₃	0.1034	106.6 ^b	107 ^e	5.78 ^g	5.02, ^j 5.6 ^f
PH ₃	0.3034	90.2 ^c	93 ^e		37.2, ^k 35 ^l
OH ₃ ⁺	0.0770	115-117 ^d	118, ^e 111.4 ^f		0.0, ^m .8 ^f
SH ₃ ⁺	0.2456				30.0 ⁱ

^a Stabilization energy (au) of the HOMO at 109.5°. ^b Reference 15. ^c Reference 16. ^d "Table of Interatomic Distances", *Chem. Soc., Spec. Publ.*, No. 18 (1965). ^e Reference 2. ^f R. Alrichs, F. Driessler, H. Lischka, and V. Staemmler, *J. Chem. Phys.*, **62**, 1235 (1975). ^g Reference 12. ^h P. Millie' and G. Berthier, *Int. J. Quant. Chem.*, **2**, 67 (1968). ⁱ Cited in ref 14. ^j A. Rauk, L. C. Allen, and E. Clements, *J. Chem. Phys.*, **52**, 4133 (1970). ^k Reference 13a. ^l Reference 13b. ^m J. W. Moscovitz and M. C. Harrison, *J. Chem. Phys.*, **43**, 3550 (1965). ⁿ J. B. Lambert, M. Urdaneta-Perez, and H.-N. Sun, *J. Chem. Soc., Chem. Commun.*, 806 (1967).

to be 106.6°¹⁵ in NH₃ and 90.2°¹⁶ in PH₃.

We have seen in the comparison of NH₃ and PH₃ that a small HOMO-LUMO gap in the planar geometry is indicative of small equilibrium bond angles and a strong preference for a pyramidal geometry (large inversion barrier). Therefore, we now inquire more generally as to how the energy of the HOMO and LUMO in AH₃ molecules varies with the identity of A. Two trends can be noted in the size of the HOMO-LUMO gap:

(1) As the central atom varies along a row of the periodic table, both the HOMO and LUMO decrease in energy as the electronegativity of A increases.¹⁷ However, because of the larger coefficient of A in the HOMO (the HOMO is, in fact, a p AO completely localized on A), this orbital decreases in energy at a somewhat faster rate than the LUMO. Therefore, we conclude that the HOMO-LUMO energy gap increases slightly as A varies across a row of the periodic table. The inversion barrier is thus expected to decrease across a row, and a parallel increase in bond angles is also anticipated. However, since the change in the HOMO-LUMO interaction across a row is expected to be small, there exists the possibility, especially in the first row, where the HOMO-LUMO energy gaps are rather large, that other effects, which our analysis neglects, can appreciably affect the barriers.

(2) As the central atom varies down a column of the periodic table, the change in the size of the HOMO-LUMO gap is more pronounced. With the decrease in electronegativity of A down a column, the energy of the

Table II
Values for the HAH Angle in Some AH₂ Molecules

	Exptl, deg	Calcd, deg		
		I ^b	II ^c	III ^d
H ₂ N ⁻		110	100-105	
H ₂ O	104.5 ^a	115	104	103.3
H ₂ F ⁺			105	111.8
H ₂ S	92.2			

^a Reference 24. ^b L. Z. Stenkamp and E. R. Davidson, *Theor. Chim. Acta*, **30**, 283 (1973). ^c Reference 2. ^d H. Lischka, *Theor. Chim. Acta*, **31**, 39 (1973).

HOMO increases. However, in contrast to what one might have anticipated, based solely on the decrease in the electronegativity of A, the LUMO drops in energy.¹⁷ Thus, the changes in the energy of both the HOMO and the LUMO work to decrease the energy gap between them. Consequently, in moving down a column from the first to the second row, a dramatic decrease in the HOMO-LUMO energy gap is anticipated. The smaller HOMO-LUMO separation in the planar geometry of molecules containing second-row elements results in a larger barrier to inversion and smaller bond angles in these molecules than in their first-row counterparts.

The foregoing qualitative predictions can be made semiquantitative by calculating, from eq 2, the stabilization energy of the lone pair in some AH₃ molecules. We have computed SE in going from a planar to a tetrahedral geometry for several members of this eight valence electron series.^{5a} The results are shown in Table I. In the subsequent columns, the geometries and inversion barriers, obtained by the methods indicated, are displayed. The parallel between the computed lone-pair stabilization energies and the geometries and inversion barriers is good, except for the barriers in the first-row series, obtained by ab initio calculations. However, many of these barriers were calculated using different basis sets, and it is, therefore, difficult to know what significance to attach to the small differences between the barriers for different first-row AH₃ molecules.

The two general principles derived above for AH₃ molecules can also be applied to AH₂ molecules in order to determine how the HAH angle depends on the identity of A. The anticipated trends in the HAH angle, based on the expected variation of the HOMO-LUMO gap in the linear molecules, are H₂N⁻ < H₂O < H₂F⁺; H₂S < H₂O. The bond angles for these molecules are shown in Table II, and again they are in accord with our expectations.

(15) L. S. Bartell and R. C. Hirst, *J. Chem. Phys.*, **31**, 449 (1959).



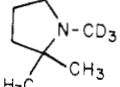
(16) E. D. Palik and E. E. Bell, *J. Chem. Phys.*, **26**, 1093 (1957).

(17) According to first-order perturbation theory,¹⁷ if the identity of the central atom in an AH₃ molecule is varied, the change in energy of the σ* MO is given by

$$\delta E_{\sigma^*} = c^2 \sigma^* A \delta \alpha_A + 6c \sigma^* A c \sigma^* H \delta \beta_{AH}$$

where $c_{\sigma^* A}$ and $c_{\sigma^* H}$ are, respectively, the coefficients of the central atom and one of the hydrogen atoms in the σ* MO, and $\delta \alpha_A$, $\delta \beta_{AH}$ are the changes in the coulombic integral of A and the A-H resonance integral, respectively. As one proceeds along a row of the periodic table, the first term dominates and the σ* MO decreases in energy as the central atom varies from C⁻ to O⁺, albeit at a slower rate than the HOMO. However, as one proceeds down a column of the periodic table, the second term apparently dominates, for the σ* MO decreases in energy, despite the decrease in the electronegativity of the central atom. It has been our experience that this trend is manifested in the results of both extended Hückel and CNDO/2 calculations [see M. D. Curtis, *J. Organomet. Chem.*, **60**, 63 (1973)], and it also appears in recent ab initio calculations [W. von Niesson, L. S. Cederbaum, and G. H. F. Ciercksen, *J. Am. Chem. Soc.*, **98**, 2066 (1976)]. Not only is this trend apparent in several different types of theoretical calculations, but experimental results also indicate its reality [see R. Bingham, *J. Am. Chem. Soc.*, **97**, 6743 (1975), for a discussion of some pertinent data].

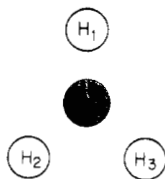
Table III
Inversion Barriers (kcal/mol) for Molecules with
Constricted RNR' Angles

	Exptl	Ab initio
$(\text{CH}_3)_2\text{N-H}$	4.4 ^a	8.6 ^b
	> 11.6 ^c	18.3 ^d
	9.0 ^e	
	8.2 ^f	

^a J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, **48**, 5058 (1968). ^b Reference 20. ^c M. K. Kemp and W. H. Flygare, *J. Am. Chem. Soc.*, **90**, 6267 (1968). ^d J. M. Lehn, B. Munsch, P. Millie, and A. Veillard, *Theor. Chim. Acta*, **13**, 313 (1969). ^e J. M. Lehn and J. Wagner, *Chem. Commun.*, **148** (1968). ^f J. M. Lehn and J. Wagner, *Tetrahedron*, **26**, 4227 (1970).

Any change that decreases the energy gap between the HOMO and LUMO in AH_3 molecules should increase the barrier to inversion and decrease the HAH angles. Such a change can be effected by replacing hydrogen with a more electronegative substituent. As the electronegativity of the substituent is increased, the LUMO decreases in energy. Since the energy of the lone pair on A in planar AH_3 remains almost unaffected by replacing H by a more electronegative atom, the HOMO-LUMO energy gap is decreased.¹⁸ The increase in the inversion barrier in NH_3 as the electronegativity of hydrogen is artificially increased has been demonstrated by the ab initio calculations of Mislow, Rauk, and Allen.¹⁹ The effect of substituent electronegativity on inversion barriers is well-known experimentally and has been discussed by several authors.²⁰

In addition to the substituent electronegativity effect, contraction of one of the HAH angles also decreases the energy of the LUMO of planar AH_3 . This MO is shown below. As the $\text{H}_2\text{-A-H}_3$ angle is constricted, the $\text{H}_2\text{-H}_3$ bonding overlap increases at a much faster rate than the already small $\text{H}_1\text{-H}_2$ and $\text{H}_1\text{-H}_3$ bonding overlaps decrease.²¹ The result is a decrease in the LUMO



energy and, consequently, in the HOMO-LUMO energy gap. We have confirmed this prediction by performing INDO calculations on D_{3h} planar ammonia and planar ammonia with one HNH angle constrained to 60° . The overlap integrals between the hydrogen atoms are shown below. The INDO calculations indicate a low-

(18) The argument neglects any conjugative effects which may be present, and is only strictly valid for planar AH_3 , where H is a hydrogen atom whose electronegativity has been artificially increased. For a further discussion, see ref 5a.

(19) K. Mislow, A. Rauk, and L. C. Allen, *Angew. Chem., Int. Ed. Engl.*, **9**, 400 (1970).

(20) J. M. Lehn, *Fortschr. Chem. Forsch.*, **15**, 311 (1970), and ref 14.

(21) This can be readily understood, since the overlap integral for two hydrogen AO's is proportional to e^{-kr} , where r is the distance between the atoms.

ering of the LUMO energy by almost 0.5 eV^{22} when the bond angle is constricted.




Atom pair	All bond angles 120°	H_2NH_3 bond angle 60°
$\text{H}_1\text{-H}_2$	0.1931	0.1431
$\text{H}_2\text{-H}_3$	0.1931	0.5101

The fact that angle constraint increases inversion barriers has been known for some time. Some pertinent experimental data is shown in Table III, while much more is available in several review articles.²⁰

Open-Shell AB_n Systems

In the previous section we dealt with systems in which the HOMO contains two electrons. As the occupation number, n , in eq 2 decreases from 2 to 1, the stabilization energy on pyramidalization or bending is anticipated to decrease. Concomitantly, the equilibrium bond angle is expected to increase, and the inversion barrier in a seven-electron AH_3 molecule is anticipated to be smaller than that in the corresponding eight-electron system. These expectations are confirmed by trends in the inversion barriers and geometries of AH_3 radicals. Thus, while the methyl anion CH_3^- is pyramidal, the methyl radical is planar.²³ However, when carbon, a first-row element, is replaced by silicon, a second-row element, the radical adopts a nonplanar geometry.²⁴ The barrier to inversion is sufficiently high that the stereochemical integrity of optically active silyl radicals is maintained.²⁵ The operation of the substituent electronegativity effect can also be seen in radicals. In particular, as the hydrogens in $\cdot\text{CH}_3$ are replaced by fluorines, the following trends in bond angles are observed:²⁶ $\cdot\text{CH}_2\text{F}$, $\sim 120^\circ$; $\cdot\text{CHF}_2$, 116° ; $\cdot\text{CF}_3$, 110° . Walborsky et al.²⁷ have demonstrated the importance of the electronegativity effect in maintaining the optical purity of substituted cyclopropyl radicals.

As one bond angle is constrained in the methyl radical, the pyramidal geometry would also be expected to be increasingly favored over the planar, as is the case in the anion. That this, indeed, happens is shown by the data below. The cyclopropyl anion is included to

			
Inversion barrier, ²⁸ kcal/mol	-3.3	4.8	36.6

illustrate the dramatic increase in inversion barrier as n is increased from 1 to 2.

The above analysis can be applied to open-shell AB_2 systems as well. An interesting case is CH_2 . In the triplet state, the MO that is stabilized by bending has an occupation number of 1. Consequently, the triplet has a relatively flat potential curve for bending with an equilibrium bond angle of 136° .^{29a} In the lowest singlet,

(22) The INDO calculations find a concomitant increase in the HOMO energy, which is unanticipated by simple one-electron analysis.

(23) T. Koenig, T. Ball, and W. Snell, *J. Am. Chem. Soc.*, **97**, 3938 (1969).

(24) P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, **91**, 3938 (1969).

(25) H. Sakurai, M. Murakami, and M. Kumada, *J. Am. Chem. Soc.*, **91**, 519 (1969).

(26) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965).

(27) H. M. Walborsky and P. C. Collins, *J. Org. Chem.*, **41**, 940 (1976).

(28) M. J. S. Dewar and M. Shansal, *J. Am. Chem. Soc.*, **91**, 3654 (1969).

(29) (a) E. Wasserman, V. J. Kuck, R. S. Hutton, and W. A. Yager, *J. Am. Chem. Soc.*, **92**, 7491 (1970); (b) J. H. Meadows and H. F. Schaefer III, *ibid.*, **98**, 4383 (1976).

Table IV
Variation of HAH Angle with Change in Occupation
Number of the Stabilized p Orbital in AH₃ Molecules

Molecule	n ^a	Angle, ^b deg
CH ₃ ⁺	0	120
CH ₃	1	115-120
CH ₃ ⁻	2	105
NH ₃ ⁺	1	120
NH ₃	2	107
PH ₃ ⁺	1	110-120
PH ₃	2	93

^a Number of electrons in "stabilized" orbital. ^b Reference 2.

Table V
Variation of HAH Angle with Change in Occupation
Number of the Stabilized p Orbital in AH₂ Molecules

Molecule	n ^a	Angle, ^b deg	
BH ₂ ⁺	0	180	
BH ₂	1	131	
BH ₂ ⁻	2	100	
CH ₂ ⁺	1	140	
CH ₂	2	103	
BH ₂	² A ₁	1	131
	² B ₁	0	180
CH ₂	¹ A ₁	2	103
	³ B ₁	1	134
SiH ₂	¹ A ₁	2	90-95
	³ B ₁	1	120-125

^a Number of electrons in "stabilized" orbital. ^b Reference 2.

however, the HOMO has an occupation number of 2; consequently, the singlet has a much larger barrier to linearity and an equilibrium bond angle of 103°. Recent *ab initio* calculations, which correctly predict the equilibrium bond angles in both states of CH₂, give a significantly smaller angle for each of the corresponding states of SiH₂, 118.2° for the triplet and 94.1° for the singlet. Indeed, bending in SiH₂ so strongly lifts the orbital degeneracy, which exists in the linear molecule, that, unlike the case in CH₂, the singlet emerges as the ground state. Further pertinent data for open-shell AH₃ and AH₂ molecules are shown in Tables IV and V.

Imines and Related Molecules

Molecules containing a doubly bonded atom, bearing a lone pair of electrons, are also amenable to analysis. As shown below, such molecules may exist in either



linear (I) or bent (II) geometries. The highest four occupied and lowest two unoccupied MO's for a linear molecule are shown in Figure 4. As bending occurs, the HOMO, which contains the lone pair, and a σ^* MO interact, thus stabilizing the bent geometry. Therefore, we expect trends in both the inversion barriers and geometries of these molecules, similar to those described above for AB₂ and AB₃ molecules. This expectation is, indeed, borne out. While little experimental data are available on inversion barriers in this class of compounds, Lehn³⁰ has computed some barrier heights by *ab initio* calculations. These are shown below and

(30) J. M. Lehn, B. Munsch, and P. H. Millie, *Theor. Chim. Acta*, **16**, 351 (1970).

Barrier, kcal/mol	H ₂ C=C ⁻ H	H ₂ C=N ⁺ H	H ₂ C=O ⁺ H
	38.9	27.9	17.2

conform to the prediction of a decrease in barrier height with an increase in the HOMO-LUMO gap, brought about by increasing the electronegativity of A.

Again, reasoning as for AH₃ molecules, if hydrogen is replaced by a more electronegative substituent, the inversion barrier should increase. Pertinent experimental data for various imine derivatives are displayed

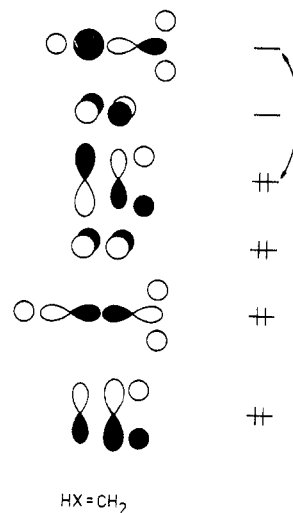


Figure 4. The highest four occupied and lowest two unoccupied MO's of a typical H₂C=AH molecule.

Table VI
Experimentally Determined Inversion
Barriers for Some Imines

	Z	ΔG^\ddagger , kcal/mol
	OCH ₃	23.2 ^a
	N(CH ₃) ₂	21.0 ^a
	CH ₃	12.2 ^b
	OCH ₃	>25 ^a
	N(CH ₃) ₂	>25 ^a
	CH ₃	19.1 ^b
	Br	>28 ^c
	Cl	>31 ^c
	OCH ₃	>39 ^c

^a H. Kessler and D. Leibfritz, *Justus Liebigs Ann. Chem.*, **737**, 53 (1970). ^b Cited in H. Kalinowski and H. Kessler, *Top. Stereochem.*, **7**, 295 (1973). ^c D. Y. Curtin and J. W. Hauser, *J. Am. Chem. Soc.*, **83**, 3474 (1961).

Table VII
Calculated Inversion Barriers for Various Substituted
Methylenimines^a

H ₂ C=N ₂ , X	Barrier, kcal/mol
H	4.6
CH ₃	13.8
NH ₂	16.0
OH	23.0
F	32.5
Cl	10.6

^a Extend Hückel calculation; see ref 31.

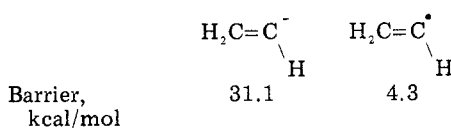
Table VIII
Inversion Barriers (kcal/mol) in
Methylenimine and Diimide

	H ₂ C=NH	HN=NH
Ab initio	27.9 ^{a, b}	50.1 ^b
EHT	4.6 ^c	11.6 ^d

^a Reference 30. ^b J. M. Lehn and B. Munsch, *Theor. Chim. Acta*, **12**, 91 (1968). ^c Reference 31. ^d J. Alster and L. A. Burnelle, *J. Am. Chem. Soc.*, **89**, 1261 (1967).

in Table VI. Additionally, the relative barriers for the parent imine with various N substituents have been calculated by the EH method,³¹ and the results are shown in Table VII. Both the experimental and calculated trends are as expected.

Similarly, the barrier to inversion is expected to increase as the methylene group is replaced by a more electronegative one. This effect is, indeed, observed, as shown by the computational results for methylenimine and diimide in Table VIII. Once again, as the occupation number of the HOMO is decreased, the inversion barrier is expected to decrease. This qualitative prediction has been confirmed by MINDO calculations on the vinyl anion and radical, as shown below.²⁸



The nitrogen cumulenes of the general formula HN=(C=)_nNH are an especially fascinating series of compounds. The first three members of the series, along with their calculated inversion barriers, are shown below.³² The inversion barrier heights of these compounds may be understood by reference to Figure 5. As bending of the linear molecules occurs, a σ^* MO mixes with the in-plane π MO's. As usual, we expect

	Barrier, kcal/mol
HN=C=NH	8.0
HN=C=C=NH	23.9
HN=C=C=C=NH	6.9

the highest of the occupied π MO's to mix with this σ^* MO to the greatest extent; therefore, we concentrate on this interaction. With $n = 1$, the π system consists of a CN double bond and an N lone-pair AO; so, it is isoconjugate with the allyl anion. With $n = 2$, the in-plane π system consists of a CN double bond and two N lone pair AO's; so, it is isoconjugate with the dianion of butadiene. From Figure 5, it is obvious that the HOMO- σ^* energy gap is smaller in the latter case, where both N lone pair AO's lie in the same plane.³³ In general, when n is odd, the π system is isoconjugate with an odd-alternate hydrocarbon of $n + 2$ carbons with $n + 3$ electrons. In the treatment of such a system by simple Hückel theory,⁷ the HOMO energy is α . When n is even, the π system is isoconjugate with an even-alternate hydrocarbon of $n + 2$ carbons and $n + 4$ electrons. The HOMO energy of such a dianion is $\alpha - 2\beta \cos [(n + 2)\pi/2(n + 1)]$, which is obviously greater

(31) F. Kerek, Z. Simon, and G. Ostrogovich, *J. Chem. Soc. B*, 541 (1971).

(32) M. S. Gordon and H. Fischer, *J. Am. Chem. Soc.*, **90**, 2471 (1968).

(33) We have carried out INDO calculations on the first two members of this series. According to these calculations, the energy gap is 15.48 eV when $n = 1$ and 13.32 eV when $n = 2$.

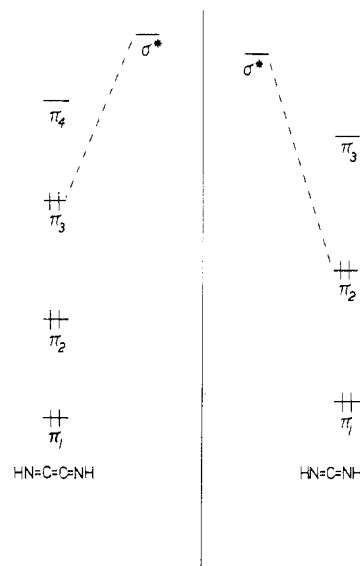


Figure 5. The σ^* and in-plane π MO's for the first two members of the HN(=C)_n=NH series.

than the energy of the HOMO of the hydrocarbons that are isoconjugate with the odd members of the series. Thus, the HOMO- σ^* energy gap is smaller, and, hence, the barrier height to inversion greater, when n is even. This gives rise to the observed alternation in the barrier height.

Conclusion

We have presented a theoretical model that is capable of qualitatively explaining the structure of and conformational barriers in a great many molecular systems.³⁴ The concept of HOMO-LUMO mixing, used here, can be related to the concept of hybridization in resonance theory, which is often invoked to interpret some of these effects.³⁹ Consider, for example, the hybridization approach for explaining the electronegativity effect on the inversion barrier of ammonia. As the electronegativity of the hydrogens is increased, it is assumed that the p character of the N-H σ bonds and, concomitantly, the s character of the lone pair are increased. The increase in p character of the NH bonds dictates smaller HNH angles and a larger barrier to inversion. In the MO approach presented here, we have

(34) The same model can also be used to explain, at least in part, the extraordinary reactivity toward cycloaddition of such molecules as silaethylene,³⁵ tetrafluoroethylene,³⁶ and methylenecyclopropane.³⁷ For instance, the central atom effect that makes silyl radicals strongly prefer a nonplanar geometry should operate to destabilize silaethylene, since a planar silicon atom is required for maximum π bonding. The same effect also acts to destabilize metaphosphate (PO_3^-) relative to nitrate (NO_3^-). In fact, calculations on planar metaphosphate show that, as would be expected, it possesses a very low-lying σ^* MO.³⁸ Analogously, the substituent electronegativity and angle constraint effects, respectively, extract an energetic price for the planarity required for optimum π bonding in tetrafluoroethylene and methylenecyclopropane.³⁷

(35) See, for instance, L. E. Gusel'nikov, N. S. Nametkin, and V. M. Vdovin, *Acc. Chem. Res.*, **8**, 18 (1975). Only recently have derivatives of silaethylene been isolated at low temperatures in inert matrices: O. L. Chapman, C.-C. Chang, J. Kolc, M. E. Jung, J. A. Lowe, T. J. Barton, and M. L. Tumej, *J. Am. Chem. Soc.*, **98**, 7844 (1976); M. R. Chedekel, M. Skoglund, R. L. Kreeger, and H. Schecter, *ibid.*, **98**, 7846.

(36) J. D. Roberts and C. M. Sharts, *Org. React.*, **12**, 1 (1962); P. D. Bartlett, *Q. Rev., Chem. Soc.*, **24**, 473 (1970).

(37) P. D. Bartlett and R. C. Wheland, *J. Am. Chem. Soc.*, **94**, 2145 (1972).

(38) L. M. Loew, *J. Am. Chem. Soc.*, **98**, 1630 (1976); **99**, 1019 (1977).

(39) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961); L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N.Y., 1960.

seen that the HOMO-LUMO interaction increases as the hydrogen electronegativity is increased. Since the LUMO is a σ^* MO with a significant contribution from the nitrogen 2s AO, the more the LUMO is mixed into the HOMO, indeed, the greater is the s character in the resulting lone pair MO. In most cases the frontier orbital approach presented in this Account is not at variance with a hybridization description of the effects discussed here. In fact, consideration of HOMO-

LUMO interactions can be seen as offering justification, in the context of MO theory, for the description of these effects that emerge from the less rigorous concept of hybridization in resonance theory.⁴⁰

(40) Note Added in Proof. In connection with the discussion of molecules containing π bonds,³⁴ it is interesting to note that the x-ray structure of a compound possessing a Sn-Sn double bond shows the tin atoms to be pyramidal: P. J. Davidson, D. H. Harris, and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 2268 (1976).

Photochemical Probes of Hydrocarbon Chain Conformation in Solution

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Concern about the shape of hydrocarbon chains began in the 1920's with the surface-tension studies of fatty acid monolayers by Langmuir.¹ For various reasons, which have been reviewed recently by Meyer and Stec,² he concluded that the normal alkanes would fold up into tight, ball-like configurations in the gas phase. This kind of argument assumes that the attractive enthalpy of pairwise contacts between remote CH_2 groups is sufficient to overcome the maximum entropy associated with the random coil. The early arguments preceded our understanding that alkanes have access to only three rotational states about each carbon-carbon bond, with trans rotamers essentially half a kilocalorie more stable than gauche.³

The point of view persists, however, that hydrocarbon chains form compact configurations in the gas phase which maximize intramolecular contacts.⁴ Various experiments have been given conflicting interpretations; however, electron diffraction studies by Bartell⁵ firmly establish that butane, pentane, hexane, and heptane achieve conformations randomly distributed among rotamers favoring trans over gauche by $E_g = 600$ cal/mol. For tetracosane in the gas phase, current evidence supports a random conformation.² The evidence is thermodynamic, and the choice in interpretation, as Meyer and Stec point out, is a rather delicate one.²

For hydrocarbon chains in solution, various points of view have been put forward. The weight of the evidence supports the contention that in dilute solution hydrocarbon chains are reasonably described as randomly oriented.^{6,7} The number of compelling experiments are few. The conclusions rest on comparisons of these experimental results with semiempirical conformational calculations. There is also a growing body of evidence

suggesting that alkane-chain-containing molecules aggregate at modest concentrations, even in nonpolar solvents.^{8,9} Contemporary interest in biological membranes and other phospholipid systems, in micelles, in microemulsions, in monolayers, and in other semi-structured systems is sufficiently intense that we can no longer be satisfied with a general picture of hydrocarbon chains in solution. Experiments are necessary which detail the shapes of these flexible molecules in dilute solution and in aggregates. These experiments in turn must be used to test the limits of current semiempirical models.

What are needed are sets of experiments which probe hydrocarbon chain shape from many points of view. Solvent effects on chain conformation must be investigated. In spite of suggestions that these effects are "small", they will be of considerable importance for our understanding if they can be described with sufficient precision. To choose an extreme example, few would doubt that a hydrocarbon chain in a phospholipid vesicle has a different average configuration than the

(1) I. Langmuir, "Third Colloid Symposium Monograph", The Chemical Catalog Co., New York, N.Y., 1925, pp 53-54.

(2) E. F. Meyer and K. S. Stec, *J. Am. Chem. Soc.*, **93**, 5451 (1971).

(3) (a) H. Morawetz, "Macromolecules in Solution", 1st ed, Interscience, New York, N.Y., 1965; (b) ref 3a, p 124; (c) ref 3a, Chapter II.

(4) J. C. McCoubrey, J. N. McCrae, and A. R. Ubbelohde, *J. Chem. Soc.*, 1961 (1951).

(5) L. S. Bartell and D. A. Kohl, *J. Chem. Phys.*, **39**, 3097 (1963).

(6) (a) G. D. Patterson and P. J. Flory, *J. Chem. Soc., Faraday Trans. 2*, **68**, 1098 (1972); (b) W. J. Leonard, Jr., R. L. Jernigan, and P. J. Flory, *J. Chem. Phys.*, **43**, 2256 (1965).

(7) M. A. Winnik, A. Lemire, D. S. Saunders, and C. K. Lee, *J. Am. Chem. Soc.*, **98**, 2000 (1976).

(8) G. W. Brady, *Acc. Chem. Res.*, **7**, 174 (1974); (b) G. W. Brady and D. B. Fein, *J. Appl. Crystallogr.*, **8**, 261 (1975); (c) G. W. Brady, C. Cohen-Addad, and E. F. X. Lyden, *J. Chem. Phys.*, **51**, 4320 (1969).

(9) (a) P. Tancrède, P. Bothorel, P. de St. Romain, and D. Patterson, *J. Chem. Soc., Faraday Trans. 2*, **73**, 15 (1977); P. Tancrède, P. Bothorel, and D. Patterson, *ibid.*, **73**, 29 (1977); (b) V. T. Lam, P. Picker, D. Patterson, and P. Tancrède, *J. Chem. Soc., Faraday Trans. 2*, **70**, 1465 (1974); M. D. Croucher and D. Patterson, *ibid.*, **70**, 1479 (1974); (c) P. Bothorel and G. Fourche, *ibid.*, **69**, 441 (1973); (d) P. Bothorel, C. Such, and C. Clément, *ibid.*, **69**, 1453 (1972); (e) C. Clément and P. Bothorel, *J. Chim. Phys.-Phys.-Chim. Biol.*, **61**, 878 (1964).

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