

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.

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

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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

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- (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).
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- (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).

Table I. Inversion Barriers and Bond Angles for First Row Compounds

	CNDO/2 ^a		INDO ^b		Mislow ^c		Reported	
	ΔE , kcal/ mol	Angle, deg	ΔE , kcal/ mol	Angle, deg	ΔE , kcal/ mol	Angle, deg	ΔE , kcal/ mol	Angle, deg
CH ₃ ⁻	16.2	107	11.7	106	5.0	112	5.2 ^d	
NH ₃	11.8	107	4.9	110	3.2	112	5.8 ^e	109.1 ^f
NH ₂ CH ₃ ^g	12.9	<i>o</i>	4.7	<i>o</i>	4.0	<i>o</i>	4.8 ^g	
NH ₂ C(CH ₃) ₃ ^h	12.2	<i>o</i>	4.4	<i>o</i>	3.5	<i>o</i>		
NH(CH ₃) ₂	13.6	<i>o</i>	4.4	<i>o</i>	(5.2)	<i>o</i>	4.4 ^h	
N(CH ₃) ₃ ⁱ	15.0	<i>o</i>	5.1	<i>o</i>	6.5	<i>o</i>	6.0 ⁱ	
NF ₃	76.8	<i>p</i>	76.3	<i>p</i>	60.6	<i>p</i>	56-59 ^j	102.2
H ₃ O ⁺	1.3	115	0	120	0	120	0 ^k	120 ^k
							1.7 ^l	117 ^m

^a Reference 10. ^b Reference 15. ^c Reference 19. ^d Ph. Millie and G. Berthier, *Int. J. Quantum Chem., Symp.*, **2**, 67 (1968). *Ab initio* result. ^e Reference 4. ^f O. Bastiansen and B. Beagley, *Acta Chem. Scand.*, **18**, 2077 (1964). ^g M. Tsuboi, A. Y. Hirakawa, and K. Tamagake, *J. Mol. Spectrosc.*, **22**, 272 (1967). ^h J. E. Wollrab and V. W. Laurie, *J. Chem. Phys.*, **48**, 5058 (1968). ⁱ C. H. Bushweller and J. W. O'Neil, *J. Amer. Chem. Soc.*, **92**, 2159 (1970). Value reported for dibenzylmethylamine. Barriers of 5-7 kcal/mol have been observed for other trialkylamines (ref 21). ^j G. W. Koepl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, *J. Amer. Chem. Soc.*, **89**, 3396 (1967), with correction reported to Gordon and Fischer (ref 18). ^k J. W. Moskowitz and M. C. Harrison, *J. Chem. Phys.*, **43**, 3550 (1965); *ab initio* calculation. ^l G. W. Koepl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, *J. Amer. Chem. Soc.*, **89**, 3396 (1967). ^m R. Savoie and P. A. Giguere, *J. Chem. Phys.*, **41**, 2698 (1964). ⁿ Transition state geometries are discussed in detail in ref 21. ^o Tetrahedral ground conformation assumed. ^p Experimental value of bond angle assumed for ground conformation.

EHT, unfortunately, predicts a planar geometry (no barrier) for NH₃. This is probably due to the inadequate modeling by EHT of the interaction of a 2s and a 2p orbital on the same center. Since a one-center 2s-2p overlap integral is zero, EHT sets the interaction to zero. However, in pyramidal ammonia, the minimum basis set SCF calculation shows the 2s-2p interaction to be several electron volts,^{16,17} which, however, drops to zero for the planar conformation. This interaction comes about through electron-electron repulsions and seems to be instrumental in determining the relative energy of planar *vs.* pyramidal conformations of inverting molecules. CNDO and INDO retain some electron-electron repulsions so it is possible that either or both methods could be used successfully for calculations of inversion barriers. INDO is the less approximate method since it uses the one-center atomic exchange integrals as well as the atomic coulomb integrals of the CNDO method.

Gordon and Fischer¹⁸ studied some simple inversion barriers about first row atoms using both CNDO and INDO. They found that CNDO gave barriers that were too high but that INDO barriers were in reasonable agreement with experiment. However, Mislow, *et al.*,¹⁹ have designed a new set of parameters for CNDO that gives for the most part reasonable agreement of calculated and experimental barriers to inversion both at N and P. Furthermore, they omitted 3d orbitals from calculations involving second row atoms, arguing that such orbitals serve mostly to unbalance the basis sets. Although their method is reasonably good over-all, they do predict several anomalies, including a high (>50 kcal/mol) pyramidal inversion barrier for (SiH₃)₃N, a molecule known to be planar,²⁰ and an unreasonable barrier sequence for NH₃, CH₃NH₂,

(CH₃)₂NH, and (CH₃)₃N. Since inversion barriers of alkylamines²¹ and haloalkylamines²² are of current concern, it was decided to investigate the relative suitability of CNDO in both standard and Mislow parametrizations and of INDO for barrier predictions and to attempt an extension of the INDO method to second row atoms.

Results and Discussion

First Row Inversions. Calculated inversion barriers for CH₃⁻, NH₃, NH₂CH₃, NH₂C(CH₃)₃, NH(CH₃)₂, N(CH₃)₃, NF₃, and H₃O⁺ are given in Table I. Calculated optimum values of bond angles are given for the hydrides. The calculations were performed with CNDO/2,¹⁰ INDO,¹⁵ and CNDO-Mislow¹⁹ in order that the three methods might be compared and evaluated. Standard values of bond lengths (Table II) were

Table II. Standard Values of Bond Lengths Used in These Calculations^a

Bond	Bond length, Å	Bond	Bond length, Å
CH	1.09	SiN	1.74
NH	1.01	PH	1.42
CN	1.47	PC	1.84
OH	0.96	SH	1.33
SiH	1.48	NCI	1.75

^a L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. 11 (1958); No. 18 (1965).

employed without optimization. This is probably the reason why these barriers are lower than those reported by Gordon and Fischer.¹⁸

Both CNDO-Mislow and INDO barriers are in reasonable agreement with experiment. INDO, however, seems to be a little better at reproducing the barrier and geometry of NH₃. INDO, moreover, gives a more realistic account of the trend in barriers, in going from NH₃ to NH₂CH₃ to NH(CH₃)₂ to N(CH₃)₃. Barriers

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(20) K. Hedberg, *J. Amer. Chem. Soc.*, **77**, 6491 (1955).

Table III. The Integrals F^2 and G^1 for Second Row INDO Calculations

Atom	F^2		G^1	
	Extrapolated	Spectral	Extrapolated	Spectral
Na	0.04361		0.07797	
Mg	0.06732		0.10297	0.08995
Al	0.09072	0.10298	0.13431	0.12577
Si	0.12046	0.11609	0.17117	
P	0.13933	0.14231	0.21325	
S	0.16491	0.16853	0.27935	
Cl	0.19145		0.31267	

$$F^2(Z) = F^2(Z-8) \frac{F^2_{\text{sto}}(Z)}{F^2_{\text{sto}}(Z-8)} \quad (1)$$

$$G^1(Z) = G^1(Z-8) \frac{G^1_{\text{sto}}(Z)}{G^1_{\text{sto}}(Z-8)} \quad (2)$$

element, Z-8 its first row analog, and the subscript "STO" refers to a theoretical integral calculated from Slater orbitals. These values for F^2 and G^1 are listed in Table III under the heading "extrapolated." There seems to be reasonable agreement of the extrapolated and spectral values.

Table IV. Inversion Barriers and Bond Angles for Second Row Compounds

	CNDO-A ^a		CNDO-B ^b		INDO-A ^c		INDO-B ^c		CNDO-Mislow ^d		Reported ^e	
	E, kcal/mol	Angle, deg	E, kcal/mol	Angle, deg	E, kcal/mol	Angle, deg	E, kcal/mol	Angle, deg	E, kcal/mol	Angle, deg	E, kcal/mol	Angle, deg
SiH ₃ ⁻	45.5	98	25.7	101	48.5	97	26.1	99	37.4	100	39.6 ^e	
N(SiH ₃) ₃	4.8	k	0	120	0	120	0	120	32.3	k	0 ^f	120 ^f
PH ₃	49.4	96	28.6	99	48.4	95	25.4	96	35.8	99	37.2 ^g	93 ^h
P(CH ₃) ₃	41.0	l	17.0	l	33.9	l	8.6	l	30.4	l	35.6 ⁱ	99 ^h
SH ₃ ⁺	25.6	99	13.0	102	21.2	99	5.2	106	25.7	101	30.0 ^e	
NCl ₃	36.3	k	26.9	k	33.5	k	24.2	k	20.3	k		109 ^h
NH ₂ Cl	13.8	k	17.2	k	13.7	k	11.1	k	9.1	k		
N(CH ₃) ₂ Cl	22.0	k	19.4	k	12.9	k	10.4	k	9.9	k	10.2 ^j	

^a Reference 11. ^b References 12 and 13. ^c See text. ^d Reference 19. ^e *Ab initio* value reported in ref 19. ^f Reference 20. ^g J. M. Lehn and B. Munch, *Chem. Commun.*, 1327 (1969); *ab initio* result. ^h See Table II, footnote a. ⁱ R. D. Baechler and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 3090 (1970). Value reported for cyclohexylmethyl-*n*-propylphosphine. ^j W. B. Jennings and R. Spratt, *Chem. Commun.*, 54 (1971). Value reported for chlorodiethylamine. ^k Tetrahedral ground conformation assumed. ^l Experimental value of bond angle assumed for ground conformation.

calculated by the CNDO/2 method are not as realistic as those of the other two methods for the compounds cited, a conclusion that corroborates previous claims.^{18,19}

INDO for the Second Row. Since the INDO method seems well suited for studies of inversion of first row compounds, it seems desirable to extend the method to cover second row atoms, both as substituents (Cl, SiH₃, etc.) and as inverting centers (P, etc.). If the electronic structure of a second row atom can be described adequately by 3s and 3p Slater orbitals (as in Santry and Segal's "sp" version of second row CNDO¹¹ and in Mislow's modification of that method¹⁹), such extension requires only the specification of parameters, since all equations for matrix elements have already been worked out. Electronegativity ($-\frac{1}{2}(I - A)$) and bonding (β^0) parameters may be taken unchanged from CNDO; so only the Slater-Condon parameters, F^2 and G^1 , for one-center exchange integrals need be worked out. For the first row, most of these were derived by Slater²³ from atomic spectral data.²⁴ Proceeding in a similar manner one can calculate G^1 values for Mg and Al from the sp and sp² configurations, respectively, and F^2 values for Al, Si, P, and S from the sp², s²p², s²p³, and s²p⁴ configurations, respectively (Table III). In principle, one should be able to obtain values of F^2 and G^1 for other atoms as well, but configuration interaction seems to perturb the atomic states and precludes any consistent results. An alternative approach to a full set of second row F^2 and G^1 parameters is to extrapolate from the standard first row values. To this end, eq 1 and 2 were employed. In these equations, Z refers to the atomic number of a second row

It remains to specify the CNDO parameters, $\frac{1}{2}(I - A)$ and β^0 , for the second row atoms. Two different sets of these parameters for CNDO calculations have been given by the Pople group, to be referred to here as CNDO-A¹¹ and CNDO-B.¹² The initial failure of CNDO-B to preserve rotational invariance has been corrected.¹³ There are some small differences between CNDO-A and CNDO-B in equations specifying matrix elements involving second row atoms, but both methods incorporate CNDO/2¹⁰ for H and first row atoms.

In this work, both CNDO-A and CNDO-B have been converted to INDO by incorporation of F^2 and G^1 integrals and the appropriate equations for one-center matrix elements and will be referred to as INDO-A and INDO-B, respectively.

Second Row Inversions. Calculated inversion barriers for SiH₃⁻, N(SiH₃)₃, PH₃, P(CH₃)₃, SH₃⁺, NCl₃, and NH₂Cl are given in Table IV. Calculated optimum values of bond angles are given for the hydrides. Standard values of bond lengths (Table II) were used without optimization. Calculations were performed with CNDO-A, CNDO-B, INDO-A, INDO-B, and CNDO-Mislow, in order that the five methods might be compared and evaluated.

Mislow, *et al.*, used the reported values of barriers in SiH₃⁻, PH₃, and P(CH₃)₃ to obtain their second row parameters; thus their method reproduces these barriers reasonably well. INDO-A is also in reasonable but not as good agreement. INDO-B and CNDO-B seem to be unsuitable for substituted phosphines, both giving very low predictions for the barrier in P(CH₃)₃. Both CNDO-A and CNDO-Mislow predict a nonplanar geometry for N(SiH₃)₃, while CNDO-B, INDO-A, and INDO-B correctly predict its planarity. The

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(24) C. E. Moore, *Nat. Bur. Stand. (U. S.), Circ.*, 467 (1949).

CNDO methods all predict an increase in barrier in going from NH_2Cl to $\text{N}(\text{CH}_3)_2\text{Cl}$, while INDO-A and INDO-B predict a decrease. A barrier decrease would seem more likely because of steric hindrance in the pyramidal conformation due to the greater size of methyl groups as opposed to H atoms. (Compare NH_3 at 5.8 kcal/mol with $\text{NH}(\text{CH}_3)_2$ at 4.4 kcal/mol.)

While the CNDO method as parametrized by Mislow has been shown to have generally good predictive power, INDO-A seems to give more realistic results in the case of alkylamines and chloroalkylamines. It is for this reason that INDO-A has been chosen for the theoretical studies of these systems to be reported in subsequent papers.^{21,22}

Computational Details

One-center integrals for calculation of F^2 and G^1 values were obtained through use of Stevens' Inde-

pendent Integrals Package²⁵ running on a Univac Series 70/46 computer.

Cartesian coordinates for the MO calculations were obtained through use of "COORD" (time sharing version)²⁶ running interactively on a DEC System 1050 computer.

The CNDO and INDO calculations were performed with a modified version of CNINDO²⁷ running on a Univac Series 70/46 computer.

Acknowledgment. The authors are grateful to the Worcester Area College Computation Center for a grant of computer time.

(25) R. M. Stevens, "Independent Integrals Package," Quantum Chemistry Program Exchange, Program No. 161.

(26) P. E. Stevenson and J. E. Merrill, "COORD (time sharing version)," Quantum Chemistry Program Exchange, Program No. 186.

(27) P. A. Dobosh, "CNINDO: CNDO and INDO Molecular Orbital Program (FORTRAN IV)," Quantum Chemistry Program Exchange, Program No. 141.

An *ab Initio* Study of the Role of d Orbitals in Chlorosilane

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Abstract: *Ab initio* LCAO-MO-SCF computations of the wave function of chlorosilane have been carried out in a moderately sized, uncontracted, Gaussian basis set with and without an appropriate manifold of d orbitals being allowed to the silicon and/or the chlorine atom. Electron-density difference plots show that conferring d character upon either the silicon or the chlorine has about the same effect on the detailed transfer of charge between the chlorine and silicon atoms, although the usual interpretation in terms of the contributing atomic orbitals leads to the conclusion that, when d character is allowed only to the silicon, there is a transfer of charge from the chlorine but, when it is allowed only to the chlorine, the effect is essentially just a polarization of this atom. The calculated variations in the orbital energies of the core electrons upon allowing or disallowing d character to the silicon or chlorine atoms are interpreted in terms of changes in the electrostatic potential in the core region.

Although a relatively important role has long been assigned¹ to d orbitals in the covalent chemistry of atoms of the third period, it has only been recently that the problem of d-orbital participation has been attacked quantitatively. Molecular optimization has shown^{2,3} that the d contributions to the linear combination of atomic orbitals (LCAO) making up a self-consistent field (SCF) wave function involves 3d orbitals exhibiting radii which are approximately the same as those of the 3s and 3p orbitals instead of the much larger 3d radii obtained from promoting a 3s or 3p electron into a 3d orbital in an atomic calculation. Furthermore, even for coordination numbers five and six, an sp description is sufficient⁴ for the molecular orbitals, and indeed LCAO-MO-SCF calculations^{5,6} on molecules such as

PF_5 illustrate that molecular-orbital charge distributions obtained using a linear combination of s, p, and d atomic orbitals differ only in fine details from those restricted to s and p orbitals for all of the constituent atoms including those of the third period.

An important role of d orbitals used in the description of atoms of both the second and third periods is as polarization functions,⁷ with no net change occurring in the charge of the atom to which the d orbital has been allowed, since whatever electron density were to be gained by the d orbitals would be lost by the s and p orbitals of the same atom. The commonly discussed $p_\pi-d_\pi$ electronic feedback⁸⁻¹⁰ where the d orbitals on a third period atom accept charge from appropriate orbitals of neighboring atoms has been demonstrated in

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