THE CALCULATION OF
MONO-CYCLIC MOLECULAR STRUCTURES USING MINDO/3

by

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ABSTRACT

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Molecular geometries of selected, small cyclic compounds were calculated using the semi-empirical, S.C.F. molecular orbital method MINDO/3. Calculated geometries are compared with experimental values to determine MINDO/3's effectiveness. It is found that the method has several systematic deficiencies. In particular, carbon-oxygen single bond distances are calculated to be too short. Also, although planar rings are dealt with accurately, MINDO/3 tends to predict non-planar cyclic compounds to be too planar. Moreover, when several unique molecular conformations are possible, MINDO/3 often incorrectly predicts the one of lowest energy. It is argued that these last two effects may be due to MINDO/3's inability to reproduce syn-gauche energy differences.

MINDO/3's effectiveness in calculating cyclic geometries is discussed with regard to the value of applying the method in calculations of reaction pathways in the ozonolysis of alkenes. It is determined that the results of such calculations would be extremely suspect.

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Peter Eilker

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I. INTRODUCTION

A BRIEF HISTORY OF MINDO

MINDO/3 is a computational method designed to yield approximate solutions to the Schroedinger equation for various molecular systems. It is the third such method in a series (the first two methods being MINDO/1 and MINDO/2) developed by M.J.S. Dewar and his at the University of Texas at Austin. During the period, primarily the 1970's, in which MINDO in its various forms has been available for use, the method has been applied to a variety of chemical systems and problems with a fair amount of success. Moreover, it has the quality of being quite bit less costly and time consuming than many other quantum chemical techniques.. These aspects make MINDO initially attractive to the chemist searching for ways to determine chemical properties that are very difficult to determine by experimentation.

Our interest is in the mechanism of ozonolysis, many aspects of which are quite difficult to ascertain in the laboratory. This paper is concerned with extending the knowledge of MINDO/3's predictive ability and to thereby test the assumption that it can be applied to the mechanism of ozonolysis with some assurance of success. Before discussing the specific problem of ozonolysis, though, it is relevant to first give a brief synopsis of MINDO's past performance. Since the amount of material is rather large, only some generalizations will be presented. However, all

MINDO publications that could be found in a literature search will be listed.

By far the most extensive work done with MINDO has been done by Dewar, et.al.. They report hydrocarbon bond lengths that are generally less than 0.02 angstroms different from experimental values(1) and bond angles in error by less than four degrees for most hydrocarbons(1) when calculated by MINDO/3. Similar values are also reported for compounds containing carbon, hydrogen, oxygen, and/or nitrogen; for compounds containing carbon, hydrogen, fluorine, and/or chlorine; and for compounds containing third row elements(1).

Calculated heats of formation at twenty-five degrees Celsius for the above types of molecules are reported to be in error by less than ten KCAL/MOL most of the time(1).

However, with both geometry and energy calculations, systematic errors were found to occur. For example, heats of formation were consistently found to be too negative for acetylenic and small ring compounds, whereas they were too positive for aromatic and compact globular molecules(1). Thus although there are reasons to be optimistic about MINDO/3's effectiveness, one must always be aware that serious deficiencies do exist.

Without any attempt to detail MINDO's performance, the following is a summary of the types of problems which MINDO has been applied to.

(1) MINDO applied to the determination of ground state molecular properties such as optimum geometries, heats of formation, dipole moments, conformational energy barriers, and vibrational energies and force constants: see references (2) to (49) and (108) and (109).

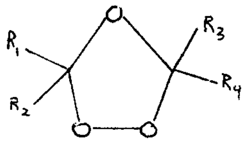
(2) MINDO applied to the determination of reaction mechanisms: see references (50) to (90).

(3) MINDO applied to the determination of excited state molecular properties and spectroscopic values: see references (91) to (107).

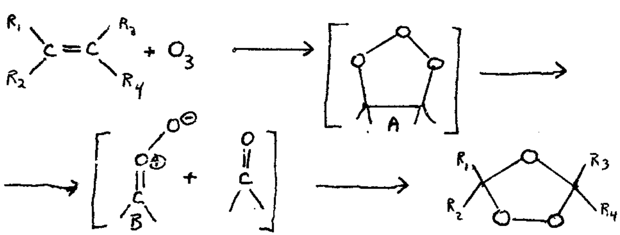
(4) Criticisms of the MINDO method: see references (110) to (113).

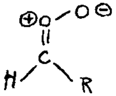
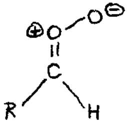
MINDO/3 AND THE MECHANISM OF OZONOLYSIS

When ozone adds to an alkene, the final product is an ozonide of the following form(114):



The predominant stereochemical product is dependent upon the substitution pattern on the alkene. To understand this and other experimental observations, Bauld, Baily, et.al. proposed the following general mechanism(114):

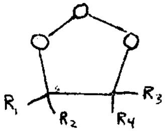


In this mechanism, A, the primary ozonide, assumes a configuration determined by the substition on the alkene(114). B, a zwitterion, takes on either a syn:  or anti configuration:  depending upon the stereochemical form of A. The product ozonide in turn has its predominant configuration determined by the form of the zwitterion. It can be seen that the stereochemistry of the reaction depends upon the alkene substition pattern.

A problem with the Bauld-Baily mechanism is how to decide the effect that the configuration of one particular intermediate has on the configuration of its immediate product(114). In fact, experiment has shown that the rules laid down by the Bauld-Baily proprosal to deduce these stereochemical effects are not always able to predict observed product distributions. (114). This is not altogether surprising since the rules mentioned above are based in qualitive arguments that many times can give only a vague idea of the relative effects resulting from various factors(114). Moreover, these qualitative arguments assume the predominant conformation of the primary ozonide to be one which need not be, necessarily, the one found in nature(114). Obviously, a determination of the geometries and energies of the various proposed intermediates would be of value. However, these species are for the most part not sufficiently stable to allow isolation and examination in the laboratory.

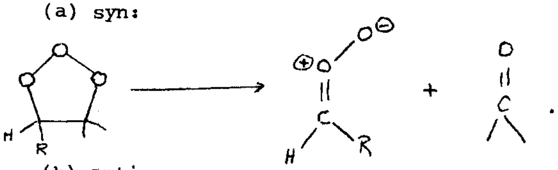
An alternative to direct experimentation is a theoretical treament. In this way one can isolate an intermediate or transition state and calculate its geometry and energy. We wish to use MINDO/3 to this end. In particular, we are interested in the energetics and stereochemistry of the following species:

(1) Primary ozonides - stable conformations:

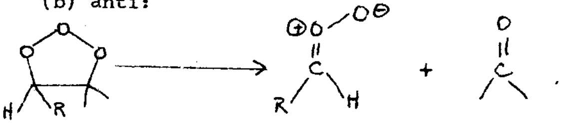


(2) Zwitterion formation;

(a) syn:



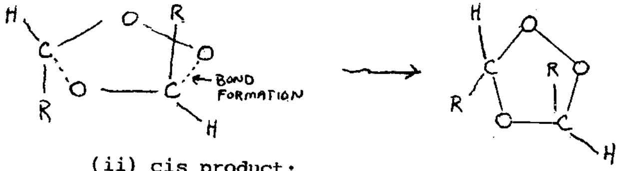
(b) anti:



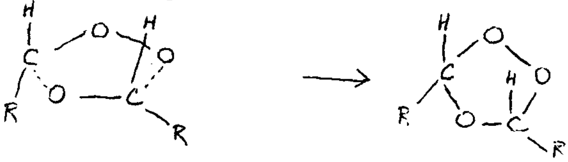
(3) Formation of the product ozonide:

(a) with syn zwitterions:

(i) trans product:

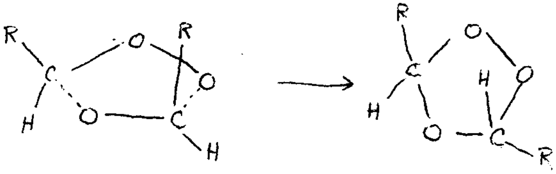


(ii) cis product:

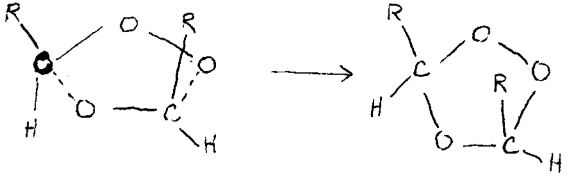


(b) with anti zwitterions:

(i) trans product:



(ii) cis product:



The theoretical technique is unquestionably advantageous if the treatment yields results that are sufficiently accurate. Since one cannot test the accuracy of a treatment by comparing its results to data taken from the system one wants to eventually treat (presumably such experimental data does not exist), a reasonable course would be to apply the treatment to similar systems that can and have been treated in the laboratory.

It is obvious that if MINDO/3 is to be applied to the mechanism of ozonolysis, it must be an accurate method for the determination of ring geometries. Since, also, the nature of proposed ozonolysis intermediates suggest that such cyclic moieties are non-planar, monocyclic structures, MINDO/3 should, in particular, be accurate in the calculation of the geometries of such compounds. To determine MINDO/3's reliability in this regard, the method will be applied to a number of test ring compounds with known experimental geometries. A comparison will then be made between MINDO/3's predictions and the actual geometries. If the comparison is favorable, then it is reasonable to suppose that MINDO/3 can be applied to elucidating the mechanism of ozonolysis.

A QUANTUM MECHANICAL INTERLUDE

S.C.F. THEORY

Describing the behavior of a molecule system is, for the most part, equivalent to solving the Schroedinger equation for that system(115).

For a one electron system (if the nucleus is held fixed) the Schroedinger equation takes the form:

$$K\nabla_{e^-}^2\Psi - \frac{Z_n e^2}{r_{ne}}\Psi = E\Psi \qquad (116)$$

where Z_n is the charge of the nucleus, and r_{ne} is the distance between the electron and the nucleus, and k is a constant. This equation can be placed in a form whereby the commutation properties of the operators on the left hand side guarantee a solution of the form $\Psi = f(x)g(y)h(z)$; where x,y,z are the co-ordinates of the electron(117). The Schroedinger equation can be solved exactly in this way(note that the nuclear position is fixed and thus need not be specified in the equation).

In systems of more than one electron (once again assuming fixed nuclei) the Schroedinger equation takes the following form(116):

$$\left(\sum_i K_i\nabla_i^2\right)\Psi - \left(\sum_A \sum_i \frac{Z_A e^2}{r_{Ai}}\right)\Psi + \left(\sum\sum_{A<B} \frac{Z_A Z_B}{r_{AB}}\right)\Psi + \left(\sum_{i<} \sum_j \frac{e^2}{r_{ij}}\right)\Psi = E\Psi$$

where $\sum_A$ indicates summation over all nuclei (as does $\sum_B$); $\sum_i$ indicates summation over all e^-'s (as does $\sum_j$); $K_i\nabla_i^2$ is the kinetic energy operator for a single electron i; Z_A is the charge on the nucleus A; r_{AB} is the distance between

A and B; and r_{ij} is the distance between electrons i and j; (r_{AB} is a constant).

Note that every operator on the left is a function of the co-ordinates of one electron except for the terms $\frac{e^2}{r_{ij}}$, since r_{ij} depends on the instantaneous positions of electron i and electron j. Because of the terms $\frac{e^2}{r_{ij}}$, Ψ cannot be assumes to have the form $f(x_1)g(y_1)\ldots k(z_n)$, where $x_1, y_1, \ldots z_n$ are as above(117). In no form do the operators have the desired commutation properties. This leads to the fact that the Schroedinger equation cannot be solved exactly for molecular systems(117). Thus to apply the Schroedinger equation to systems larger than the hydrogen atom (or analogous one electron structures) approximate methods of solution are needed(117).

<u>The Orbital Approximation</u>: If we put aside, for the moment, the nuclear repulsion terms in the equation for a molecular system, then the equation becomes one dealing with electron position and the energy of electrons due to kinetic energy, attractions by nuclei, and repulsions by other electrons: $\hat{H}_{EL}\Psi_{EL} = E_{EL}\Psi_{EL}$.

$$\text{where} \quad \hat{H}_{EL} = \sum_i K_i \nabla_i^2 - \sum_i \sum_A \frac{Z_A e^2}{r_{iA}} + \sum_{i<j} \sum \frac{e^2}{r_{ij}} \qquad (116).$$

Now $\hat{H}_{EL} \neq \hat{H}_1 + \hat{H}_2 + \ldots + \hat{H}_n$, where $\hat{H}_i$ is dependent only on the co-ordinates of electron 1,etc.. We can, however, assume such a form for $\hat{H}_{EL}$, which although not correct is nevertheless a reasonable physical approximation. That is, $\hat{H}'_{EL} = \hat{H}_1 + \hat{H}_2 + \ldots + \hat{H}_n$, if $\hat{H}_i$ is taken as:

$$\hat{H}_i = K_i \nabla_i^2 + \sum_j \left(\frac{e^2}{r_{ij}}\right)_{\substack{\text{AVERAGED OVER}\\ \text{THE POSITIONS OF } j}} - \sum_A Z_A e^2 / r_{Ai} \qquad (117)$$

$\hat{H}_i$ then only depends on the instantaneous position of electron i.

The Schroedinger equation with this approximation reduces to the set of equations $\hat{H}_i \psi_i = E_i \psi_i \quad i = 1, 2, 3, \ldots n$ (117), where $\psi'_{EL} = \psi_1 \psi_2 \psi_3 \ldots \psi_n$. Notice that $\sum_i E_i$ does not approximate the total electronic energy E_{EL}. This is due to the fact that the electron repulsion terms are counted twice in $\sum_i E_i$ (117)(i.e., once for electron i and once for electron j). To get an approximation for E_{EL},

$\frac{1}{2} \sum_i \sum_j \left(\frac{e^2}{r_{ij}}\right)_{\substack{\text{AVG.}\\ \text{OVER } j}} = \sum_{i<j} \sum \left(\frac{e^2}{r_{ij}}\right)_{\text{AVG. OVER } j}$ must be subtracted from $\sum_i E_i$. (117).

$$E_{EL} \cong \sum_i E_i - \sum \sum \left(\frac{e^2}{r_{ij}}\right)_{\text{AVG. OVER } j} .$$

Does ψ'_{EL} approximate the true wavefunction ψ_{EL}? One might think not since $\sum_i E_i \not\approx E_{EL}$ and ψ'_{EL} is the eigenfunction with eigenvalue $\sum_i E_i$, whereas ψ_{EL} is the eigenfunction with eigenvalue E_{EL} . Nevertheless consider $H'_{EL} \psi'_{EL} = \left(\sum_i E_i\right) \psi'_{EL}$. If each side is subtracted by $\left[\sum_{i<j} \sum \left(\frac{e^2}{r_{ij}}\right)_{\text{AVG. OVER } j}\right] \psi'_{EL}$, then one has

$$\left[H'_{EL} - \sum_{i<j} \sum \left(\frac{e^2}{r_{ij}}\right)_{\text{AVG. OVER } j}\right] \psi'_{EL} = \left[\sum_i E_i - \sum_{i<j} \sum e^2/r_{ij}\right] \psi'_{EL} .$$

Notice that the energy term on the right approximates E_{EL}(117). The operator on the left approximates H_{EL}(117). It is thus reasonable to assume that $\psi_{EL} \approx \psi'_{EL} = \psi_1 \psi_2 \psi_3 \ldots \psi_n$.

This method is termed the orbital approximation(117).

What is the physical nature of the approximation $\frac{e^2}{r_{ij}} \cong \left(\frac{e^2}{r_{ij}}\right)_{\text{AVG. OVER } j}$, and said approximation's consequences through its use in the Schroedinger equation?

Examine the set of equations $\hat{H}_i \psi_i = E_i \psi_i$; $i = 1, 2, \ldots n$, (which represents $\hat{H}_{EL} \psi_{EL} = E_{EL} \psi_{EL}$). Because each equation is dependent on one electron, the physical system must be one where each electron moves about independently of the motions of all other electrons(117). The only effect the other electrons have on electron i is to produce a constant (with time) electric field throughout which i moves. This [illegible] will tend to overestimate the actual electronic energy(117). The following will illustrate why.

Take electron i at position p different from $j_{avg.}$ position. The calculated energy from this situation is the weighted average energy of i at p for j at all its possible positions. Consider, though, j right at p. The weighted average energy includes the repulsion corresponding to this. In reality, i will tend to move away due to repulsion as j gets close, so that there are actually no energy contributions to i's energy for j sufficiently close to i(117). Thus the orbital approximation of $\psi'_{EL} = \psi_1 \psi_2 \ldots \psi_n$ overestimates the coulomb repulsion energy between electrons(117). The effect is the result of neglect of what is termed electron coulomb correlation(117).

The various one electron wavefunctions resulting from the orbital approximation are called orbital energies. By examining $\int \Psi^{*\prime} \Psi' d\tau$, it is evident that the probability density for a given electron, i, is given exclusively by $\psi_i^* \psi_i$ (117). Physically, one can describe electron i as "occupying" the orbital ψ_i.

Slater Determinants: Although Ψ' given above approximates solutions to the Schroedinger equation, the approximation can be made more physically correct. This is due to the fact that there are properties of quantum systems which are not specified by the Schroedinger equation, but [illegible], which are known to exist. One must therefore construct approximate solutions in such a way as to take at least partial account of these properties.

The most important property of the above kind is electron spin.

Electrons are known to have intrinsic angular momentum (which can be illustrated classically by a spinning ball) (117). This spin is quantized and may take two different values for the electron(117).

Spin can be represented by the eigenvalue equation: $\hat{S}_z \sigma = \pm \hbar/2 \ \sigma$, where σ is either α, the eigenfunction with eigenvalue $\hbar/2$, or β, the eigenfunction with eigenvalue $-\hbar/2$, and where σ depends on what are called the spin co-ordinates of the electron (α and β are orthonormal) (117).

In constructing the orbital approximation wave function one takes account of spin by multiplying each spatial orbital ψ_i by either α or β (117). One calls these new orbitals, spin orbitals(117).

This construct is not arbitrary. The one electron operator $\hat{S}_{zi}$ commutes with H_i(117). It follows that both operators have a common set of eigenfunctions. Since (a) $\hat{H}_i\psi_i = E_i\psi_i$, (b) $\hat{S}_{zi}\sigma_i = \pm\hbar/2\,\sigma_i$, (c) $\hat{H}_i$ does not operate on σ_i except in ways that result in product functions wherein the spatial co-ordinates form a function that is multiplied by a function of the spin co-ordinates, and (d) the same relation applies to $\hat{S}_{zi}$ and ψ_i ; then we can construct spin orbitals by multiplying $\hat{H}_i\psi_i = E_i\psi_i$ by σ_i and $\hat{S}_{zi}\sigma_i = \pm\frac{\hbar}{2}\sigma_i$ by ψ_i so that:

$$\hat{H}_i(\psi_i\sigma_i) = E_i(\psi_i\sigma_i) \quad \text{and} \quad \hat{S}_{zi}(\sigma_i\psi_i) = \pm\frac{\hbar}{2}(\sigma_i\psi_i) .$$

By inspection a common set of eigenfunctions is $\psi_i\sigma_i$.

With the approximations introduced above one has the following: $H'_{EL}\psi'_{EL} = E'_{EL}\psi'_{EL}$ where

$$\psi'_{EL} = \psi_1(1)\sigma_1(1)\psi_2(2)\sigma_2(2)\ \dots\ \psi_n(n)\sigma_n(n)$$

and where $\psi(1)$ indicates that ψ depends on the spatial co-ordinates of electron 1 (117), $\sigma(1)$ indicates that σ depends on the spin co-ordinates of electron 1, etc.(117), and where n equals the number of electrons in the system. This is still deficient in one respect, though.

Consider an interchange of electrons 1 and 2. Because electrons are indistinguishable particles, the physical states described by ψ'_{EL} and ψ''_{EL} below must be the same(116).

$$\psi'_{EL} = \psi_1(1)\psi_2(2)\ldots\psi_n(n)\sigma_1(1)\sigma_2(2)\cdots\sigma_n(n).$$

$$\psi''_{EL} = \psi_1(2)\psi_2(1)\ldots\psi_n(n)\sigma_1(2)\sigma_2(1)\ldots\sigma_n(n).$$

This condition corresponds to the following:

$$\psi'^{*}_{EL}\,\psi'_{EL} = \psi''^{*}_{EL}\,\psi''_{EL} \quad \text{or} \quad \psi'_{EL} = \psi''_{EL} \qquad (116).$$

It is a result of experiment that for the interchange of two electrons: $\psi'_{EL} = -\psi''_{EL}$ (117). This is called the antisymmetry principle(116).

Obviously the above construct does not obey the antisymmetry principle (i.e. $\psi'_{EL} \neq -\psi''_{EL}$). ψ'_{EL} must be further manipulated to correspond to known physical reality. This is done by equating ψ'_{EL} to the following (116):

$$\psi'(1,2,\ldots n) = N \begin{vmatrix} \psi_1(1)\sigma_1(1) & \psi_2(1)\sigma_2(1) & \cdot\;\cdot\;\cdot & \psi_n(1)\sigma_n(1) \\ \psi_1(2)\sigma_1(2) & \psi_2(2)\sigma_2(2) & \cdots & \\ \vdots & & & \\ \psi_1(n)\sigma_1(n) & \cdots & & \psi_n(n)\sigma_n(n) \end{vmatrix}$$

where n is the number of electrons in the system and where N is a normalization constant.

That the above is consistent with the antisymmetry principle is evident due to the fact that interchanging two electrons corresponds to interchanging two rows of the determinant(116). From linear algebra this results in reversing the sign of the determinant(116).

In practice, Ψ' is many times modified to make things simpler still. That is, in ground state, closed shell molecules (molecules with equal numbers of electrons having opposite spin) one uses one spatial function ψ_i for the spin orbitals of two electrons but differentiates the spin orbitals by multiplying ψ_i by α for one and by β for the other spin orbital(116). It is a property of Ψ' and the determinant which it equals, that a given spatial function ψ_i cannot be assigned to more than two electrons. If it were assigned to more than two then there would necessarily be two identical columns in Ψ' and the determinant would equal zero(116).

In the ground state:

$$\Psi' = N \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(1)\beta(1) & \psi_2(1)\alpha(1) & \cdots & \psi_n(1)\alpha(1) & \psi_n(1)\beta(n) \\ \psi_1(2)\alpha(2) & \psi_1(2)\beta(2) & \cdots & & & \\ \vdots & & & & & \\ \psi_1(n)\alpha(n) & \cdots & & & \psi_n(2n)\alpha(2n) & \psi_n(2n)\beta(2n) \end{vmatrix}$$

where 2n equals the number of electrons in the ground state, closed shell system(116).

By considering the form of Ψ' just given, which is called a Slater determinant(116), one can arrive at a conclusion that is useful in interpreting some of the results to be given below. Say, for example, one made ~~the~~ second column above the same as the first. Physically this corresponds to two electrons occupying the same spatial orbital <u>and</u> having [illegible]. If this is the [illegible] [illegible] cludes the el[illegible] [illegible] spin and to stay away from each other(117). This is a rough [illegible] the same spin. If this is the case, Ψ' equals zero. From this, one concludes that electrons of the same spin tend to stay away from each other(117). This a rough statement of the Pauli principle(117) and leads to a lowering of the electronic energy.

The Variation Method: There is another technique that must be outlined before specific molecular orbital methods are described. This is the variation method.

Slater determinants approximate the true electronic wavefunctions of molecular systems. However, how can one actually use these approximate wavefunctions to calculate the electronic structure of a molecule, if to do so one must know the operators $\hat{H}_i$? Knowing these operators implies that the average positions of the electrons are, in fact, known. They could be known if the electronic structure of the molecule were known, but this is what is being sought. The variation method provides a way out of this bind. It allows one to make a guess at Ψ'_{EL} and then to vary it in order to get a better approximation to the true electronic wavefunction, all while working within the Slater determinant framework.

At the basis of the variation method is the following theorem: Given Ψ', a function with the same boundary conditions as Ψ, the true ground state eigenfunction of $\hat{H}$, then $E_0 = \dfrac{\int \Psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau} \leq \dfrac{\int \Psi'^* \hat{H} \Psi' d\tau}{\int \Psi'^* \Psi' d\tau} = E$ (117).

Thus $E = f(\psi', \hat{H})$. E_0 is the minimum of $f(\psi', \hat{H})$. Because this is the case $\delta E = \delta f(\psi', \hat{H}) = 0$ if $E = E_0$, for any small change δf in f(116). This fact is very useful in that it allows one to determine just how close ψ' is to the true wavefunction ψ (116). Thus one need only take an initial guess at ψ', vary ψ' by way of parameters until it gives a minimum E, and then take the modified $\psi' \approx \psi$ (116).

The Hartree-Fock Method with use of LCAO (Linear combinations of atomic orbitals): Consider the expectation value for the energy of a system with Hamiltonian $\hat{H}$ and approximate eigenfunction ψ' equal to the Slater determinant. Also, for this system consider only the closed shell, ground state. $E = \iint \psi' \hat{H} \psi' d\tau d\sigma \big/ \iint \psi'^2 d\tau d\sigma$, where ψ' is real(117).

(At this point an additional approximation will be made. Since non-valence electrons contribute nothing (to a good approximation) to bonding and the chemical nature of a molecule(117), these electrons will treated along with the nucleus as essentially a point with an effective charge determined by the number of protons, the number of non-valence electrons, and the relative effects of each of these on charged species outside the non-valence shells(117). This simplification is termed the core approximation.

The core approximation does not significantly affect calculated heats of formation or other reaction energetics because the core persists in reactants and products with little or no change(117). Moreover, the core approximation does not affect the minimization of molecular energy much due to the fact that core electrons, being relatively close to nuclei, are not able to be moved away without the input of energy. Thus regardless of the molecular environment (which changes in the course of energy minimization), core electrons can reasonably be taken as always existing as part of the core (117).)

With the ground state and core assumptions the Slater determinant becomes:

$$\psi'_{EL} = N \begin{vmatrix} \psi_1(1)\alpha(1) & \psi_1(1)\beta(1) & \psi_2(1)\alpha(1) & \cdots & \psi_n(1)\beta(1) \\ \psi_1(2)\alpha(2) & & & & \vdots \\ \vdots & & & & \vdots \\ \psi_1(2n)\alpha(2n) & & \cdots & & \psi_n(2n)\beta(2n) \end{vmatrix}$$

where 2n is now the number of valence electrons.

Now call $\hat{H} = \hat{H}_i + \sum_{i<j}\sum e^2/r_{ij}$, where $\hat{H}_i = k_i \nabla_i^2 - \sum_A Z_A e^2/r_{Ai}$ (117) so that $\hat{H} = \hat{H}_{EL}$ = the operator for the total electron energy of the system.

Thus $$E = \frac{\left(\iint \psi' \sum_i \hat{H}_i \psi' d\tau\, d\sigma + \iint \psi' \left(\sum_{i<j}\sum e^2/r_{ij}\right)\psi' d\tau\, d\sigma\right)}{\iint \psi'\psi' d\tau\, d\sigma} \approx E_{EL}.$$

By expanding the determinant ψ' and by requiring the orthonormality of the ψ_i's and σ_i's the following expression for E is obtained: $E = 2\sum_i H_{ii} + \sum_i\sum_j 2J_{ij} - 2\overset{\uparrow}{\sum_i}\overset{\uparrow}{\sum_j} K_{ij}$ (117).

$$E = 2\sum_i H_{ii} + \sum_i\sum_j \left(2J_{ij} - K_{ij}\right) \quad (117).$$

$\overset{11}{\Sigma}$ implies summation only over spin orbitals with the same spin eigenfunction and:

$$H_{ii} = \int \psi_i(m)\hat{H}_i\psi_i(m)\,d\tau_m \equiv \text{core integral (117),}$$

$$J_{ij} = \iint \psi_i(m)\psi_i(m)\left(e^2/r_{mn}\right)\psi_j(n)\psi_j(n)\,d\tau_m d\tau_n \equiv \text{coulomb integral,}^{(117)}$$

$$K_{ij} = \iint \psi_i(m)\psi_j(m)\left(e^2/r_{mn}\right)\psi_i(n)\psi_j(n)\,d\tau_m d\tau_n \equiv \text{exchange integral.}^{(117)}$$

To apply the variation method to this expression for E, it is possible to use the ψ_i's themselves as parameters(116). This is called the Hartree-Fock method and it yields a set of differential equations, one equation for each electron.(116) A comparatively easier method to use, and one that is used predominantly in practice, involves parametrizing the ψ_i's by representing them as linear combinations of atomic orbitals φ_μ's. Thus $\psi_i = \sum_\mu a_{\mu i}\varphi_\mu$, where the $a_{\mu i}$ are constants(116).

A natural question at this point is "How many atomic orbitals does one use?". A common method, and the one used in MINDO/3, is to include all valence atomic orbitals on the atoms involved in the molecule(116). More orbitals, although yielding somewhat greater accuracy, results in substantially more computation time. Less than a valence set would lead to spurious results since valence atomic orbitals seem to be the most important atomic orbitals involved in bonding and chemical reactivity.

Another aspect of the LCAO approximation which we must consider deals with the form of the atomic orbitals to be [illegible] used. For most atoms these orbitals cannot be known exactly in functional form(117). The orbitals used in LCAO make use of the core approximation and hydrogen-like or approximately hydrogen-like orbital functions(117). Essentially, the core of a given atom is given an effective charge determined by the variation method(117). This charge in turn is plugged in where applicable to functions of the s,p,d hydrogen type or into functions that approximate this form(117). The latter type functions are most often used and are called Slater-Zener orbitals(117). To apply the variation method to the LCAO form of the following is done:

(a) $\sum_{\mu} a_{\mu i} \varphi_{\mu}$ is substituted for ψ_i in either the expressions for orbital energies or the total energy E_{EL}.

(b) The E_i's (and thus EEL) or E_{EL} are minimized by applying the conditions $\partial E_i / \partial a_{\mu i} = 0$ for all μ and i (117), or $\partial E'_{EL} / \partial a_{\mu i} = 0$ for all μ, i (117).

Step (b) is equivalent to requiring the following to be true: $\sum_{\nu} \left(F_{\mu\nu} - E_i S_{\mu\nu}\right) a_{\nu i} = 0$ for $\mu = 1,2,3,\ldots n$ (Equation #I),

where n is the number of atomic orbitals being used and

where $F_{\mu\nu} = H_{\mu\nu} + \sum_i \sum_{\lambda\sigma} 2a_{\lambda i} a_{\sigma i} \left[(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\nu\sigma)\right]$

or $F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma} \left[(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\nu\sigma)\right]$ (116)

Also $H_{\mu\nu} \equiv \int \varphi_\mu(i) \hat{H}_i \varphi_\nu(i)\, d\tau_i = \int \varphi_\mu(i) \left[K_i \nabla_i^2 + \sum_A \frac{Z_A e^2}{r_{Ai}}\right] \varphi_\nu(i)\, d\tau_i \equiv$ a core integral with respect to atomic orbitals(116);

$(\mu\nu|\lambda\sigma) \equiv \iint \varphi_\mu(i) \varphi_\nu(i) \frac{e^2}{r_{ij}} \varphi_\lambda(j) \varphi_\sigma(j)\, d\tau_i\, d\tau_j$ $\equiv$ either a coulomb or exchange integral with respect to atomic orbitals. (116)

$P_{\lambda\sigma} \equiv 2 \sum_i a_{\lambda i} a_{\sigma i}$. $S_{\mu\nu} \equiv \int \varphi_\mu(i) \varphi_\nu(i)\, d\tau_i \equiv$ overlap integral.

For the solutions to equation #I (i.e., the $a_{\nu i}$) to be non-trivial, linear algebra tells us that

$$\begin{vmatrix} F_{11} - E_i S_{11} & F_{12} - E_i S_{12} & \dots & F_{1n} - E_i S_{1n} \\ F_{21} - E_i S_{21} & & \cdot & \\ \vdots & & \cdot & \\ & & \cdot & \\ F_{n1} - E_i S_{n1} & \dots & & F_{nn} - E_i S_{nn} \end{vmatrix} = 0 \qquad \text{(Equation \#II)},$$

where n equals the total number of atomic orbitals in the basis set.

Equation #II is designated as $|F_{\mu\nu} - E_i S_{\mu\nu}| = 0$ (117).

Equation is n linear homogeneous equations in n unknowns (i.e., the $a_{\nu i}$'s). There are in turn analogous sets of equations for every molecular orbital ψ_i. These equations are a necessary condition for the total E_{EL} to be a minimum.

Notice that it is implied that $F_{\mu\nu} - E_i S_{\mu\nu}$ is known in the equations represented by equation #I, for the only unknowns are the $a_{\nu i}$. But one must know the molecular orbital ψ_i in order to find E_i. Thus one has to solve equation #I to find the ψ_i's, yet one needs the ψ_i's to be able to solve equation#I. Similary, notice that one needs to know the values for the co-efficients $a_{\nu i}$ to know $F_{\mu\nu}$, and $F_{\mu\nu}$ must be known to be able to find the $a_{\nu i}$.

To deal with this problem, one begins with a guess of the [illegible] of the 's (which equal [illegible] ; (117). Using th the forms of the ψ_i's (which equal $\sum_{\mu} a_{\mu i}\varphi_{\mu}$) (117). Using these ψ_i's, one can generate the $F_{\mu\nu}$ terms and the $S_{\mu\nu}$ terms. The E_i's are found by making use of equation #II (117). This equation is one of degree n in E_i, and thus n values of E_i will fit the equation(117). One takes these roots as the energies E_i of the molecular orbitals, ψ_i's(117). The first n lowest energies in a 2n electron system are assigned to the occupied molecular orbitals.

Now the co- efficients in equation #I are known and the different sets can be solved to give new $a_{\nu i}$'s. The new $a_{\nu i}$'s can then be used to generate new $F_{\mu\nu}$'s (which taken together are called the Fock or F matrix), $S_{\mu\nu}$'s and E_i's (117). The prcedure keeps going until, ideally, no change occurs in the values above(117). This is called the self- consistent field or S.C.F. method(117). The energy convergence point is called the Hartree-Fock energy limit. This energy value is the nearest to the true physical value that can be found using the orbital approximation (if an unlimited basis set is used).(116) It is, in general, greater than the true energy, though, due to the neglect of electron coulomb correlation(117).

Some Physical Interpretations: It is useful at this point to examine some of the quantities that appear in the equations #I and II, and to give to them a physical interpretation.

(1) $P_{\lambda\sigma} = 2\sum_{i} a_{\lambda i}\, a_{\sigma i}$ and $S_{\lambda\sigma} = \int \varphi_{\lambda}(i)\,\varphi_{\sigma}(i)\,d\tau_i$

The total number of electrons in a closed shell system equals

2n.

$$2n = 2\sum_i \int \psi_i \psi_i \, d\tau_i = 2\sum_i \int \left(\sum_\sigma a_{\sigma i}\varphi_\sigma\right)\left(\sum_\lambda a_{\lambda i}\varphi_\lambda\right) d\tau_i \quad (117).$$

$$2n = 2\sum_i \sum_{\lambda\sigma} a_{\lambda i} a_{\sigma i} \int \varphi_\lambda \varphi_\sigma \, d\tau_i = \sum_{\lambda\sigma} P_{\lambda\sigma} \int \varphi_\sigma \varphi_\lambda \, d\tau_i = \sum_{\lambda\sigma} P_{\lambda\sigma} S_{\lambda\sigma} \quad (116).$$

$\sum_{\lambda\sigma} P_{\lambda\sigma} S_{\lambda\sigma}$ = total electron population.

$S_{\lambda\sigma}$ is basically a property of the individual atomic orbitals involved. Since the $P_{\lambda\sigma}$'s are constants charateristic of the molecule, the $S_{\lambda\sigma}$ values must be numbers that are in "units of electrons". Thus $S_{\lambda\sigma}$ can be thought of (in a probabilistic sense) as a charge cloud which results from the overlap of φ_λ with φ_σ (116). The quantity $P_{\lambda\sigma}$ then, measures the amount of total electronic charge in a molecule that resides in a given charge cloud, $S_{\lambda\sigma}$ (117).

(2) $H_{\mu\nu}$ $\equiv$ core integral

$$E_T^C = \sum_i \int \psi_i H_i \psi_i \, d\tau_i = \sum_i \sum_{\mu\nu} a_{\mu i} a_{\nu i} H_{\mu\nu} = \sum_{\mu\nu} P_{\mu\nu} H_{\mu\nu} \quad (117);$$

where E_T^C is the core energy of all the electrons in the molecule. Using again the charge cloud idea, it appears that since $H_{\mu\nu}$ is an energy term, it represents the energy due to all the cores of the molecule in their interaction with the charge cloud residing in the φ_μ , φ_ν overlap(117). $P_{\mu\nu}$ is a measure of $H_{\mu\nu}$'s contribution to a given molecule's energy.(117)

(3) $J_{\mu\nu\sigma\lambda} \equiv (\mu\nu \mid \sigma\lambda)$ $\equiv$ coulomb integral.

Say one takes a small amount of charge in the charge cloud residing in the overlap of φ_μ and φ_ν . This small amount can be represented: $dq_i = e\left(\varphi_\mu(i)\varphi_\nu(i)\,d\tau_i\right)$ (117). Now consider a similar amount in the overlap of φ_σ and φ_λ

which is a distance r_{ij} from the first. The energy of repulsion resulting from these two bits of charge can be represented as:

$$dJ = \varphi_\mu(i)\,\varphi_\nu(i)\,{}^{e^2}\!/_{r_{ij}}\,\varphi_\sigma(j)\,\varphi_\lambda(j)\,d\tau_i\,d\tau_j \qquad (117)$$

If one wishes to find the total repulsion energy between the two clouds then one need only integrate dJ over $d\tau_i$ and $d\tau_j$:

$$J = \iint \varphi_\mu(i)\varphi_\nu(i)\,{}^{e^2}\!/_{r_{ij}}\,\varphi_\sigma(j)\varphi_\lambda(j)\,d\tau_i\,d\tau_j \qquad (117)$$

This is precisely the form of the coulomb integral $(\mu\nu|\lambda\sigma)$. Thus these integrals represent the energy of repulsion between two charge clouds, residing in the overlap of φ_σ and φ_λ, and in the overlap of φ_σ and φ_λ (117). Moreover, since the charge cloud is only a "cloud" when viewed through time, the integral $(\mu\nu|\lambda\sigma)$ represents some form of time averaged repulsion energy.

(4) $K_{\mu\nu\lambda\sigma}$ $\equiv$ exchange integral

It might be wondered why an integral that looks like a repulsion integral $(\mu\nu|\lambda\sigma)$ should serve to produce the opposite effect on the total energy by virtue of its sign. A clue may be had by considering the total energy in the non-LCAO Hartree-Fock method. Here the K_{ij} term results from a sum only over spin orbitals with the same spin eigenfunction(117). Moreover, it is a fact that in the Hartree Method, where electron spin and the antisymmetry principle are not accounted for, the exchange terms do not appear at all(117).

It appears that the K integrals represent terms in the total energy which are directly a result of introducing spin [illegible] or [illegible]

(117)
and the antisymmetry principle into the orbital approximation. This makes sense physically because the Pauli principle a result of the antisymmetry principle) states, in a rather simplified form that electrons of parallel spin tend to stay away from each other(117). Thus the energy of repulsion between electrons of parallel spin will be less than that of electrons of antiparallel spins(117). The exchange integrals reflect this fact in the expression for the total electronic energy(117). This is called exchange correlation(117). Exchange correlation is not ignored in methods using Slater determinants(117).

SEMI-EMPIRICAL METHODS

Although the Hartree-Fock method with LCAO represents a reasonably accurate solution to the Schroedinger equation for atomic and molecular systems, there are reasons that in practice the method is not well suited to many such systems.

First, computation time must be considered. The method involves the evaluation of a tremendous number of integrals. Even by computer, molecules of a relatively few number of atoms are not feasibly treated (117). Moreover, the Hartree--Fock limit is often not a sufficiently accurate representation to allow reliable predictions of molecular properties to be made based on the results of such calculations(especially in systems where coulomb correlation is important(117).

To try to remedy these faults, Pople, Dewar, and others have developed treatments within the Hartree-Fock with LCAO framework which are empirical in that they assign parametric values to some or all of the integrals in the Fock matrix based on: (a) agreement with experiment of the calculated results, and (b) the physical significance of the various integrals(116). The methods are labelled semi-empirical(116). In them, calculation time is reduced by eliminating the need to evaluate a large number of integrals. Moreover, it is hoped that by parametrization greater accuracy can be achieved(117).

The Zero-Differential Overlap Approximation(ZDO): At the basis of semi-empirical SCF-MO methods is the zero-differential overlap approximation(116). This involves taking the following to be true: $(\mu\nu|\lambda\sigma) = \delta_{\mu\nu}\delta_{\lambda\sigma}$ (where the δ's are Kronecker delta) (116). Before attempting to justify this, consider the elements of the Fock matrix ($F_{\mu\nu}$):

Without approximation $F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda\sigma} P_{\lambda\sigma}\left[(\mu\nu|\lambda\sigma) - \frac{(\mu\lambda|\nu\sigma)}{2}\right]$

With approximation $H_{\mu\nu}$ is, in general, not affected, for reasons to be given later(116). $J_{\mu\nu\sigma\lambda} = (\mu\nu|\sigma\lambda) = \delta_{\mu\nu}\delta_{\lambda\sigma}$(116). Thus, the integral survives for $\mu = \nu$ and $\lambda = \sigma$. Similary the exchange integrals: $(\mu\lambda|\nu\sigma)$ equal $\delta_{\mu\lambda}\delta_{\nu\sigma}$ (116). Thus, $F_{\mu\nu}$ becomes with ZDO(116):

$$F_{\mu\mu} = H_{\mu\mu} + \sum_{\lambda} P_{\lambda\lambda}(\mu\mu|\lambda\lambda) - \frac{1}{2} P_{\mu\mu}(\mu\mu|\mu\mu)$$

$$F_{\mu\nu} = H_{\mu\nu} - \frac{1}{2} P_{\mu\nu}(\mu\mu|\nu\nu) \quad \text{for } \mu \neq \nu .$$

Moreover, since $S_{\mu\nu} = \int \varphi_\mu(i)\varphi_\nu(i)\,d\tau_i$. $S_{\mu\nu}$ is also taken as zero for $\mu\neq\nu$ in the Fock matrix(116).

The variation equations become or

$\sum_{\nu}(F_{\mu\nu}-E_i\delta_{\mu\nu})a_{\nu i}=0$ (116), and $|F_{\mu\nu}-E_i\delta_{\mu\nu}|$ (116).

How can such an approximation with such drastic consequences be justified?

It may be argued that the integrals which are eliminated are known to be close to zero(116). However, the large number of these integrals could counteract their small values taken singly and make their collective contribution a large one indeed(116).

A better defense of the method is that neglect of the energy integrals (coulomb and repulsion integrals) will result in a change in $\int\psi'\hat{H}\psi'd\tau$. However, neglect of $S_{\mu\nu}$ integrals ($\mu\neq\nu$) will change the normalization constant $1/\int\psi'\psi'd\tau$. The total energy $E = \int\psi'\hat{H}\psi'd\tau / \int\psi'\psi'd\tau$ will not change as much as one would expect by applying ZDO because the numeraton changes roughly in proportion to the denominator(117). Moreover, it can be shown that for some φ_μ and φ_ν , neglecting $H_{\mu\nu}$ will not give this same sort of cancelling effect(117). In the ZDO treatment $H_{\mu\nu}$ is replaced by a parameter (designated $\beta_{\mu\nu}$) which is varied to give the best agreement with experiment(117). This parameter is not meant to be equated with $H_{\mu\nu}$. Instead $\beta_{\mu\nu}$ represents a necessary correction to be introduced in place of $H_{\mu\nu}$ in the situation where the normalization constant $1/\int\psi'\psi'd\tau$ is affected by neglect of the $S_{\mu\nu}$ (117).

Most semi-empirical SCF-MO theories differ basically in the degree to which the ZDO overlap approximation is applied(116). Three such methods, the last being MINDO/3, will be considered here.

CNDO/1 - Complete Neglect Of Differential Overlap: In CNDO/1, the ZDO approximation is applied tp every integral to which it is applicable(116). The following Fock matrix is thus applicable:

$$F_{\mu\mu} = H_{\mu\mu} - \tfrac{1}{2} P_{\mu\mu}(\mu\mu|\mu\mu) + \sum_{\lambda} P_{\lambda\lambda}(\mu\mu|\lambda\lambda) \quad (116)$$

$$F_{\mu\nu} = H_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu}(\mu\mu|\nu\nu) \text{ for } \mu \neq \nu \quad (116).$$

There are difficulties encountered here, however. To be specific, any method used, if it is to give meaningful results, must not give answers that depend on specific choices of the co-ordinate system. While a total Hartree-Fock with LCAO treatment does not cause difficulties in this regard,(118) introducing the ZDO approximation does(118).

Murrell and Harget give the following development(118): Consider the integral $(p_A^2|s_B^2)$ where p_A is a p atomic orbital on atom A and s_B is an s orbital on atom B, and where p_A has the xy plane as a symmetry element. In CNDO/1 $(p_A^2|s_B^2)$ equals zero. If we now rotate the co-ordinate axes about the z axis by the angle θ then $p_A = (\cos\theta)p_{xA} + (\sin\theta)p_{yA}$, $S_B = S_B$.

$$(s_B^2|p_A^2) = (\cos^2\theta\, p_{xA}^2|S_B^2) + (\sin^2\theta\, p_{yA}^2|S_B^2) + 2\cos\theta\sin\theta(p_{xA}p_{yA}|S_B^2)$$

In CNDO/1 the integral $(p_{xA}p_{yA}|S_B^2)$ equals zero because in general, $p_{xA} \neq p_{yA}$. Thus, $(p_A^2 \,|\, s_B^2)$ equals $\cos^2\theta(p_{xA}^2 \,|\, s_B^2)$ + $\sin^2\theta(p_{yA}^2 \,|\, s_B^2)$. This can only be true if $(p_A^2 \,|\, s_B^2)$ equals $(p_{xA}^2 \,|\, s_B^2)$ equals $(p_{yA}^2 \,|\, s_B^2)$.

To meet invariance conditions of the above kind, CNDO/1 essentially makes all valence orbitals on a given atom equivalent so that the integral $(\varphi_{\mu A}\varphi_{\mu A}|\varphi_{\nu B}\varphi_{\nu B})$ (where $\varphi_{\mu A}$ is on atom A and $\varphi_{\nu B}$ on atom B) equals a value γ_{AB} which is dependent only on the nature of atoms A and B and the distance between them(116).

Now consider the integrals $H_{\mu\mu}$ and $H_{\mu\nu}$ in the Fock matrix. The operator $K_i \nabla_i^2 + \sum_A \frac{Z_A e^2}{r_{iA}}$ which is contained in these integrals represents the operator for the kinetic energy of electron i and the potential of electron i due to the attractive forces of all the cores in the molecule(116). There are three cases to be considered(116):

(a) $H_{\mu\mu}$

Given orbital φ_μ on atom A, then the integral can be divided into terms involving only A and terms involving φ_μ and other atoms. $H_{\mu\mu} = U_{\mu\mu} - \sum_{B \neq A} (\mu|V_B|\mu)$ (116), where $U_{\mu\mu}$ represents the sum of the kinectic energy of electron i plus its potential due to the core of A, and V_B is the operator representing the potential of electron i due to its interaction with the core of atom B(116). To give $H_{\mu\mu}$ rotational invariance it can be shown that $(\mu|V_B|\mu)$ cannot depend on the form of the orbital φ_μ on A(116). Thus $(\mu|V_B|\mu) = V_{AB}$ in CNDO/1 where V_{AB} is dependent only on the natures of atom A and B and their distance.(116).

(b) $H_{\mu\nu}$ where φ_μ and φ_ν are both on A.

$H_{\mu\nu} = U_{\mu\nu} - \sum_{B \neq A} (\mu|V_B|\nu)$ (116). CNDO/1 sets $U_{\mu\nu}$ equal to zero by assuming the basis orbitals φ_μ and φ_ν have the symmetry of hydrogen-like atomic orbitals(116). The term $(\mu|V_B|\nu)$ for μ, ν on A is taken as zero to be consistent with theZDO treatment of the coulomb and exchange integrals.(116)

(c) $H_{\mu\nu}$ where φ_μ is on A and φ_ν is on B

This term is the term which Dewar has shown cannot be neglected and which must be replaced by $\beta_{\mu\nu}$ (117). $\beta_{\mu\nu}$ must meet two requirements. First, it must be of a form whereby its value decreases as the atoms A and B get farther away, for this is a property of $H_{\mu\nu}$. To deal with this, $\beta_{\mu\nu}$ is set equal to $\beta^0_{\mu\nu} S_{\mu\nu}$ where $\beta^0_{\mu\nu}$ is a constant(116). (Note that $S_{\mu\nu}$ <u>here</u> is not taken to be zero.) Second, $\beta_{\mu\nu} = \beta^0_{\mu\nu} S_{\mu\nu}$ must be invariant to rotations of the co-ordinate axes. To make this so, the constant $\beta^0_{\mu\nu}$ must be dependent only upon the characters of the atoms A and B(116). In CNDO/1 $\beta_{\mu\nu} = \beta^0_{\mu\nu} S_{\mu\nu}$ and $\beta_{\mu\nu}$ is termed a core resonance integral(117).

At this point every term in the Fock matrix has been subjected to the necessary ZDO approximations and to some sort of correction to meet invariance conditions.

The final form of the matrix for CNDO/1 is the following:

$$F_{\mu\mu} = U_{\mu\mu} + (P_{AA} - \tfrac{1}{2} P_{\mu\mu})\gamma_{AA} + \sum_{B \neq A} (P_{BB}\gamma_{AB} - V_{AB}) \quad (116)$$

$$F_{\mu\nu} = \beta^0_{AB} S_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu}\gamma_{AB}, \quad \mu \neq \nu \quad (116)$$

where $P_{AA} = \sum_\lambda P_{\lambda\lambda}$ for all λ on A ($P_{AA} = \sum_\lambda^A P_{\lambda\lambda}$)(116). Note that when B equals A, $F_{\mu\nu} = -\tfrac{1}{2} P_{\mu\nu}\gamma_{AA}$, for $S_{\mu\nu}$ is taken as zero(116).

In practice the elements of the Fock matrix for the CNDO/1 meth is then taken as zero(116).

In practice the elements of the Fock matrix for the CNDO/1 method are assigned functional forms approximately consistent with physical reality(116). All or part of them are then treated as parameters and are varied to give best fit with experiment(116).

The functional forms for CNDO/1 (and INDO) will not be dealt with here. Only those for MINDO/3 will be sketched.

INDO - Intermediate Neglect of Differential Overlap:

In CNDO/1 exchange integrals of the form $(\mu\nu|\mu\nu)$ are neglected. This approximation in many systems introduces considerable error, especially for φ_μ and φ_ν on the same atom(116). To illustrate, consider φ_μ and φ_ν. The exchange integral involving these two orbitals can be thought of as an energy lowering term due to the fact that the two electrons represented in the integral have parallel spins and thus tend to stay away from each other(116). Moreover, as φ_μ and φ_ν become closer there is more overlap in general. The amount of charge represented by the charge cloud residing in the overlap increases. The exchange effect therefore becomes greater in magnitude because the two electrons represented in $(\mu\nu|\mu\nu)$ have a greater chance of being near each other and thus of experiencing the effect(117).

To take this into consideration INDO counts some integrals that have differential overlap. These integrals are the exchange integrals $(\mu\nu|\mu\nu)$ where φ_μ and φ_ν are on the same atom(11[illegible]).

same atom(116). With this the Fock matrix os as follows(118):

$$F_{\mu\mu} = U_{\mu\mu} + \sum_{\nu} P_{\nu\nu}\left[(\mu^2|\nu^2) - \tfrac{1}{2}(\mu\nu|\mu\nu)\right] + \sum_{B}(P_{BB}\gamma_{AB} - V_{AB})$$

$F^{A}_{\mu\nu} = \tfrac{1}{2} P_{\mu\nu}\left[3(\mu\nu|\mu\nu) - (\mu\mu|\nu\nu)\right]$; where $F^{A}_{\mu\nu}$ implies μ, ν on A.

$F_{\mu\nu} = \beta_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu}\gamma_{AB}$; μ on A, ν on B.

Since any terms of the form $(\mu\nu|\lambda\sigma)$ above involve only atomic orbitals on the same atom, they will necessarily be invariant to rotation of the co-ordinate axes.

<u>MINDO/3 - Modified INDO</u>: MINDO includes the same types of integrals as INDO does in the Fock matrix. That is to say the ZDO approximation is applied to the same degree in both.(119) The difference between the two methods is the way in which the evaluation of the Fock matrix integrals are handled.

Before looking at the forms of the functions used to calculate the Fock matrix, consider some simplifications that may be made (these are directly results of ZDO).

Because the molecular orbitals are normalized:

$$\int \psi_i \psi_i \, d\tau = 1 = \int \sum_{\mu\nu} a_{\mu i} a_{\nu i} \varphi_\mu \varphi_\nu \, d\tau = \sum_{\mu\nu} a_{\mu i} a_{\nu i} \int \varphi_\mu \varphi_\nu \, d\tau .$$

If the φ's are normalized (which is required of the basis set) and differential overlap is neglected, then:

$$\int \psi_i \psi_i \, d\tau = \sum_{\mu} a_{\mu i}^2 \int \varphi_\mu^2 \, d\tau = \sum_{\mu} a_{\mu i}^2 = 1$$

Summing over all molecular orbitals $2\sum_{i}\int \psi_i^2 \, d\tau = 2n = \sum_{\mu} P_{\mu\mu}$. $\sum_{\mu} P_{\mu\mu}$ equals the number of electrons in the system(117). Because of ZDO, $P_{\mu\mu}$ represents that contribution to the total electron population that can be represented as an electron "cloud" residing in the atomic orbital φ_μ(117).

$P_{\mu\mu}$ is defined as the charge density of φ_μ and is given the symbol q_μ (117).

An alternate term for $P_{\mu\nu}$ for $\mu \neq \nu$ is the bond order of φ_μ and φ_ν (117).

Now consider the term V_{AB}, which represents the interaction of an electron in an atomic orbital of atom A with the core of B. If we designate as $(\mu\mu, B)$ the energy of interaction between an electron in φ_μ (on A) with the neutral atom B then $(\mu\mu, B) = V_{AB} + \sum_\nu^B c_\nu (\mu\mu|\nu\nu)$ (117), where $\sum_\nu^B c_\nu$ plus the charge of core B equals zero. c_ν thus represents the electron population of φ_ν (on B)(117).

Now since $(\mu\mu, B)$ represents the energy of interaction between a neutral species (i.e.,B) and a charged species, one might expect it to be small in value and perhaps zero, depending upon the charge distribution within B. In practice $(\mu\mu, B)$ is small and these values are neglected(117).

With neglect of $(\mu\mu, B)$ (which are termed penetration integrals) $V_{AB} = -\sum_\nu c_\nu (\mu\mu|\nu\nu) = -Z_B \gamma_{AB}$ (117), where Z_B is the charge on the core of B (117) and where $(\mu\mu|\nu\nu) = \gamma_{AB}$, as do all other integrals of this form in MINDO/3, INDO, and CNDO/1.

The Fock matrix for MINDO/3 reads:

$$F_{\mu\mu} = U_{\mu\mu} + \sum_\nu^A q_\nu \left[(\mu^2|\nu^2) - \tfrac{1}{2}(\mu\nu|\mu\nu) \right] + \sum_B (P_{BB} - Z_B)\gamma_{AB}$$

$$F_{\mu\nu}^A = \tfrac{1}{2} P_{\mu\nu} \left[3(\mu\nu|\mu\nu) - (\mu\mu|\nu\nu) \right]$$

$$F_{\mu\nu} = \beta_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu} \gamma_{AB} \qquad \mu \text{ on } A,\ \nu \text{ on } B.$$

Now consider the functional forms of the integrals in the Fock matrix:

(a) One center core integrals, $U_{\mu\mu}$; one center coulomb and exchange integrals, $(\mu\mu|\nu\nu)$ and $(\mu\nu|\mu\nu)$, where μ, ν are on A:

All these integrals represent valence state atomic values since they deal only with one center, and they are valence orbitals. The values of the integrals can thus be determined by best-fitting to spectroscopic data dealing with the valence of the particular atom in question(120). This is what is done in MINDO/3(120). The actual forms used for the integrals will not be given here as without development they are meaningless, and space does not permit development.

(b) Two center repulsion and exchange integrals between an atomic orbital on atom A and one on atom B:

In MINDO/3: $$\gamma_{AB} = e^2\left[R_{AB}^2 + .25\left(\frac{e^2}{g_A} + \frac{e^2}{g_B}\right)\right]^{-\frac{1}{2}} \qquad (119),$$

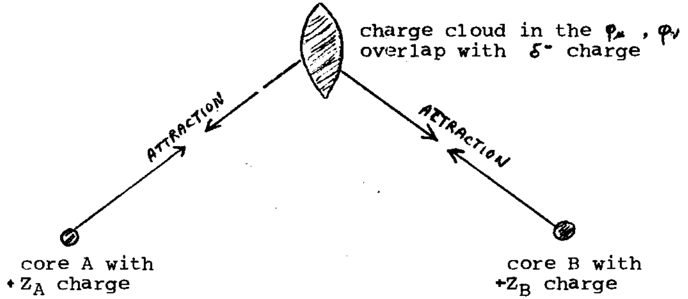
where R_{AB} is the internuclear distance between A and B, g_A is the average repuosion energy of an electron on atom A with another electron on A, and g_B has an analogous definition.

One might ask why this is the form that is used. First, since one electron is on A and another on B, one might expect that as A and B get very far apart the motions of the electron on A about its atom and those of the electron on B about its atom would not affect the distance between the two much. In this case, this distance can be taken as the average distance between the two (i.e., R_{AB}). The repulsion energy is then $\lim_{R_{AB}\to\infty} \gamma_{AB}$ with γ_{AB} given as above. It equals e^2/R_{AB}. The function has the desired behavior.

Second, this function has worked well in other quantum chemical treatments(119).

(c) Core resonce integrals, $\beta_{\mu\nu}$, for φ_μ on A, φ_ν on B..

The $\beta_{\mu\nu}$ terms can be thought of roughly as representing the energy of the following situation:



Because of electrostatic attraction, A is drawn toward the charge cloud as is B. As a result A and B are drawn toward each other. $\beta_{\mu\nu}$ measures the energy of the interaction. It is a measure of the bonding energy between A and B(119).

With this in mind consider the form of $\beta_{\mu\nu}$ used in MINDO/3: $\beta_{\mu\nu} = S_{\mu\nu}(I_\mu + I_\nu) f_2(R_{AB})$ (119), where I_μ and I_ν

are the atomic valence state ionization potentials corresponding to electrons in atomic orbitals φ_μ and φ_ν respectively, and where $f_2(R_{AB})$ is a parameter(119).

Is this reasonably physically?

As outlined above $S_{\mu\nu}$ can be thought of as representing a cloud of a given amount of electronic charge. The larger $S_{\mu\nu}$, the larger the wlwctron "population" in the cloud. Since the energy of attraction represented in the picture above is proportional to the charge of the cloud,then it is reasonable to set $\beta_{\mu\nu} \propto S_{\mu\nu}$ (117).

Also, notice the electron cloud is in the field of two cores. Moreover, it is in part of the atomic orbital φ_ν and part of φ_μ . To take the charge cloud away from the atomic orbitals and make the cloud essentially "free" of attraction from the cores is analogous to ionizing atom A by emtying φ_ν and ionizing atom B by emtying φ_μ. Thus $\beta_{\mu\nu}$, which measures the energy of stabilization to be had by placing the charge cloud in the φ_μ , φ_ν overlap os approximately proportional to the ionization potential of the valence state of A and that of B(117).

Finally, because it is an electrostatic attraction that results in $\beta_{\mu\nu}$, $\beta_{\mu\nu}$ should be a function of the distance between the cloud and core A and the cloud and core B. This distance is in turn related to the internuclear distance R_{AB}. Thus, $\beta_{\mu\nu} \propto f_2(R_{AB})$.

(d) Core-core repulsion:

The total energy of a molecule is not given by the electronic energy alone. The cores within molecules also contribute to the energy both kinetically and potentially. In many attempts (such as MINDO/3) to solve the Schroedinger equation for a molecular system, the core kinetic energy is ignored because including it would complicate things considerably (this neglection and its consequences are dealt with below).

The potential terms are dealt with though, so that

$$E_{TOT} = E_{EL} + E_{\substack{CORE-CORE \\ REPULSIONS}} = E_{EL} + E_{C-C} \qquad (119).$$

In most treatments, the cores of atoms in a molecule are treated as point charges and the corresponding electrostatic potential function is used(119) MINDO/3 cannot do this because other approximations must be compensated for(119).

Recall that $V_{AB} \cong -Z_B \gamma_{AB}$ if penetration integrals are neglected. In reality V_{AB} is closer to $(\mu\mu, B) - Z_B \gamma_{AB}$. Since the electrons of neutral B can distort away from an electron charge cloud, there will be more attraction represented by $(\mu\mu, B)$ than repulsion. Thus $(\mu\mu, B)$ will be negative. By neglecting the penetration integrals $(\mu\mu, B)$ one underestimates the attractive energy V_{AB}(119). With all else "correct" the net energy of attraction between atoms in the molecule will be underestimated(119). In part, this is dealt with by giving E_{C-C} the same form as V_{AB} so that the neglect of penetration integrals, in essence, cancels out. E_{C-C} is set [illegible]

[illegible]

will be [illegible] attracted [illegible] repelled [illegible] equal to $Z_AZ_B\gamma_{AB}$ where Z_A and Z_B are the core charges(119). If this is the case for all R_{AB}, however, then neutral atoms will be neither attracted nor repelled at any distance by any coulombic forces(119):

(a) Core-core repulsion energy between A and B $= Z_AZ_B/R_{AB}$

(b) electrons of A with core of B- attractive energy $= -Z_AZ_B/R_{AB}$

(c) electrons of B with core of A -attractive energy $= -Z_AZ_B/R_{AB}$

(d) electrons of A with electrons of B -repulsive energy $= Z_AZ_B/R_{AB}$

Thus, the total coulombic energy equals zero between two neutral atoms at any distance.

The exchange energy, however, becomes more negative as R_{AB} goes toward zero. In any geometry optimization to the energy minimum using E_{C-C} equal to $Z_AZ_B\gamma_{AB}$ for all R_{AB}, then the optimum geometry will be a collapsed molecule due to this exchange effect(119).

To make allowances for neutral atom repulsion at small inter-nuclear distances, while also making such repulsion go to zero as R_{AB} goes to infinity, E_{C-C} is set equal to

$E_{C-C} = Z_A Z_B\left[\gamma_{AB} + \left(e^2/R_{AB} - \gamma_{AB}\right) f_3(R_{AB})\right]$ (119), where f_3 goes to zero as R_{AB} goes to infinity, f_3 goes to one as R_{AB} goes to zero, and where f_3 is parametrized(119).

In addition to $f_2(R_{AB})$ and $f_3(R_{AB})$ being parametrized, the MINDO/3 method uses as parameters the effective charges on the cores of the different atom types involved(119). The optimum values for all these parameters were found by fitting calculated values to experimental heats of formation and experimental geometries(119).

In MINDO/3, heats of formation are taken as being equal to the total calculated energy of the molecule minus the total calculated energy of component atoms(119). Thus heats of formation are equated to negative energies of atomization as calculated by MINDO/3.

The procedure for calculating heats of formation is not strictly correct since MINDO/3 takes no account of any kinetic energy other than that of electrons. Translational, vibrational, and rotational kinetic energy of the cores is ignored. Moreover, the value of this total core kinetic energy will, in general, change in the course of a reaction and cancelling will not occur. MINDO/3, to deal with this, absorbs the source of error in the values for its parameters.(119)

<u>Molecular Geometry Optimization</u>: The MINDO/3 method tacitly assumes that the molecular structure corresponding to the lowest combined electronic and internuclear energies is the structure that is actually observed in the laboratory. This is a reasonable assumption, given no marked vibrational anharmonicity, since an average of vibrational motions would be very near this optimum geometry. To find the geometry of lowest electronic-internuclear energy, MINDO/3 employs the

Davidon-Fletcher-Powell minimization algorithm(121). The form of thes algorithm is too complicated to be dealt with here, nevertheless two features related to geometry optimization must be mentioned.

First, energy minima determined by the MINDO/3 algorithm need not be absolute minima. It is possible to find two or more minima for any given molecule. These mey be interpreted as different conformers of the same compound. The actual calculated optimum geometry is dependent upon the original input geometry.

Second, the MINDO/3 program is equipped with an option that permits one to hold various structural parameters constant. It is used with molecules in which symmetry considerations suggest that two or more particular bond lengths, bond angles, or dihedral angles should have the same value.

Configuration Interaction: Suppose one takes two different Slater determinants with the same number of spin orbitals: Ψ' and Ψ''. Now suppose one takes a linear combination of Ψ' and Ψ'': $\Psi = A'\Psi' + A''\Psi''$, where A' and A'' are parameters(117). Using the variation method, A' and A'' can be determined by minimizing the expectation value of the electronic energy of the state represented by Ψ (117). The energy determined this way is an approximation to the true electronic energy of the molecular system(117) since Ψ' and Ψ'' are equally valid ways to approximate the true wavefunction. Notice, however, that the nature of the approximation to the true [illegible] in this case than in the case where only one determinant is used(117).

to the true E_{EL} is different in this case than in the case where only one determinanr is used(117).

One Slater determinant represents a system in which all electron-electron repulsion terms are dependent on the instantaneous co-ordinates of one electron and the average co-ordinates of the other electrons. These average co-ordinates will, in general, change from those of the first. Taking a linear combination of two Slater determinants as Ψ, the wavefunction, and applying the variation method thus corresponds to a system in which two different average electron spatial arrangements are taken into account.

If an infinite number of different Slater determinants representing a system are combined linearly and the variation method applied, then an infinite number of average electron positions are taken into account. This, in turn, corresponds to actually taking into account the instantaneous co-ordinates of both electrons in the determination of the energy of electron-electron repulsion. Coulomb correlation has been taken into account(117). The value for E_{EL} no longer converges to the Hartree-Fock limit, it converges to the true value for the electronic energy of the system(117). This linear combination of Slater determinants method is termed configuration interaction(CI) (117).

It can be shown using perturbation theory that CI introduces no significant advantage in accuracy to make up for the greatly increased time needed for the calculations [illegible] (117). [illegible] 117) and [illegible] (119) [illegible] in ground state, closed shell systems(117). However, for excited state(117) and radical species(119) CI offers a significant advantage. Indeed, it has to be used in order to describe the system accurately(117).

The MINDO/3 computer program offers a CI option. It is used for systems in which significant advantage will be gained by its use.

III. DATA AND DISCUSSION

MOLECULES STUDIED

The wish to test MINDO's ability in calculating small ring geometries necessitated a literature search for experimental structure data. Unfortunately, the search for small, non-planar cyclic structures has not been particulary fruitful. The lack of data is in large part due to the difficulty of applying experimental structure determination techniques to com½ounds of the above sort.

Microwave studies, which determine a molecule's rotational sptectrum and hence, ultimately its moment of inertia and structure, could have ceen applied to molecules of interest to us. However, such molecules have relatively small conformational energy barriers with regard to changing the shape of the ring. As a result, the rotational spectrum of such a molecule has contributions from more than just the lowest energy form. This considerably complicates the interpretation of the spectrum and the deduction of a geometry.

X-ray crystallography is also hampered, to a degree, by the nature of the molecules we desire to use. The problem is in getting the compounds to crystallize. Fairly non-polar bonds and the high symmetry of rings make for low melting points.

It is no accident that oxygen is a component of most of the molecules which were demed suitable for our purposes.

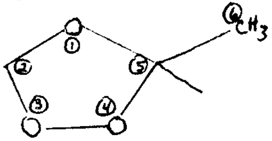
A ring containing oxygen is less "floppy" in a conformational sense than are analogous molecules without oxygen. Microwave studies are thus simplified. Also, oxygen-carbon bonds are polar enough such that electrostatic interactions between molecules may make crystallography feasible.

The following is a list of the molecules that were studied:

1. equatorial- Propylene ozonide
2. Ethylene carbonate
3. Diglycollic anhydride
4. Trioxane
5. 1,3-Dioxalan
6. 1,2-Cylcobutanedicarboxylic acid
7. β -Propiolactone
8. Trimethylene oxide
9. 3-Methylene-cyanocyclobutane
10. Chlorocyclobutane

Each of these molecules will be dealt with below individually. Assumptions made in the calculations will be detailed, and pertinent features of the results will be outlined.

1.e-Propylene Ozonide



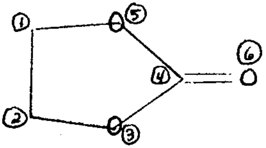
Symmetry conditions: The methyl hydrogen C-C-H angles and C-H distances were assumed to be equal.

Table 1.

	calculated	calculated	observed(122)
1,2	1.393 A	1.389 A	1.423 A
2,3	1.394	1.398	1.399
3,4	1.404	1.404	1.471
4,5	1.381	1.379	1.411
5,6	1.505	1.506	1.534
1,2,3	109.9°	109.8°	105.6°
2,3,4	106.3	107.0	99.7
3,4,5	106.5	106.1	99.2
6,5,4	111.9	112.6	108.3
1,2,3,4	10.5	-0.4	41.0
2,3,4,5	-7.2	3.5	-49.2
conformation	O-O half chair	C-O half chair	O-O half chair
heat of formation (25° C)	-77.70 KCAL/MOL	-77.76 KCAL/MOL	-------

Two different minima were found corresponding to heats of formation of insignifant energy difference. Carbon-oxygen bond distances were found to be too short. Internal ring angles were calculated to be too large. This is especially true of those containing oxygen at the vertex of the angle. Finally, ring puckering wsa underestimated by a large amount, errors in ring dihedral angles being on the order of 30-50°.

2. Ethylene Carbonate



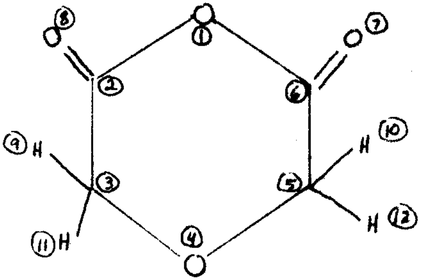
No symmetry was assumed.

Table 2.

	calculated	observed(123)
1,2	1.518 A	1.52 A
2,3	1.378	1.40
3,4	1.374	1.33
4,5	1.374	1.33
4,6	1.215	1.15
1,2,3	105.7°	102°
2,3,4(3,4,5)	109.4	109
3,4,6	125.4	124.5
1,2,3,4	5.7	20

The C-O single bond distance involving the saturated carbon was underestimated. The C-O double bond distance was overestimated. The C-O single bonds involving the unsaturated carbon are overestimated. Internal ring angles are fairly well reproduced, however, the 1,2,3,4 ring dihedral is underestimated.

3. Diglycollic Anhydride:



Symmetry conditions: 3,4 and 4,5 bond distances were held equal, as were 2,3 and 5,6; 2,8 and 6,7; 3,9 and 5,10; and 3,11 and 5,12. Bond angles 1,2,8 and 1,6,7 were set equal as were 2,3,9 and 6,5 10; and 2,3,11 and 6,5,12.

Table 3.

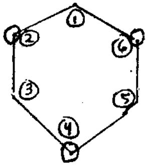
	calculated	calculated	observed(124)
1,2	1.347	1.349	1.386
2,3	1.521	1.513	1.491
3,4	1.366	1.362	1.409
4,5	1.366	1.362	1.413
1,6	1.347	1.349	1.386

Table 3.(continued)

	calculated	calculated	observed(124)
6,7	1.207	1.208	1.187
1,2,3	111.7	111.9	116.7
2,3,4	116.0	117.3	112.0
3,4,5	122.4	124.9	110.0
2,1,6	133.4	133.4	121.2
1,2,3,4	-15.2	-12.0	-20.0
2,3,4,5	34.0	22.8	57.3
3,2,1,6	-3.5	1.9	-16.5
conformation	chair	boat	chair
heat of formation (KCAL/MOL) 25° C.	-174.80	-174.73	-----

It is evident that carbon-oxygen single bonds were underestimated. Carbon-oxygen double bonds were overestimated. The ring was predicted to be too planar. Two minima were found with insignificant energy differences. These minima correspond to boat and chair conformers, respectively. The chair conformer is the experimentally determined structure.

4. Trioxane:



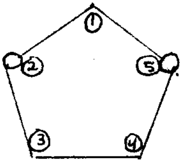
No symmetry conditions were imposed.

Table 4.

	calculated	calculated	observed(125)
1,2	1.369	1.369	1.421
2,3	1.370	1.372	1.422
3,4	1.371	1.368	1.421
4,5	1.369	1.367	1.422
5,6	1.369	1.367	1.421
1,2,3	118.1	118.4	110.4
2,3,4	119.3	119.7	109.6
1,2,3,4	-19.3	343.3	-58.9
2,3,4,5	27.0	2.2	58.9
3,4,5,6	-18.3	11.5	-58.9
conformation	chair	boat	chair
heat of formation (KCAL/MOL) 25° C.	-119.97	-120.20	-----

Two conformers of trioxane were found. One corresponds to a boat conformation, the other to a chair. The boat was predicted to be the more stable by about 0.2 KCAL/MOL whereas experiment has determined the chaor form to be energetically favored. In addition, C-O single bonds were underestimated. The ring angles were calculated to be too large. Ring dihedral angles were found to be much too small.

5. 1,3-Dioxalan



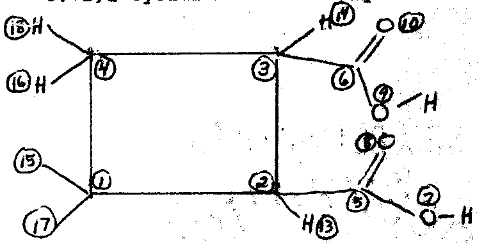
No symmetry conditions were imposed.

Table 5.

	calculated	observed(126)
1,2	1.383	1.42
2,3	1.378	1.42
3,4	1.513	1.54
4,5	1.378	1.42
1,2,3	106.8	108(approx.)
2,3,4	106.7	108(approx.)
1,2,3,4	7.0	puckered non-planar ring
2,3,4,5	-7.6	

There is a considerable lack of experimental data for this molecule. With the data that is available, it is evident that bond lengths are underestimated for C-O single bonds. Internal ring angles are calculated to within two degrees of observed values. The calculated ring is puckered as experiment has shown it to be, although the accuracy of the predicted extent of puckering cannot be determined.

6. 1,2-Cyclobutanedicarboxylic Acid:



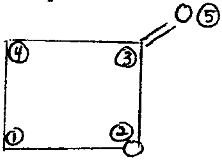
All symmetry conditions imposed dealt with the hydrogen atoms. Bond lenghts 2,13 and 3,14 were held equal as were bond lengths 1,17; 1,15; 4,18; and 4,16. Angles 1,2,13 and 2,3,14 were held equal as were 2,1,15; 2,1 17; 3,4,16; and 3,4,18. These assumptions are not entirely justifiable except that they probably do not significantly affect the form of the calculated ring geometry.

Table 6.

	calculated	observed(127)
1,2	1.544	1.553
2,3	1.578	1.517
3,4	1.545	1.553
2,5	1.523	1.493
3,6	1.518	1.493
1,2,3	88.6	-----
2,3,4	88.5	88.8
1,2,3,4	-8.3	-31

From the table it is evident that C-C bond distances were not reproduced entirely accurately, but there is no systematic deviation. Ring bond angles are accurate. Experiment predicts a non-planar ring with a dihedral angle of about thirty one degrees. MINDO/3 does, indeed, predict a puckered ring, but the calculated geometry is flattened compared the experimental data.

7. β-Propiolactone



No symmetry conditions were imposed.

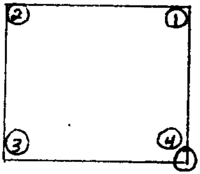
Table 7.

	calculated	observed(128)
1,2	1.389	1.45
2,3	1.373	1.45
3,4	1.521	1.53
3,5	1.198	1.19
1,2,3	94.4	89
1,2,3,4	0.6	0

β-Propiolactone is one of a group of four membered rings whose preffered geometry is planar, whereas this fact would, by no means, be evident just from considerations of the bonding in the molecule. MINDO/3 predicts this planarity. However, C-O single bond lengths are underestimated by 0.06

to 0.08 angstroms. Also, the C-O-C angle within the ring is greater by about 5 degrees than the observed value.

8. Trimethylene Oxide



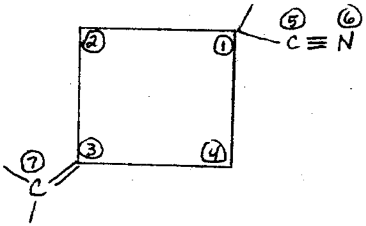
No symmetry conditions were imposed.

Table 8.

	calculated	observed(129)
1,2	1.513	1.54
2,3	1.511	1.54
3,4	1.389	1.46
1,2,3	83.3	88.5
1,2,3,4	-0.03	0

Trimethylene oxide also has a planar experimental structure, which is not obvious from bonding considerations. MINDO/3 is quite accurate in predicting this planarity. However, C-O single bond distances are calculated to be too short.

9. 3-Methylene-1-cyanocyclobutane



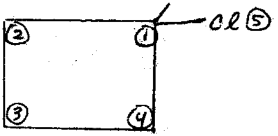
No symmetry conditions were imposed.

Table 9.

	calculated	observed(130)
1,2	1.544	1.540
2,3	1.519	1.496
3,4	1.520	1.496
3,7	1.330	1.340
5,6	1.161	1.159
1,2,3	91.5	-----
2,3,4	89.4	-----
1,2,3,4	2.7	17.2

The experimental structure given is a reasonable, but it may be the actual one. This is because the microwave study was done for only one isotopic species. Nevertheless, a planar ring was ruled out. Moreover, the dihedral angle given is quite close to that of other cyclobutanes(130). MINDO/3 predicts, inaccurately, a cyclic structure that is very close to planar. Besides this, the other geometrical values agree quite closely with the given experimental ones.

10. Chlorocyclobutane



No symmetry conditions were imposed.

Table 10.

	calculated	observed(131)
1,2	1.521	1.525
2,3	1.527	1.550
1,5	1.786	1.775
1,2,3	89.3	-----
2,3,4	90.3	-----
1,2,3,4	3.4	20 ± 1

As in 3-Methylene-1-cyanocyclobutane, bond lengths are very accurately reproduced by MINDO/3. However, the ring dihedral angle is, again, considerably smaller than the experimental value.

DISCUSSION AND CONCLUSIONS

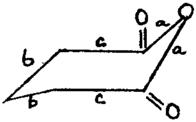
DISCUSSION OF DATA

The performance of MINDO/3 in calculating certain cyclic geometries is to a certain degree evident from the above data and discussion. The following is an attempt to further explane marked trends and their possible interconnections. In addition, MINDO/3's inaccuracies and their implications with regard to calculations of ½ossible ozonolysis reaction pathways are discussed.

There are four systematic deficiencies evident from our MINDO/3 calculations. These four are to some degree connected. First, MINDO/3 underestimates the bond distance between singly bonded carbon and oxygen. Second, MINDO/3 tends to overestimate internal ring angles. Third, as found by Dewar, et.al.(133) for cyclohexane and cyclohexene, the method predicts ring geometries which are considerably closer to planarity than observed structures. Finally, MINDO/3 does not seem to be able to lowest energy cyclic conformers.

Consider first the prediction of shortened carbon-oxygen single bonds. The trend is also present in Dewar, et.al.'s calculations on open chain molecules(132). Thus, it is probable that the deficiency is one inherent in MINDO/3's treatment of the atoms involved and is fairly independent of the molecular context of the atoms. Perhaps, though, this shortcoming has something to do with the other deficiencies of the method in predicting cyclic structures.

For instance, in diglycollic anhydride:



the a and b bonds are all predicted to be short compared to experimental data. If one imagines starting with the observed and moving towards MINDO/3's C-O distances while holding the rest of the ring static, it is evident that angle a-a and angle b-b will both open up. The ring will in turn flatten, or, in other words, the b-c-a dihedral angles will decrease. Now it is not entirely valid to assume that the remainder of the ring would not change during this process, but it is certainly true that it would not change as much as the C-O bonds using a full MINDO/3 optimization. For, the method treats carbon-carbon and oxygen-oxygen distances with better accuracy than carbon-oxygen bond distances. Also, in trioxane all the ring bond distances are shortened from observed values. This could occur to simply produce a smaller MINDO/3 trioxane of unchanged experimental shape,

yet such a form would have shorter non-bonded carbon-carbon and oxygen-oxygen distances. One would expect that such shortened distances are not favored by MINDO/3 for these pairs of atoms. Thus, it is plausible to expect that as oxygen-oxygen and carbon-carbon pairs are being brought closer by closer by the tendency to shorten carbon-oxygen bonds, there is simultaneous angle opening which acts to separate the carbon-carbon and oxygen-oxygen pairs. The result is a more planar ring.

Although carbon-oxygen bond shortening may be part of the reason for ring flattening and internal angle opening, it cannot be the only answer. Both cyclohexane and cylohexene are flattened by MINDO/3(133). Certain cyclobutyl compounds are predicted to be more planar than they actually are. Obviously carbon-oxygen bonds could not have produced the effect in these molecules.

The tendencies of MINDO/3 to open ring angles and to flatten rings are closely related. Strictly from the geometry of the ring compounds opening internal angles necessitates a more planar ring. The converse is also true. One might wonder just what the "driving force" for these simultaneous effects is.

It is possible that errors in MINDO/3 serve to overestimate certain bond angles without regard to molecular context. However, if this were true, bond angles would be overestimated in open chain molecules too. Although there some evidence indicating a tendency to overestimate angles involving singly bonded carbon and oxygen with an oxygen at the vertex of the angle(132), the trend is, by no means, pronounced. It certainly is not of the magnitude observed in our calculations. Moreover, C-C-C angles are predicted accurately(133), yet cyclohexane, cyclohexene, and species of cyclobutane are nevertheless flattened by MINDO/3.

Dewar, et.al. have suggested that ring flattened is due to an overestimation of non-bonded hydrogen-hydrogen repulsions(133). Flattening cyclic compounds increases axial hydrogen distances and is thus energetically favored to a certain degree. However, there is evidence that this is not plausible reason. First, Dewar, et.al. have found that MINDO three underestimates barriers to rotation about single bonds.(133) In particular, the barrier for the C-C bond of ethane is underestimated by 2.0 KCAL/MOL(133). If non-bonded H-H repulsion were overestimated one would expect an overestimation of the barrier to rotation. Second, we have done calculations on cyclohexane and trioxane in which both full and partial geometry optimizations have been used. The partial optimization consisted of optimizing the hydrogen degrees of freedom while holding the ring skeleton in its experimental structure. Comparing two center energies between the two types of calculations for each molecule, it was found that the change in the H-H energies was only a small portion of the change in the total energy(see table 11.). A large negative energy change would be expected for these energies in going from partial to full optimization given that H-H repulsion were a driving force in ring flattening.

Table 11.

	Partial opt.	Full opt.	Change
Trioxane:			
Two-center H-H energies	1.629 eV	1.564 eV	-0.065 eV
Total energy	-1402.556 eV	-1403.387 eV	-0.831 eV
Cyclohexane:			
Two center H-H energies	4.446 eV	4.798 eV	0.352 eV
Total energy	-939.643 eV	-940.022 eV	-0.379 eV

The underestimation of barriers to rotation by MINDO/3 is interesting in another way. It suggests that syn conformers may be more favored energetically than they should be in open chain molecules. If the deficiency is also true with regard to cyclical molecules, then one would expect that the calculated geometries of puckered rings might be too planar. Given that energy decreases for particular degrees of freedom upon flattening a ring, the flattening will not be compensated for properly in an energetic sense due to the underestimation of the energies of syn(or close to syn) conformers. Thus, MINDO/3's errors with regard to rings may be directly related to an inability to accurately reproduce syn-gauche energy differences.

With the above in mind, one can address some of the calculations of ring conformers. For instance, the difference between boat and chair conformers of six-membered rings is that the boat form has two syn interactions within the ring while the chair has two gauche interactions. With diglycollic anhydride the two conformers are calculated to be of neglible energy difference. The boat form of trioxane is calculated to be more stable than the chair by about 0.2 KCAL/MOL. With both, the experimental structure is the chair conformer. The errors in predicted relative energies may be a result of the underestimation of syn-gauche energy differences.

The actual mathematical and/or theoretical reasons for the MINDO/3 trends detailed above are quite difficult to ascertain. One might look at various components of the MINDO/3 total electronic and nuclear-nuclear repulsion energy to try to determine if any are inaccurate. However, for this, "absolute" values are needed from experiment or other theoretical techniques. It is beyond the scope of this paper to obtain such values even if they were possible to obtain. Moreover, if an accurate component analysis were available for molecules which interest us, they would be of dubious value. MINDO/3 is parametrized to reproduce experimental heats of formation. An effect of this parametrization is to introduce errors in individual energy modes which on the average absorb those errors introduced by the Born-Oppenheimer approximation, the assumption that the molecule os free from all outside forces, etc.. Therefore an appraisal of each energy mode in and of itself would be meaningless unless such examination exposed modes that were extraordinarily and consistently inaccurate.

One might also examine the MINDO/3 energy components when molecular structures move from experimentally determined to fully optimized ones. The rationale here is that those energy modes which MINDO/3 does not handle correctly will account for the greatest part of the energy difference between experimental and completely optimized geometries. However, this need not be the case. For example, MINDO/3's errors in predicting rings to be too planar may be in the underestimation of the energy increase of a certain mode upon flattening. Too little a positive energy could be the problem instead of too great a negative change. This would be undetectable in an examination of the above type.

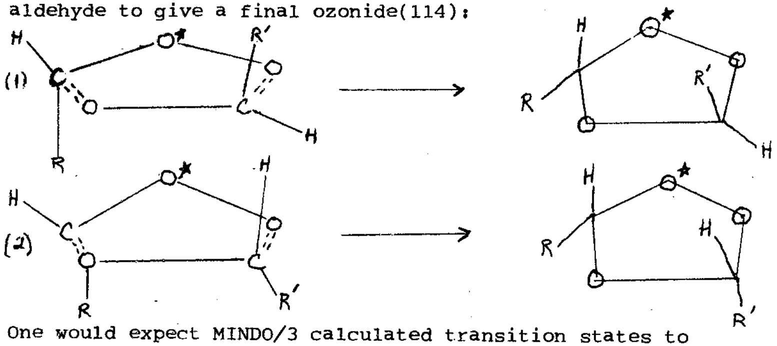
In general, an analysis leading to MINDO/3's theoretical deficiencies is too intricate to be dealt with here.

MINDO/3 AND THE MECHANISM OF OZONOLYSIS

Three considerations with regard to MINDO/3's performance in calculating ring geometries lead one to suspect that the results of calculations on ozonolysis reaction paths might be of dubious value.

First, carbon-oxygen single bonds are shortened by

MINDO/3. This could be a serious defect in the calculation of the geometries of intermediates and products, as shown above. Moreover, this deficiency could also render calculations on reaction paths inaccurate. For example, consider possible reactions of a zwitterion with a substituted aldehyde to give a final ozonide(114):



One would expect MINDO/3 calculated transition states to have shorter C-O distances than is actually the case. This, in turn, would affect other transition state interactions(114) such as that of the R' group with the lone pairs of the terminal oxygen on the zwitterion. Moreover, the effect on various interactions would not, in general, be the same for reaction (1) and reaction (2). Thus, calculated relative activation energies for the two reactions would be in error. Since ozonolysis involves a great deal of C-O bond cleavage and formation, the same kind of argument can be applied to the other postulated steps of the mechanism.

Second, MINDO/3 calculates ring geometries to be too planar. This could also introduce serious error into the into the calculation of reaction paths. Consider again the zwitterion- aldehyde reaction detailed above, where the starred oxygens represent ones that bend up out of the plane of the other four ring atoms. MINDO/3 would probably calculate a transition state in which the starred oxygens would not be far enough out of the planes. Transition state interactions, such as the R'-O^* one, would be affected differently for the two reactions. Again, relative transition state energies would be in error. Moreover, since other cyclic intermediates and transition states are important in the ozonolysis mechanism predictions of favored reaction paths for these steps based on MINDO/3 energies must also be held suspect.

Finally, MINDO/3 does not consistently predict energetically favored ring conformers. Especially pertinent is the fact that the O-O half-chair conformation of equatorial propylene ozonide cannot be said to be the lowest energy conformer if one goes by the MINDO/3 calculations. Since, assumptions in the proposed mechanisms of ozonolysis deal explicitly with the predominant conformations of cyclic intermediates, then MINDO/3's capability to check these assumptions is severely limited. Moreover, since transition states in the mechanism are probably cyclic forms then it is obvious that errors in the predictions of energetically favored conformers could play a large, undesirable role in calculated activation energies.

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