Theoretical Conformational Analysis of Saturated Heterocycles with Adjacent Heteroatoms. Primary and Final Ozonides

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Abstract: All 12 conformers of the *cis*- and *trans*-2-butene ozonide (a 1,2,3-trioxolane) have been investigated using two semiempirical methods, CNDO/2 and EHT. The two methods yield different results for the relative stability and geometry of these conformers. These results indicate that an appraisal of these methods for use in heterocyclic conformational analysis is necessary. Recently available microwave data for ethylene (final) ozonide (a 1,2,4-trioxolane) were used to compare the methods directly. The theoretical conformational analyses for three conformers of ethylene ozonide clearly show that the CNDO/2 method is appropriate for heterocycles with adjacent heteroatoms while the extended Hückel theory is not. Pertinent conformers of *cis*- and *trans*-2-butene primary ozonides were restudied using a second, more appropriate geometry, and the conclusions reached indicate that a possible mechanism for the ozonolysis of olefins which depends on the conformation of the primary ozonide needs further analysis.

The reaction of ozone with olefinic compounds frequently results in the formation of an intermediate five-member heterocycle with three adjacent oxygen atoms, a 1,2,3-trioxolane or primary ozonide. It is postulated that this intermediate then decomposes/rearranges to produce an ozonide plus a mixture of polymeric peroxides and alkoxy hydroperoxides. The original mechanism for this reaction was proposed by Criegee[1] and is shown in Figure 1. The primary ozonide decomposes into a zwitterion and a carbonyl fragment which recombine within the solvent cage to form the final ozonide. Experimental evidence summarized elsewhere[2–5] indicates that the Criegee mechanism alone is insufficient to explain the apparent transfer of stereochemical information from the original olefin to the final ozonide. Two mechanisms have been proposed to explain the new results. Murray, *et al.*,[3,6] have made several proposals for the formation of ozonides including the existence of a seven-membered heterocyclic intermediate formed by the reaction of the primary ozonide with a carbonyl compound (see Figure 2). This mechanism is consistent with the new stereochemical data and, in addition, explains the presence of ^{18}O in the peroxide oxygen of the final ozonide, when ^{18}O-labeled carbonyl compounds are introduced into the reaction mixture.[7] Story, *et al.*,[8] have offered a unified approach to ozonolysis mechanisms which ties together the many different facets of the ozonolysis reaction.

Bailey, *et al.*,[4] have suggested a refinement of the Criegee mechanism which depends on the primary ozonide assuming a conformation which has clearly identifiable axial and equatorial substituent positions (see Figure 3). When the primary ozonide decomposes, equatorial substituents produce anti zwitterions and axial substituents produce syn zwitterions which then react preferentially with carbonyl compounds to orient bulky groups to produce cis and trans final ozonides, respectively. One test of Bailey's mechanism would be an investigation of which conformers of the primary ozonide are lowest in energy.

The analysis of which interactions will be most important in determining which conformations of the primary ozonide are most stable is complicated by the presence of heteroatoms in the ring.

The presence of adjacent heteroatoms in a five- or six-membered ring makes analogy to carbocyclic rings unclear. In general carbon–heteroatom bond lengths differ from the carbon–carbon bond length. Differences in electronegativity give rise to polar bonds within the ring and the possibility of dipole–dipole interactions which are absent in carbocyclic rings. In addition the presence of lone pairs on heteroatoms in a ring reduces nonbonded interactions.[9] Therefore, when calculating the energy of various conformers, the method used should adequately reflect these factors. For these reasons and others to be discussed below, an investigation of all the conformers of primary ozonides was performed using CNDO/2 and extended Hückel (EHT) methods.

Most of the theoretical studies on heterocyclic molecules have dealt with those molecules of biochemical interest such as the purine and pyrimidine bases. In general these studies were concerned with the electronic structure of these molecules, which contain delocalized electrons, with particular interest in optical properties and charge distributions. Typical of these studies are the semiempirical studies by Pullman on tautomerism in purine bases[10] and Pullman[11] on conjugated heterocycles and the *ab initio* calculations of Clementi,[12] *et al.*, on the guanine–cytosine base

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[1] R. Criegee, *Rec. Chem. Progr.*, **18**, 111 (1957).

[2] R. W. Murray, R. D. Youssefyeh, and P. R. Story, *J. Amer. Chem. Soc.*, **88**, 3143 (1966).

[3] R. W. Murray, R. D. Youssefyeh, and P. R. Story, *ibid.*, **89**, 2429 (1967).

[4] N. L. Bauld, J. A. Thompson, C. E. Hudson, and P. S. Bailey, *ibid.*, **90**, 1822 (1968).

[5] J. Renard and S. Fliszar, *ibid.*, **92**, 2628 (1970).

[6] P. R. Story, R. W. Murray, and R. D. Youssefyeh, *ibid.*, **88**, 3146 (1966).

[7] P. R. Story, C. E. Bishop, J. R. Burgess, R. W. Murray, and R. D. Youssefyeh, *ibid.*, **90**, 1907 (1968).

[8] P. R. Story, J. A. Alford, W. C. Ray, and J. R. Burges, *ibid.*, **93**, 3044 (1971).

[9] E. L. Eliel and M. C. Knoeber, *ibid.*, **90**, 3444 (1968).

[10] B. Pullman in "Proceedings of the Jerusalem Symposium on Quantum Chemistry and Biochemistry," Vol. II, E. Bergmann and B. Pullman, Ed., Jerusalem Academic Press, Jerusalem, 1970, p 292.

[11] A. Pullman in "Sigma Molecular Orbital Theory," O. Sinanoglu and K. W. Wiberg, Ed., Yale University Press, New Haven, Conn., 1970, p 280.

[12] E. Clementi, J. Mehl, and W. von Niessen, *J. Chem. Phys.*, **54**, 508 (1971).

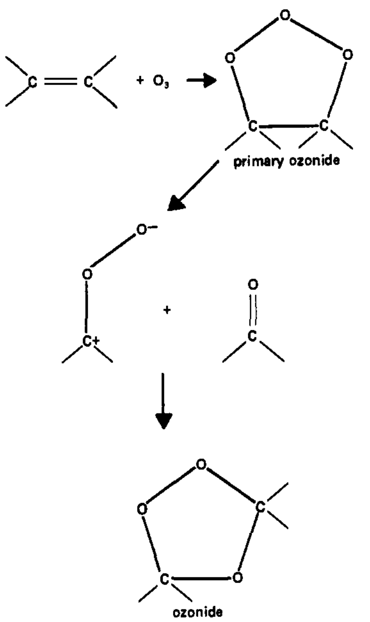

Figure 1. Criegee mechanism for ozonide formation.

pair. Adam has studied lone-pair interactions in nitrogen heterocycles.[13,14]

Several *ab initio* studies involving 1-2 diheteroatom interactions have been reported. Davidson and Allen,[15] and Veillard[16] have reported both the cis and trans barriers for hydrogen peroxide; Wong, *et al.*,[17] have theoretically predicted structures for diimide. These LCAO-SCF-MO calculations provide accurate descriptions of the barriers involved and would be most appropriate although difficult for the ozonides considered here. Diimide has also been studied using CNDO/2;[18] however, it should be noted that only oxygen-oxygen single bonds are involved in the ozonides.

The conformations of heterocycles have been studied using both classical and semiempirical methods. Seip, *et al.*,[19] have studied the conformations of ethylene ozonide and tetrahydrofuran using the Westheimer-Hendrickson[20,21] method. Renard and Fliszar[5,22] have studied four conformers for a variety of symmetrical and unsymmetrical primary ozonides using extended Hückel theory and concluded that Bailey's assumption, that the predominant conformation of the primary ozonide was the carbon half-chair, was correct.

A wealth of experimental data on five- and six-membered heterocycles has been gathered by Romers, *et al.*,[23] and Eliel.[24]

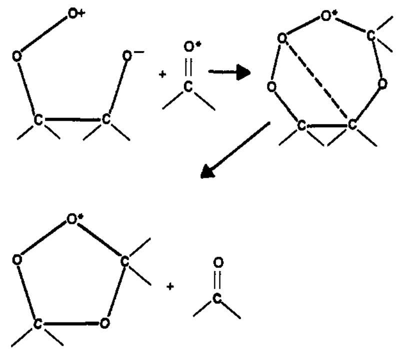

Figure 2. Mechanism for ozonide formation proposed by Murray, *et al.*

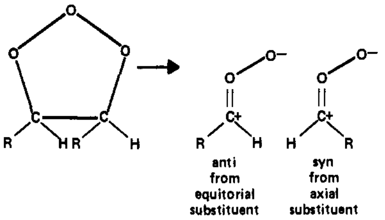

Figure 3. Refinement of Criegee's mechanism proposed by Bailey, *et al.*

Choice of Theoretical Methods

Both the CNDO/2[25] and EHT[26] semiempirical methods are all valence electron approximations to the LCAO-MO method developed by Roothaan[27] and Hall.[28] Table I presents the approximation to the Roothaan equations which are made in both methods. Fock matrix elements in EHT do not depend on the linear combination coefficients, hence no SCF procedure is possible. In addition these matrix elements do not explicitly include electron repulsion contributions which must be important in any conformational calculation, particularly one involving lone pair-lone pair interactions. The molecular energies calculated by EHT are sums of one electron energies and do not include nuclear repulsion energies. The CNDO/2 method does contain explicit inclusion of electron repulsion and nuclear repulsion; Fock matrix elements depend explicitly on linear combination coefficients and hence an SCF procedure is possible. The parameters used in the EHT calculations were those used by Renard and Fliszar.[5] The CNDO/2 parameterization is described in ref 25.

Because it appeared that CNDO/2 explicitly includes factors which must be important in determining the conformation of heterocycles, it would be a natural choice for such calculations. Since EHT had been applied to primary ozonide conformations both methods were used and compared for all the possible primary ozonide conformers.

Calculations. Five-membered rings exhibit pseudorotation in which the ring goes through a maximum of 20 possible conformations, lingering in conformers having the lower energies, and flexing rapidly through the others. Because of symmetry, the primary ozonides

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(13) W. Adam, A. Grimison, and R. Hoffmann, *J. Amer. Chem. Soc.*, **91**, 2590 (1969).

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(20) F. H. Westheimer, "Steric Effects in Organic Chemistry," Wiley, New York, N. Y., 1956.

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(22) S. Fliszar, J. Renard, and D. Z. Simon, *ibid.*, **93**, 6953 (1971).

(23) C. Romers, C. Altona, H. R. Buys, and E. Havinga, *Top. Stereochem.*, **4**, 39 (1969).

(24) E. L. Eliel, *Accounts Chem. Res.*, **3**, 1 (1970).

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

(26) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

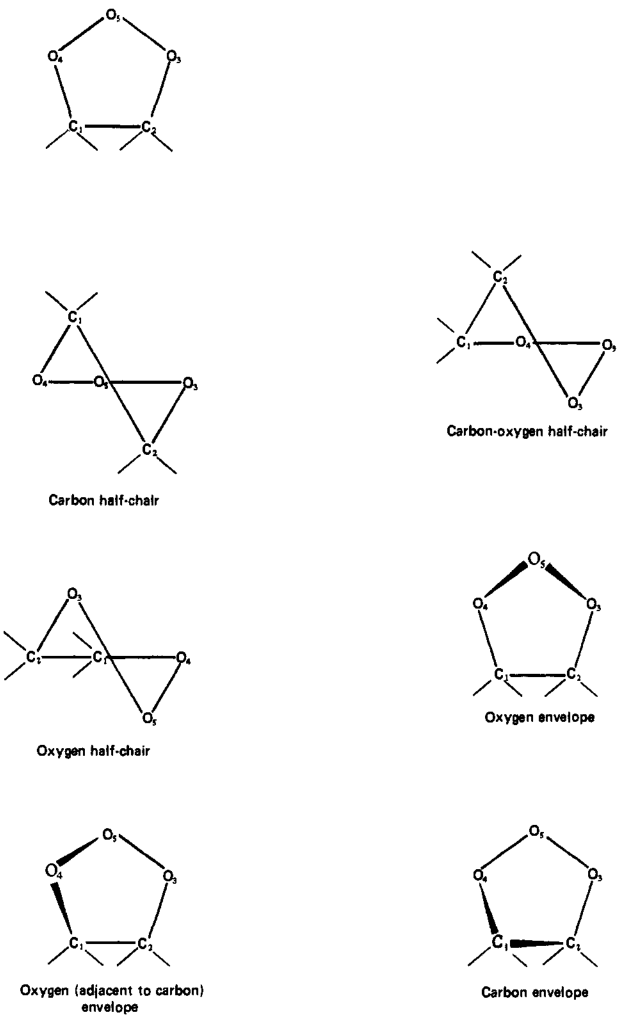
(27) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

(28) G. G. Hall, *Proc. Roy. Soc., Ser. A*, **205**, 541 (1951).

Table I. Comparison of EHT and CNDO/2 Methods

	EHT	CNDO/2[a]
Molecular orbitals	$\psi_i(1) = \sum_{\mu=1}^{m} C_{\mu i}\phi_\mu(1)$ m AO's	$\psi_i(1) = \sum_{\mu=1}^{m} C_{\mu i}\phi_\mu(1)$
Roothaan's equations	$\sum_{\mu=1}^{m} (F_{\mu\nu} - \epsilon_i S_{\mu\nu})C_{\nu i} = 0$ $i = 1, 2\ldots, m$	$\sum_{\mu=1}^{m} (F_{\mu\nu} - \epsilon_i \delta_{\mu\nu})C_{\nu i} = 0$
$F_{\mu\mu}$	Valence state ionization potentials	$\frac{1}{2}(I_\mu + A_\mu) + \left(q_A - \frac{1}{2}q_\mu\right)\gamma_{AA} + \sum_{B(\neq A)} \gamma_{AB}q_B$
$F_{\mu\nu}$	$0.5(F_{\mu\mu} + F_{\nu\nu})S_{\mu\nu}{}^*K$ $K = 1.75$ $S_{\mu\nu} = \int\phi_\mu(1)\phi_\nu(1)d\tau_1$ $P_{\mu\nu}$ = element of bond order matrix	$\frac{1}{2}(\beta^0{}_A + \beta^0{}_B)S_{\mu\nu} + \frac{1}{2}P_{\mu\nu}\gamma_{AB}$

[a] $\gamma_{AB} = \iint[2s_A(1)]^2(1/r_{12})[2s_B(2)]^2\, d\tau_1 d\tau_2$; A_μ = electron affinity for the electron in orbital ϕ_μ; I_μ = ionization potential for the electron in atomic orbital, ϕ_μ; q_A = atomic charge on atom A; q_μ = electronic charge in orbital ϕ_μ; $\beta_A{}^0$ = bonding parameter determined by comparison to minimal bases set *ab initio* calculations.



Carbon half-chair

Carbon-oxygen half-chair

Oxygen half-chair

Oxygen envelope

Oxygen (adjacent to carbon) envelope

Carbon envelope

Figure 4. Conformers of primary ozonide.

exhibit only 12 of these conformers, six half-chairs and six envelopes. Envelopes are formed when one atom is lifted out of the plane formed by the other four atoms (see Figure 4). Starting from the planar molecule, half-chairs are formed by twisting two adjacent atoms out of the plane, leaving one atom above the plane of the remaining three atoms and one atom below it. The six conformers shown in Figure 4 have six counterparts formed by pushing one atom down (envelopes) or twisting the adjacent atoms counter-clockwise (half-chairs).

The specific primary ozonide used in these exploratory calculations is 2-butene primary ozonide; both cis and trans isomers are considered. Renard and Fliszar,[5] using EHT, have reported results for four of the conformers, the carbon half-chair and carbon envelope.

The calculations presented here consider all 12 conformers, calculating the energy of each conformer as a function of twist angle; increments of 1° were used for the half-chairs and 5° for the envelopes. The twist angles are defined in Table II. The positive angles are illustrated in Figure 4. Analysis of dihedral angles between substituents on the carbon atoms *vs.* twist angle indicates that the carbon envelope relieves substituent eclipsing most, followed by the carbon half-chair, carbon–oxygen half-chair, oxygen (adjacent to carbon) envelope, and oxygen half-chair. If relieving substituent interaction were the most important factor in determining ring conformation, then stability of conformers should follow this order. If, on the other hand, relieving lone pair–lone pair or lone pair–bonding pair interactions is the most important, conformations such as the previously unconsidered oxygen half-chair or oxygen (adjacent to carbon) envelope would need to be considered. It should be noted that the only conformer with clear cut axial and equatorial substituent positions is the carbon half-chair.

Table II. Definition of Twist Angles for Conformers of Primary Ozonide

Conformer	Twist angle[a]
Carbon half-chair	C_1–C_2–O_5 and C_1–C_2–O_3
Carbon–oxygen half-chair	C_2–O_3–O_4 and C_2–O_3–O_5
Oxygen half-chair	O_3–O_5–C_1 and O_3–O_5–O_4
Oxygen envelope	O_4–C_1–C_2–O_3 and C_1–C_2–O_5
Carbon (adjacent to oxygen) envelope	C_1–C_2–O_3–O_5 and C_2–O_3–O_4
Carbon envelope	C_2–O_3–O_5–O_4 and O_3–O_5–C_1

[a] The twist angle is the dihedral angle between the planes listed in this column. See Figure 4 for atom numbering.

The geometry for the primary ozonide was taken from Renard and Fliszar. All ring bond lengths are chosen to be 1.44 Å; external carbon–carbon bonds are 1.54 Å, ring carbon–hydrogen bonds are 1.08 Å, and other carbon–hydrogen bonds are 1.09 Å. This geometry is a very severe approximation to an appropriate geometry; and the justification of 1.44 Å for the carbon–carbon bond length is based on the incorrect assumption of substantial double bond character between the carbon atoms. Although severely lacking, the geometry is used here for direct comparison to the results for Renard and Fliszar.

Results

Extended Hückel Theory. The results of a conformational analysis on the 12 conformers of 2-butene primary ozonide using EHT are summarized in Table III.

Table III. Summary of EHT Results for the Conformers of *cis*- and *trans*-2-Butene Primary Ozonides[a]

	Isomer[b]			
	Trans		Cis	
Conformer	Twist angle, deg	*E*, kcal/mol	Twist angle, deg	*E*, kcal/mol
Carbon half-chair	18	7.2	23	19.1
	−20	6.4	a	a
Carbon–oxygen half-chair	15	2.9	21	9.2
	−16	1.0	−21	9.5
Oxygen half-chair	17	1.7	19	2.7
	−15	0.6	−19	2.2
Oxygen envelope	nm	nm	nm	nm
	a	a	nm	nm
Oxygen (adjacent to carbon) envelope	15	3.7	15	7.4
	nm	nm	−15	7.0
Carbon envelope	10	1.9	15	12.2
	−10	3.8	−15	12.4

[a] Energies in kcal/mol below planar conformations. [b] nm = no minima found for this conformer. a = no separate conformer by symmetry.

In agreement with Renard and Fliszar and in support of Bailey's mechanism, the carbon half-chair was found to be the most stable conformer, followed by the carbon envelope; next came the previously unexplored carbon–oxygen half-chair, oxygen (adjacent to carbon) envelope, oxygen half-chair, and oxygen envelope which showed no conformation lower in energy than the planar structure. Since the oxygen envelope shows no minimum and does not change substituent interactions, the EHT is not reflecting the alleviation of lone-pair interactions which the oxygen envelope should provide. This could also account for the low standing of the oxygen half-chair in the order of stability. The minima in the envelope curves correspond to one methyl group being moved away from the center of the ring into a pseudoequatorial position. The minima for the half-chair conformers correspond to one methyl group moving into an equatorial position in the carbon half-chair and pseudoequatorial positions in the other half-chairs. The order of stability in the half-chairs coincides with the reduction of substituent interaction for each conformer. The only difference between the carbon half-chair calculations here and those of Renard and Fliszar is that for *trans*-2-butene primary ozonide, the (a,a) conformation of the methyl groups was found to be higher in energy than the (e,e) conformation; the previous results indicated that both (a,a) and (e,e) conformations were equal in energy.

CNDO/2. The results of the CNDO/2 conformational analysis are presented in Table IV. In general the energies are smaller than EHT and the order of stability is different. The carbon–oxygen half-chair is lowest in energy followed by the carbon envelope, carbon half-chair, and the remaining conformers which are very close in energy. The oxygen envelopes exhibit minima relative to the planar structure; hence the CNDO/2 calculations are reflecting the reduction in lone-pair interaction expected for these conformers. It is difficult to separate those conformers whose energies are less than 1 kcal/mol below the planar energy from the planar structure but probably they are slightly more stable than the planar structure.

Table IV. Summary of CNDO/2 Results for the Conformers of *cis*- and *trans*-2-Butene Primary Ozonide[a]

	Isomer[b]			
	Trans		Cis	
Conformer	Twist angle, deg	*E*, kcal/mol	Twist, angle, deg	*E*, kcal/mol
Carbon half-chair	11	1.2	12	1.9
	nm	nm	a	a
Carbon–oxygen half-chair	14	1.7	15	2.1
	−13	<0.5	−16	2.8
Oxygen half-chair	13	0.8	+16	1.4
	−11	<0.5	−14	<0.5
Oxygen envelope	10	0.8	+10	<0.5
	a	a	−10	1.3
Oxygen (adjacent to carbon) envelope	5	0.6	+10	1.4
	nm	nm	−10	<0.5
Carbon envelope	nm	nm	+10	2.1
	−10	1.4	−10	2.3

[a] Energies in kcal/mol below planar conformation. [b] nm = no minimum found for this conformer. a = no separate conformer by symmetry.

The detailed curves for *trans*-2-butene primary ozonide are shown in Figures 5 and 6. The envelope minima correspond to at least one methyl group moving into a pseudo-equatorial position. The half-chair results have minima where methyl groups move into equatorial positions (carbon half-chair) and pseudo-equatorial position (oxygen and oxygen adjacent to carbon) half-chairs. The order of half-chair stability does not follow the order of reduction of substituent interactions. Since the carbon–oxygen half-chair is third on the list for relieving substituent interactions it must owe its stability to the alleviation of lone pair–lone pair and lone pair–bonding pair interactions. The one result out of place is that there are only small or no minima for the negative twist angles of the half-chairs. This could be due to the choice of ring geometry.

Comparison of EHT and CNDO/2 Results. Comparison of Tables III and IV shows that the EHT and CNDO/2 methods give quite different results for the order of stability of the primary ozonide conformers and their twist angles. In addition the magnitudes of the various energies are considerably less for CNDO/2.

It would not be surprising to find these CNDO/2 energies to be smaller than EHT when the results of CNDO/2 barrier-to-internal-rotation calculations[29] are

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[29] M. Gordon, *J. Amer. Chem. Soc.*, **91**, 3122 (1969).

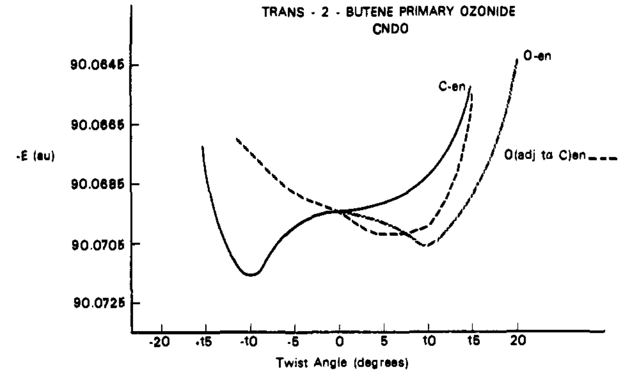

Figure 5. CNDO/2 results for *trans*-2-butene primary ozonide envelopes.

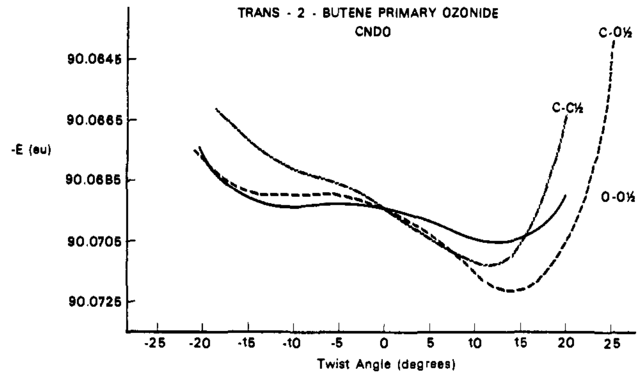

Figure 6. CNDO/2 results for *trans*-2-butene primary ozonide half-chairs.

considered, but the differences indicated for the primary ozonide results are too large to be explained in this manner. Since CNDO/2 explicitly includes nuclear repulsions and electron repulsion contributions to the total energy, it should be more sensitive than EHT to the types of interactions important in these heterocyclic molecules. Also the cases where EHT was successful in conformational determination involve molecules with no adjacent heteroatoms.

Since, not unexpectedly, CNDO/2 and EHT give different results for the primary ozonide conformational analysis, it would be most useful to compare those two methods with a molecular conformational problem involving a heterocycle with adjacent heteroatoms. A natural choice would be a final ozonide. While early electron diffraction results[19] were not conclusive, recent microwave data provide the geometry of ethylene ozonide.[30]

Ethylene Ozonide Conformational Analysis

Kuczkowski and Gillies recently reported the microwave structure for ethylene ozonide;[30] the results are summarized in Figure 7 and Table V. The molecule has C_2 symmetry with nonequivalent hydrogen atoms; the hydrogen atom labeled H_A is the equatorial hydrogen. The carbon–peroxide oxygen bond length, 1.395 Å, is smaller than most carbon–oxygen bond lengths in heterocycles and adds to the arguments against the choice of geometry in the previous primary ozonide conformational calculations.[5,22] This geometry was modified slightly to obtain internal consistency. The O–O–C angle used here is 99.22°; this is within experimental error and guarantees that the epoxide oxygen position is the same regardless of which direction around the ring one goes in determining the coordinates of this atom. This also modifies the C–O–C angle to 102.85°, again clearly within experimental error.

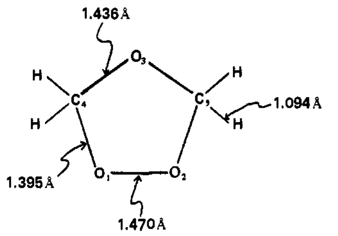

Figure 7. Experimental ethylene ozonide geometry (oxygen half-chair, C_2 symmetry).

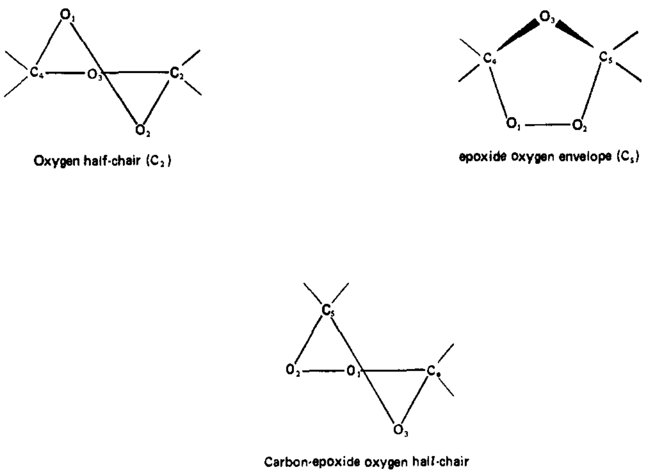

Figure 8. Ethylene ozonide conformers.

Table V. Ethylene Ozonide Geometry

Bond angle	Deg	Dihedral angle	Deg
C–O–C	102.83	C_4–O_3–C_5–O_2	16.60
C–O–O	99.23	C_5–O_2–O_1–C_4	50.24
O–C–O	106.25	O_3–C_4–O_1–O_2	41.27
H–C–H	112.93	C_4–O_3–C_5–H_A	132.09
O_3–C–H_A	109.43	C_4–O_3–C_5–H_B	103.90
O_3–C–H_B	109.08		

The planar molecule is formed by flattening out the ring and pushing the two carbon atoms into the plane of the three oxygen atoms. This yields the following ring angles: O–O–C, 108.56°; O–C–O, 106.25°; and C–O–C, 110.38°. The C–O–C–H dihedral angles for the hydrogens were taken to be 120 and 240°. Other angles and bond lengths were the same as the experimental geometry. For reasons to be discussed below, a planar geometry with average O–C–H angles was also used; in all other aspects, the second planar geometry is identical with the one described above.

Three conformers of the ethylene ozonide were considered: the C_2 oxygen half-chair, the C_s epoxide oxygen envelope, and the carbon–epoxide oxygen half-chair. These conformers are illustrated in Figure 8. The oxygen half-chair is constructed by pushing C_4 below the O_1–O_2–O_3 plane and pulling C_5 above it. The shape of the conformer is defined by a twist angle

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(30) R. L. Kuczkowski and C. Gillies, *J. Amer. Chem. Soc.*, **94**, 7609 (1972).

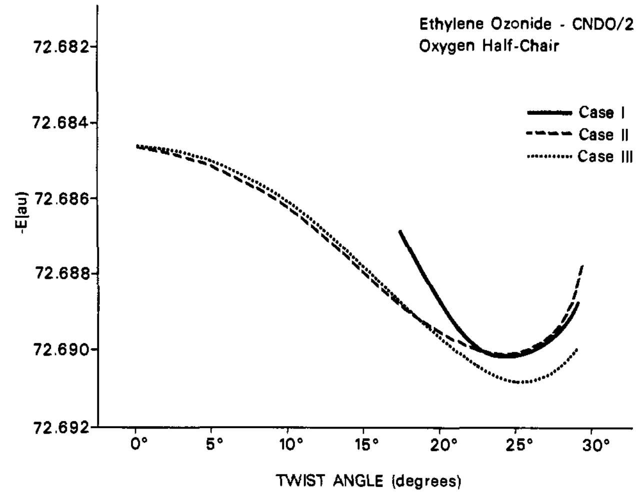

Figure 9. CNDO/2 calculations for three slightly different oxygen half-chair geometries of ethylene ozonide.

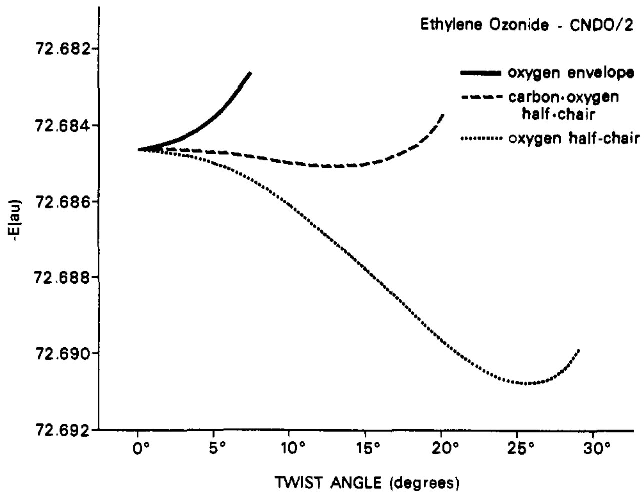

Figure 10. CNDO/2 calculations for three ethylene ozonide conformers.

which is a dihedral angle between two planes within the molecule. For the oxygen half-chair this twist angle is the dihedral angle between the O_1–O_2–O_3 plane and the O_1–O_2–C_5 or O_1–O_2–C_4 plane; experimentally the twist angle was found to be 25.12°.

Three slightly different geometries were investigated with the oxygen half-chair. Case I consisted of using experimental C–O–C–H dihedral angles for twist angles close to the experimental twist angle; it is only appropriate in this region because one would expect the C–O–C–H dihedral angle to change with changes in the twist angle. Case II takes into account the change in C–O–C–H with twist angle. Starting at 120 and 240 ° in the planar conformation, case II C–O–C–H angles are made proportional to the twist angle so that at 25.12° the dihedral angles are equal to the experimental dihedral angles. Since there is no experimental evidence for the epoxide oxygen envelope or carbon–epoxide oxygen half-chair, there is no external method which can be used to fix the C–O–C–H angles. Therefore they need to be calculated and are defined as 120 and 240° minus the C–O–C–O dihedral angle; the latter dihedral angle is calculated from ring geometry for each twist angle. In addition average O–C–H angles (109.255°) are used for these conformers as there is no way to determine if or how the hydrogens are not equivalent. Case III for the oxygen half-chair, then, consisted of using C–O–C–H dihedral angles calculated in the same way as for the other conformers studied and using average O–C–H angles.

The epoxide oxygen envelope and carbon–epoxide oxygen half-chair were investigated using geometries determined in the manner described above and used in case III oxygen half-chair. The oxygen envelope is formed by pulling O_3 out of the C_4–O_1–O_2–C_5 plane; the twist angle is defined as the dihedral angle between the O_1–O_2–O_3 plane and the C_4–O_1–O_2–O_5 plane. The carbon–epoxide oxygen half-chair is formed by pushing O_2 below the C_5–O_3–O_1 plane and pulling C_4 above it (see Figure 8). The C_4–O_3–C_5–O_2 dihedral angle and the C_5–O_3–C_4–O_1 dihedral angles were used to fix the hydrogens on C_5 and C_4, respectively. The carbon–epoxide oxygen half-chair twist angle is the dihedral angle between the C_5–O_3–O_1 plane and the O_2–C_5–O_3 or C_5–O_3–C_4 planes. For the oxygen half-chair twist angle increments of 1° were used in locating minima; for the other two conformers increments of 5° were used.

Results. The energies of the three ethylene ozonide oxygen half-chairs are shown as a function of twist angle for the CNDO/2 method in Figure 9. The CNDO/2 results indicate that all three geometries yield essentially the same twist angle and energy for the minimum energy conformation. In contrast, the extended Hückel results show a scatter in both twist angle and minima. The differences between the three geometries is small in the vicinity of the experimental twist angle, and the CNDO/2 calculations indicate this much more than do the EHT results. The twist angles and energies relative to planar are listed in Table VI.

Table VI. Minimum Energies of Three Ethylene Ozonide Conformers[a]

	CNDO/2		EHT	
	Twist angle, deg	*E*, kcal/mol	Twist angle, deg	*E*, kcal/mol
Oxygen half-chair (C_2)				
Case I	24	3.5	20	2.9
Case II	24	3.5	15	2.1
Case III	25	3.9	15	1.1
Epoxide oxygen envelope	No minimum		15	8.4
Carbon–epoxide oxygen half-chair	10	<0.2	20	2.4
Experimental geometry	25.12	3.5	25.12	−1.1

[a] In kcal/mol below the planer conformation.

The energy *vs.* twist angle curves for the three conformers of ethylene ozonide are shown in Figure 10. These CNDO/2 results clearly indicate that the oxygen half-chair is the lowest in energy of the three conformers; in fact the epoxide oxygen envelope does not exhibit a minimum lower than the planar conformation. The extended Hückel results, listed in Table VI, indicate the opposite order of stability of the three conformers. The results for all three conformers are summarized in Table VI. From these calculations it is

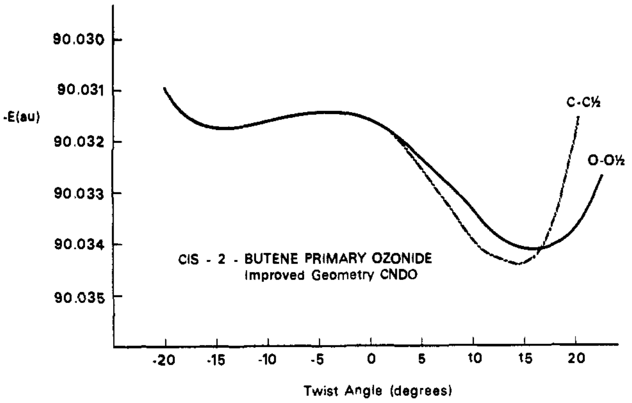

Figure 11. CNDO/2 results for *cis*-2-butene primary ozonide using the improved geometry.

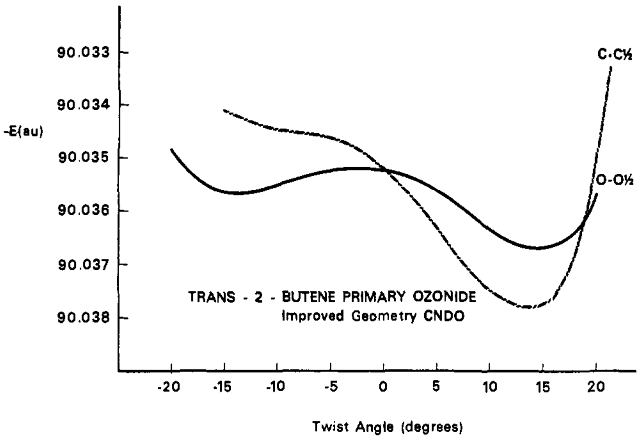

Figure 12. CNDO/2 calculations for *trans*-2-butene primary ozonide using the improved geometry.

clear that the CNDO/2 method correctly predicts the ethylene ozonide conformations while the extended Hückel theory does not. Also in Table VI are listed the energies of the oxygen half-chair experimental geometry. The CNDO/2 energy is the same to two significant figures as cases I and II but slightly lower when the absolute energies are compared. The extended Hückel experimental energy is actually above the planer energy.

Improved Primary Ozonide Geometry

Since the initial geometry used for the primary ozonide calculations was not accurate, an improved geometry was used to investigate several conformers of 2-butene primary ozonide. The new geometry was synthesized from the work of Kuczkowski and Gillies[30] and from five-membered ring geometries reported by Eliel and Knoeber.[9] The following ring bond lengths were chosen: C–O, 1.39 Å, O–O, 1.47 Å, and C–C, 1.52 Å. Other C–C distances were 1.54 Å and C–H distances were 1.09 Å. The C–O–O bond angle was chosen to be 107°; this yields a O–C–C angle of 108.2° and a O–O–O angle of 109.6° in the planer conformation. This choice of geometry also yields angles characteristic of nonplanar five-membered rings, for instance, the O–C–C angle of 102.8° at the 20° twist angle of the carbon and oxygen half-chairs. The former was chosen because it was used by Bailey, *et al.*, to illustrate their proposed ozonolysis mechanism and has clearly identifiable axial and equatorial positions. The latter conformer is the one found experimentally for ethylene final ozonide and has pseudo-axial and pseudo-equatorial positions typical of most ozonide conformers. Both *cis*- and *trans*-2-butene primary ozonides were studied. Calculations were performed at 5° intervals.

Results. The energies of the *cis*-2-butene primary ozonide half-chair using the improved geometry are presented in Figure 11. The twist angles are defined as before. The results are similar to those obtained with the crude geometry: minima are predicted for conformers which place a methyl group in an equatorial or pseudo-equatorial position (positive twist angle half-chairs). No or small minima were observed for negative twist angles; hence ring geometry does not affect this result, contrary to earlier predictions.

The conformers of *trans*-2-butene primary ozonide are shown in Figure 12. Again results closely parallel those using the crude geometry. Minima observed for positive twist angles represent conformers where both methyl groups are clearly equatorial (carbon half-chair) or pseudo-equatorial (oxygen half-chair). While the results with the improved geometry are not markedly different from those with the crude geometry, they do confirm, using a more accurate geometry, the fact that the carbon and oxygen half-chairs are very close in energy, certainly close enough to have similar populations at the temperatures present during ozonolysis reactions and much closer than indicated by previous EHT calculations, which had predicted differences of 5 to 17 kcal/mol. Hence one cannot assume that a primary ozonide conformer with clearly defined axial and equatorial positions (carbon half-chair) is the dominant conformer. Other conformers without such clearly defined substituent positions are present in essentially the same concentration. To the Bailey, *et al.*, ozonolysis mechanism, these results mean that primary ozonide conformers in which one cannot clearly identify which substituent would produce syn or anti zwitterions are present in concentrations comparable to the carbon half-chair, the only conformer with clearly identifiable axial and equatorial positions. Hence one would expect that many primary ozonide molecules would decompose to zwitterions following a route different from that proposed by Bailey, *et al.*

Table VII. Summary of CNDO/2 for *cis*- and *trans*-2-Butene Primary Ozonide with the Improved Geometry[a]

	Isomer[a]			
	Trans		Cis	
Conformer	Twist angle, deg	E, kcal/mol	Twist angle, deg	E, kcal/mol
Carbon half-chair	15	1.6	15	1.8
	nm	nm	a	a
Oxygen half-chair	15	0.9	15	1.7
	−15	<0.5	−15	<0.5

[a] Energies in kcal/mol below planer conformation. [b] nm = no minimum found for this conformer. a = no separate conformer by symmetry.

Conclusion

A consideration of all twelve conformers of *cis*- and *trans*-2-butene primary ozonide (a 1,2,3-trioxolane) using EHT and CNDO/2 methods has yielded conflicting results for the geometry and relative stability of the conformers. When these two semiempirical methods are applied to ethylene ozonide (a 1,2,4-trioxolane), the CNDO/2 accurately predicts the experimental conformation while EHT does not. These two results clearly indicate that earlier studies of primary ozonide conformation and the associated conclusions concerning the mechanism of ozonolysis of olefins need to be reconsidered. This reconsideration included the use of a more reliable geometry for the primary ozonide ring. The improved relative stabilities of the primary ozonide conformers are similar to those obtained using the crude geometry and confirm that conformers with pseudo-axial and pseudo-equatorial substituent positions are present in concentrations similar to conformers with clearly defined axial and equatorial positions. These conclusions raise questions concerning the ozonolysis mechanism proposed by Bailey, *et al.*

Acknowledgments. I thank Robert W. Murray for many helpful discussions which led to these calculations, John R. Sabin for the CNDO/2 computer program, and Robert L. Kuczkowski for making the microwave structure of ethylene ozonide available before publication. The University of Missouri—St. Louis Computer Center provided a grant under which these calculations were performed.

Electronic Structure of Reactive Intermediates. The Nitrenium Ions NH_2^+, NHF^+, and NF_2^+ [1]

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Abstract: The nitrenium ions NH_2^+, NHF^+, and NF_2^+ have been studied using *ab initio* techniques and have been compared with the isoelectronic carbenes CH_2, CHF, and CF_2. We find the triplet ground state of NH_2^+ (150°) 45 kcal/mol below the singlet (120°), while the singlet ground state of NF_2^+ (105°) is 33 kcal/mol below the triplet (122°). The ordering of the multiplicities is essentially in accord with the isoelectronic carbenes and as in CHF the singlet and triplet states of NHF^+ are essentially degenerate, the triplet (135°) lying 4 kcal/mol below the singlet (107°), an inversion of the carbene order. We find that although fluorine substitution destabilizes both the singlet and triplet states the triplets are destabilized to a greater extent. The effects contributing to the destabilization are analyzed and quantified. Finally, an analysis of the charge distribution indicates that the charge on the N atom varies from +0.10 to +0.96 as we go from NH_2^+ to NF_2^+.

Nitrenium ions[3] are compounds bearing a positive charge and containing a formally divalent nitrogen atom. For every nitrenium ion there is an isoelectronic carbene obtained by decreasing the divalent nitrogen's atomic number from 7 to 6. There is also an isomorphic relationship between nitrenium ions and primary and secondary carbonium ions, the former being obtained from the latter by coalescing a proton and the carbon nucleus formally associated with the carbonium ion center. The resulting nitrenium ion is isoelectronic with the parent carbonium ion and also hosts a positive charge. Whether one traces the nitrenium ion's lineage to a carbene or carbonium ion one anticipates that insight into the chemistry of the nitrogen species will accrue from a careful analysis of the parent–offspring electronic structure.

In this study we will concern ourselves with the nitrenium ions NH_2^+, NHF^+, and NF_2^+ and the corresponding isoelectronic carbenes CH_2, CHF, and CF_2.

Calculations

For N and F we use the gaussian-lobe function representation of Huzinaga's[4] 9s,5p set contracted to 4s,2p while for H we use his 4s set contracted to 2s. All contractions are as recommended by Dunning.[5] A common scale factor of 1.2 was obtained for both hydrogen functions by optimizing the SCF energy for the $^1A_1$ state of NH_2^+. This scale factor will be used in all calculations reported.

A N–H distance of 1.9055 au was obtained by optimizing the SCF energy of the $^1A_1$ state of NH_2^+ while a N–F distance of 2.5766 au was assumed. The Hartree–Fock–Roothaan[6] equations were solved for the lowest doubly occupied singlet state of NH_2^+, NHF^+, and NF_2^+ in the previously described basis as a function of angle. The results are presented in Figure 1 along with the results for the isoelectronic carbenes.[7]

In all cases the highest occupied MO has a significant nitrogen lone-pair component, and we will refer to this orbital as the σ_1 MO. So in NH_2^+, $\sigma_1 \equiv 3a_1$, in NHF^+, $\sigma_1 = 7a'$, while in NF_2^+ it is $6a_1$. Also, the lowest empty MO is essentially a N p orbital perpendicular to

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[1] Supported in part by a grant from Research Corporation.

[2] National Science Foundation Undergraduate Research Participant, summer 1971.

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[4] (a) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965). (b) By "lobe function representation" we mean that each nuclear centered p orbital is replaced with an antisymmetric combination of 1s gaussians, the exponent (α) being the same as that of the p function being mimicked while the lobe separation is taken as 0.03 $\alpha^{-1/2}$ following J. D. Petke, *et al.*, *J. Chem. Phys.*, 51, 256 (1969).

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