Theoretical determination of molecular structure and conformation. III. The pseudorotation surface of 1,2,3-trioxolane and 1,2,4-trioxolane[a)]

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The potential surfaces of 1,2,3-trioxolane (primary ozonide) and 1,2,4-trioxolane (final ozonide) have been explored by *ab initio* MO theory using large augmented basis sets. Extensive optimization of geometry has been perfomed with and without polarization functions. Results indicate that the latter are necessary in order to obtain reliable theoretical predictions with regard to the degree and mode of puckering of the two five-membered rings and with regard to their conformational barriers. Contrary to previous quantum chemical calculations the envelope form (C_s symmetry) of the primary ozonide is found to be the most stable conformation. Pseudorotation is hindered by a barrier of 3.5 kcal/mole which is about half as high as the barrier to planarity (7.7 kcal/mole). Similar barrier heights are calculated for the final ozonide (3 kcal/mole vs 6 kcal/mole), but in this case the twist conformation (C_2 symmetry) corresponds to the conformational minimum. The electronic features determining the conformational tendencies of the trioxolanes are analysed in detail using hydrogen trioxide and hydrogen peroxide as alicyclic model compounds.

I. INTRODUCTION

Among the cyclic polyoxides, the trioxolanes certainly play the most prominent role. Since 1942, when Rieche[1] confirmed that one group of reaction products of ozone and olefins in solution possesses the constitution of 1,2,4-trioxolanes, they have found widest chemical interest. One decade after Rieche's studies, Criegee[2] made his famous proposal in which he described the ozonolysis by a three-step mechanism. According to Criegee, the reaction receives its exotic nature by the conversion of an initially formed 1,2,3-trioxolane, the so-called primary ozonide, to a 1,2,4-trioxolane, the so-called final ozonide. About 25 years of experimental work have substantiated the Criegee mechanism as the major reaction path for the ozonolysis in solution. However, mechanistic refinements have also proved to be necessary in order to account for the stereospecificity of the reaction. Bailey *et al.*[3] pointed out that nonplanar conformations of the intermediate trioxolanes are crucial. Assuming conformation If (Fig. 1) for the primary ozonide and conformation IIb for the final ozonide, they were capable of explaining most of the available experimental data.

Convincing experimental evidence has been given for the actual formation of the 1,2,3-trioxolanes by cycloaddition of ozone to the CC double bond of an alkene.[4] But due to their high instability even at low temperatures no conformational study has been successful. Therefore, various theoretical attempts have been made to verify assumptions concerning the preference of certain trioxolane conformations.

Using the EHT method, Renard and Fliszár[5] investigated two modes of puckering of the 1,2,3-trioxolane ring. A comparison of the calculated conformational energies showed the twist form If of the primary ozonide to be far more stable than the envelope form Ia which was in line with the first of the Bauld–Bailey assumptions. Later, Rouse[6] doubted the adequacy of the EHT method for heterocycles with adjacent hetero atoms. He demonstrated that CNDO/2 calculations yield a different order of stabilities than that obtained with EHT. For the conformers of *cis*- and *trans*-2-butene primary ozonide, conformations Id and Ic were found to be lowest in energy. Recently, complete optimization of all structural parameters of 1,2,3-trioxolane has been performed by Klopman and Andreozzi at the MINDO/3 level of theory.[7] Their computed equilibrium structure suggests a planar ring slightly distorted from C_{2v} symmetry.

Two *ab initio* studies have been published on the primary ozonide. The first, by Leroy and Sana,[8] was pri-

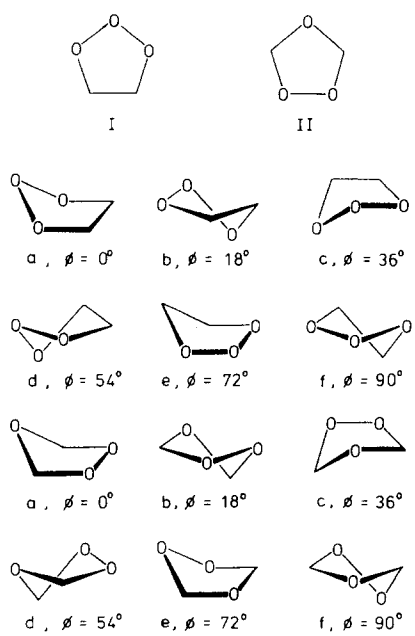

FIG. 1. Conformations of 1,2,3-trioxolane (I) and 1,2,4-trioxolane (II).

[a)]Paper II: D. Cremer, J. Chem. Phys. **69**, 4456 (1978), and referred to as Paper II throughout text.

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marily designed to describe the transition state of the ozone–alkene cycloaddition process. Only the energy of the planar primary ozonide is quoted by the authors. The second study, published by Hiberty,[9] heavily relied on an orbital symmetry analysis given by Lattimer, Kuczkowski, and Gillies[10] who attributed a key role to the asymmetrical conformation Ic in the decomposition of the primary ozonide. Actually, Hiberty's calculations confirmed this conformation to be more stable by almost 3 kcal/mole than the twist form If if the minimal STO-3G basis was employed. However, an improvement of the basis set to split valence shell quality reduced this energy difference to 1 kcal/mole. No attempt was made to find out whether other conformations of lower energy exist.

While the first Bauld–Bailey assumption is neither verified nor contradicted by theory,[11] their description of the most probable 1,2,4-trioxolane conformation is at variance with experimental observations. A first analysis of gaseous 1,2,4-trioxolane by the electron diffraction method[12] was not very conclusive since experimental intensity values could satisfactorily be fitted both to a symmetrical twist (C_2) and an envelope (C_s) model of the molecule. The x-ray crystal structure determination of 3-carbomethoxy-5-anisyl-1,2,4-trioxolane proved similarly inconclusive with regard to conformation.[13] The first unambiguous evidence about the structure and conformation of the final ozonide was gathered by Gillies and Kuczkowski.[14] By means of an analysis of the microwave spectra of seven isotopic species of ethylene ozonide, conformation IIf of the molecule was established. This conformation was also found for propene ozonide and *trans*-2-butene ozonide.[10] No experimental evidence of either ring inversion or pseudorotation could be obtained from the experimental spectra.

Theoretical investigations of 1,2,4-trioxolanes have been performed with the Westheimer–Hendrickson model[15] and the semiempirical CNDO/2 method,[6,16] both attributing conformational preference to IIf. A MINDO/3 calculation of the equilibrium geometry of II comes to the conclusion that the molecule is nonpuckered.[7] No *ab initio* study has been reported so far on 1,2,4-trioxolanes.

Recently, we have evaluated the internal rotational potential of hydrogen trioxide employing a large augmented basis set and correcting the single determinant restricted Hartree–Fock (RHF) values for possible correlation errors. [See Paper II, reference citation a) of this paper.] From an investigation of the rotational modes of the geminal double rotor, we concluded that H_2O_3 is well-suited as a model compound for 1,2,3-trioxolane. The expected relationship between the conformational tendencies of both molecules led us to the prediction that the C_s envelope rather than the C_2 twist form of the primary ozonide should be located at the minima of the conformational surface. In addition, we were able to predict a barrier to pseudorotation of about 3–4 kcal/mole and a barrier to inversion about twice as large.

Since our predictions are at variance with the reported quantum chemical studies of the primary ozonide, the principal aim of this paper is the theoretical verification of our previous assumptions. We will approach this objective by first establishing a well-defined conformational model of the five-membered ring, then by studying the effects of geometry optimization and basis set enlargements and, finally, by analyzing the electronic features which dominate the conformational tendencies of compounds I and II. The conclusions drawn out of this analysis should aid a theoretical treatise of the ozonolysis mechanism.[17]

II. THE CONFORMATIONAL MODEL USED FOR TRIOXOLANES

Both trioxolanes under consideration possess nine atoms and, hence, 21 internal degrees of freedom. In order to get the most accurate and complete picture of the conformational tendencies of the two ring compounds, a rather extensive scan on the complete hypersurface would be necessary. As this is prohibited because of computational reasons one has to decide whether to cut down on the accuracy of a single point or to reduce the number of points to be calculated. The latter is possible if a conformational model is used which defines the number of unique conformational modes of a ring of size N (N = number of ring atoms) and relates these modes to a subset out of the complete set of the internal ring coordinates. By definition, this subset of internal coordinates should account for most of the conformational flexibility of the ring and, hence, span the conformational space of the N-membered ring. A less time consuming evaluation of the conformational potential V can be performed by mapping the $3N$-6 dimensional hypersurface onto the conformational subspace. In a first approximation to V, only changes in the subspace coordinates are considered for the description of the conformational modes of the ring. Later, a refinement of V may be achieved by regarding all degrees of freedom of conformations with unique energy properties, i.e., for minima, maxima, and saddlepoints of the surface.

Recently, we have proposed the concept of ring puckering coordinates.[18] According to this, a N-membered ring possesses a subset of N-3 puckering coordinates spanning its conformational space. If N is odd, the total conformational space can be divided into (N-3)/2 pseudorotational subspaces each of dimension 2. A subspace is spanned by the puckering coordinates q ($q > 0$) and ϕ, the first describing the degree and the second the mode of ring puckering.

In case of a five-membered cyclic trioxide, just a single (q, ϕ) pair has to be considered.[19] Setting $\phi = 0°$ and $\phi = 90°$ for $q > 0$ and numbering the ring atoms according to Fig. 2,[20] two basis conformations are defined, namely the envelope form Ia (IIa) and the twist form If (IIf) of Fig. 1. These conformations are located at the axes of the pseudorotational space while the planar form is at its origin. Every ring conformation out of the N-3 dimensional (q, ϕ) space can be viewed as a "linear combination of the basis forms" a and f characterized by the values of q and ϕ. An interconversion of the envelope form with $\phi = 0°$ to the twist form with $\phi = 90°$ may traverse the conformations with $\phi = 18°$, 36°, 54°, and 72° which are also shown in Fig. 1.

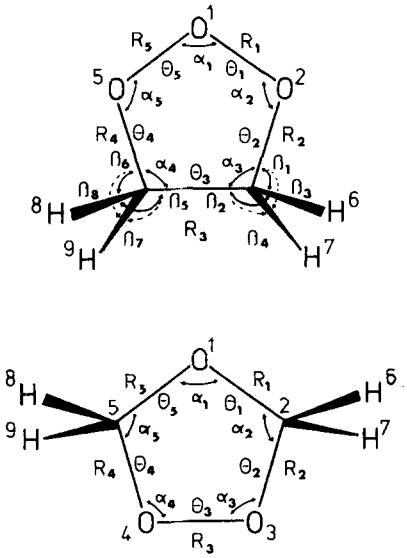

FIG. 2. Numbering of ring atoms and definition of geometrical parameters.

The Cartesian coordinates of conformations a–f have been evaluated by defining an unique mean plane of the puckered five-membered ring.[18] The atom displacements z_i perpendicular to the mean plane are related to the puckering coordinates by[18]

$$z_i = (\tfrac{2}{5})^{1/2} q \cos(\phi + 4\pi(i-1)/5)\,. \tag{1}$$

By means of the z_i values, the lengths of the five ring bonds, and two of the ring angles the remaining coordinates have been determined.

The pseudorotational potential V is analytically described by using a truncated Fourier expansion in ϕ. Then, the dependence of each Fourier term V_h on the puckering amplitude q is expressed by a Taylor series. Thus, the potential $V(\phi, q)$ can be written as[18]

$$V(\phi,q) = V_{00} + V_{02}q^2 + V_{04}q^4 + V_{22}q^2\cos 2\phi + V_{24}q^4\cos 2\phi + V_{42}q^2\cos 4\phi + V_{44}q^4\cos 4\phi + \cdots . \tag{2}$$

Equation (2) is used to describe the conformational surface of both primary and final ozonide.

III. COMPUTATIONAL DETAILS

All calculation have been performed on the basis of single determinant restricted Hartree–Fock (RHF) theory[21] which has previously been shown to give satisfactory conformational energies for H_2O_2[22] and H_2O_3 (Paper II) due to a cancellation of intrapair and interpair correlation contributions to the *ab initio* barriers to internal rotation. A series of basis sets has been used with successive refinements of the theory. First estimates on both structure and conformation have been gained with Pople's minimal STO-3G basis set,[23] henceforth called basis *A*. Basis *B* possesses split valence quality and represents a $(8s4p/4s)$ $[3s2p/2s]$[24] contracted basis of Gaussian type functions (GTF).[25] It has been shown[22] (and Paper II) that *B* provides reasonable estimates of experimental OO bond lengths due to a fortuitous cancellation of errors in theory and basis set. To obtain reliable energies for polyoxides the inclusion of polarization functions in the basis is mandatory. For this purpose, we have employed two further basis sets, namely basis *C* and *D*. Basis *C* includes six *d*-type GTF's on nonhydrogenic atoms as well as more precise inner-shell functions than *B*. It may be described as a $(10s4p1d/4s)$ $[3s2p1d/2s]$ contracted GTF basis.[26]

The most elaborate basis used in this work is basis *D*. It has been derived from Dunning's double-ζ basis[27] by adding a set of *d*-type polarization functions to the heavy atoms and a set of *p*-type polarization functions to the hydrogens, thus giving a $(9s5p1d/4s1p)$ $[4s3p1d/2s1p]$ basis. Scale factors of basis *D* have been optimized using H_2O_2[22] and CH_4 as reference molecules. Table I summarizes the corresponding ζ values which have been employed for compounds I and II in order to get accurate energies of near HF quality.

Our procedure to explore the conformational surface is as follows. First, we have fixed the ring puckering angle ϕ to multiples of $\pi/10$. For $\phi = 0°$ or $90°$, this implies C_s or C_2 symmetry of the ring. Then, the puckering amplitude and the remaining degrees of freedom of the ring framework have been optimized (see definition of parameters in Fig. 2), including also the case where q is held at a zero value, i.e., optimization of the planar ring. As for the geometry of the CH_2 groups, preliminary tests showed that the CH bond lengths hardly change with q and ϕ and can, therefore, be set to a standard value of 109 pm for both molecules. Since the destabilization resulting from methylene group eclipsing turned out to be an important portion of the overall stability of the molecule, all external bond angles, which determine the position of the H atoms relative to the ring, have been optimized for the primary ozonide. For the final ozonide, the positions of the hydrogen atoms are less crucial, thus justifying a CH_2 geometry with the angle HCH being tetrahedral and the remaining angles preserving local C_{2v} symmetry.

After an initial guess of the C_s and C_2 conformations had been obtained with basis *A* a complete optimization of the conformations Ia–If and IIa–IIf was performed with basis *B*. The determination of the degree of puck-

TABLE I. Scale factors used for the contracted GTF's of basis set *D*.[a]

GTF	Oxygen	Carbon	GTF	Hydrogen
s	1.0	1.0	*s*	1.235
s'	1.001	1.0	*s'*	1.241
s''	0.824	1.0	*p*[b]	1.074
s'''	0.862	1.0		
p	1.018	1.0		
p'	1.014	1.0		
p''	0.995	1.0		
d[b]	0.976	0.935		

[a]Exponents α of basis *D* are given in Ref. 27.
[b]Scale factors of polarization functions correspond to values of $\alpha = 1.0$. If $\zeta = 1.0$, the following exponents result according to $\zeta^{GAUSS} = \zeta^2\alpha$: $\alpha(d_O) = 0.953$; $\alpha(d_C) = 0.874$; $\alpha(p_H) = 1.154$.

TABLE II. Total energies (hartree) (*A*) and relative energies (kcal/mole) (*B*) of 1,2,3-trioxolane and 1,2,4-trioxolane.

Molecule	Pseudo-rotation angle ϕ	Symmetry	Basis *A* [2*s*1*p*/1*s*]	Basis *B* [3*s*2*p*/2*s*]	Basis *C* [3*s*2*p*1*d*/2*s*]	Basis *D* [4*s*3*p*1*d*/2*s*1*p*]
			A.			
1,2,3-trioxolane	planar	C_{2v}	−298.59416	−301.98090	−302.40996	−302.49607
	0°	C_s	−298.60614	−301.98900	−302.42252	−302.50832
	18°	C_1		−301.98890		
	36°	C_1		−301.98865		
	54°	C_1		−301.98823		
	72°	C_1		−301.98796		
	90°	C_2	−298.59671	−301.98785	−302.41769	−302.50281
1,2,4-trioxolane	planar	C_{2v}	−298.63160	−302.06102	−302.50567	−302.59000
	0°	C_s	−298.63463	−302.06298	−302.51042	−302.59474
	18°	C_1		−302.06320		
	36°	C_1		−302.06398		
	54°	C_1		−302.06531		
	72°	C_1		−302.06691		
	90°	C_2	−298.63855	−302.06788	−302.51567	−302.59959
			B.			
1,2,3-trioxolane	planar	C_{2v}	7.52	5.08	7.88	7.69
	0°	C_s	0	0	0	0
	18°	C_1		0.07		
	36°	C_1		0.22		
	54°	C_1		0.48		
	72°	C_1		0.65		
	90°	C_2	5.92	0.72	3.03	3.46
1,2,4-trioxolane	planar	C_{2v}	4.36	4.30	6.28	6.02
	0°	C_s	2.46	3.08	3.30	3.04
	18°	C_1		2.69		
	36°	C_1		2.45		
	54°	C_1		1.62		
	72°	C_1		0.61		
	90°	C_2	0	0	0	0

ering of C_s and C_2 forms was repeated by reoptimization of the crucial parameters q and α_1, with basis *C* holding all other parameters at the basis *B* values. Finally, single point calculations for the best geometries thus obtained were implemented with basis *D*.

All calculations have been performed with the *ab initio* program package COLOGNE 76.[28,29] A direct energy minimization technique had to be used to obtain convergence for RHF/basis *D* calculations. For this purpose a program based on the univariate search method of Seeger and Pople[30] was written by the author. An efficient optimization of the structural parameters was achieved with a Quasi-Newton algorithm which represents an improved version of the complementary Davidon–Fletcher–Powell method.[31] This procedure is incorporated into COLOGNE 76 together with the program RING[32] which uses the concept of ring puckering parameters. The study of the conformations with C_1 symmetry demanded the optimization of a maximum of 16 parameters (I). Due to carefully chosen initial guesses not more than three optimization cycles were necessary to achieve an accuracy of 0.2 pm for bond lengths and 0.2° for bond angles.

IV. RESULTS AND DISCUSSION

Results obtained by the procedure outlined in Sec. III are summarized in the Tables II–VI. Table II.A contains the total energies computed with basis sets *A*–*D* while Table II.B lists energies relative to the conformational minima of 1,2,3-trioxolane and 1,2,4-trioxolane. Tables III and IV depict the structures of minimum, maximum, and saddlepoint conformations. Equilibrium geometries obtained with basis *B* for the C_1 conformations b, c, d, and e are shown in Tables V (primary ozonide) and VI (final ozonide).

A. 1,2,3-Trioxolane

At all calculational levels, puckered forms of the primary ozonide are found to be more stable than the planar ring. Contrary to the results of other quantum chemical calculations so far published,[5–9] the envelope conformation turns out to correspond to the global minimum of the potential surface. Pseudorotation of the ring is the energetically favored interconversional process. It is hindered by a barrier determined by the relative energy of the twist form. The barrier to inversion through the planar form is 2–4 kcal/mole higher than the barrier to

TABLE III. RHF structural parameters for 1,2,3-trioxolane (distances in picometer, angles in deg).[a]

ϕ, deg	Symmetry	Parameter	Basis A[b]	Basis B	Basis C
planar	C_{2v}	α_1	111.3	107.9	108.6
		α_2	108.7	109.3	108.8
		α_3	105.6	106.7	106.9
		R_1	141.0	146.3	
		R_2	144.5	143.2	
		R_3	154.9	154.2	
		β_1		107.8	
		β_2		111.9	
0	C_s	q	45.1	43.2	47.0
		α_1	103.8	101.8	101.3
		α_2	102.4	103.9	102.3
		α_3	102.8	104.2	104.1
		θ_1	49.5	45.1	48.9
		θ_2	28.8	27.5	29.5
		θ_3	0	0	0
		R_1	140.2	145.4	
		R_2	145.3	143.7	
		R_3	156.1	155.1	
		β_1		109.7	
		β_2		111.9	
		β_3		106.5	
		β_4		113.4	
90	C_2	q	31.9	39.2	41.6
		α_1	110.4	106.1	106.6
		α_2	106.6	106.0	105.0
		α_3	102.6	102.4	101.9
		θ_1	11.1	13.6	14.3
		θ_2	27.1	33.7	35.5
		θ_3	33.2	41.9	44.6
		R_1	141.2	147.4	
		R_2	144.5	143.3	
		R_3	154.2	151.8	
		β_1		110.0	
		β_2		112.1	
		β_3		106.5	
		β_4		114.0	

[a]Only absolute values of calculated dihedral angles are given in Tables III–VI.
[b]β parameters have not been optimized.

pseudorotation depending on the basis set employed and the degree of optimization.

Since our predictions (see Paper II) deduced from a study of the internal rotational potential of H_2O_3 are confirmed, we conclude that the same electronic features dominate the conformational behavior of both trioxides, namely dipole–dipole interactions between OX (X = H, C) bond dipole moments and lone pair delocalization out of the p_π(O) orbitals into suitably oriented polar bonds.[33] In the planar form, destabilizing dipole–dipole repulsion associated with the two O–CH_2 groups of the molecule is highest. Destabilization is reinforced by the eclipsing of the methylene groups, although this effect probably contributes only a small fraction to the total driving force for puckering. At least, this is suggested by the energy of the *syn*-periplanar (*sp*, *sp*) form of H_2O_3 (22 kcal/mole) (Paper II) and the one of eclipsed ethane (3 kcal/mole)[34] each seen relative to the energies of their conformational minimum. Puckering of the ring should provide the opportunity to lower dipole–dipole repulsion and, in addition, to gain some stabilization due to a hyperconjugative interaction of the lone pair p_π orbital of atoms O(2) or O(5) with the σ^* orbital of the neighboring OO bond. The hyperconjugative effect increases with increasing torsion around the OO bonds tending to a maximum if the p_π(O) and the σ^*_{OO} orbital are coplanar which, of course, is not possible for the ring.

According to the observations made for H_2O_3, we expect the lone pair delocalization to show up in the computed OO bond lengths (Tables III and V). The shortest OO distances are found for phase angles between $\phi = 18°$ and $\phi = 54°$ (basis B, $R_1 = 144.9$ to 145.4 pm). Ring conformations characterized by these ϕ values exhibit a

TABLE IV. RHF structural parameters for 1,2,4-trioxolane (distances in picometer, angles in deg).

ϕ, deg	Symmetry	Parameter	Basis *A*	Basis *B*	Basis *C*
planar	C_{2v}	α_1	106.2	111.4	109.9
		α_2	109.1	106.7	107.8
		α_3	107.8	107.6	107.2
		R_1	143.4	141.7	
		R_2	145.1	144.1	
		R_3	140.6	146.9	
0	C_s	q	31.4	28.6	35.0
		α_1	102.2	106.9	103.4
		α_2	106.7	105.4	105.8
		α_3	106.3	106.1	105.0
		θ_1	32.8	31.2	37.6
		θ_2	20.7	18.7	23.1
		θ_3	0	0	0
		R_1	143.2	141.5	
		R_2	145.3	143.9	
		R_3	141.1	147.6	
90	C_2	q	40.1	41.0	44.7
		α_1	104.0	107.9	105.8
		α_2	106.2	104.6	105.4
		α_3	102.2	101.7	100.2
		θ_1	13.5	14.0	15.3
		θ_2	36.3	35.6	38.9
		θ_3	43.7	44.2	47.4
		R_1	144.2	142.6	
		R_2	144.9	143.3	
		R_3	140.2	146.7	

strong torsion at the bond O(1)O(2), being of the order of 40°, and a 10°–20° lower torsion at the bond O(5)O(1). Consequently, the lone pair of O(2) more strongly interacts with the σ^*_{OO} orbital of the neighboring OO bond than O(5) does. This leads to a shortening of R_1 and a lengthening of R_5 (relative to R_1 of the C_{2v} form) due to a shift of electron charge into the antibonding OO orbital. The resulting net stabilization for the molecule is reflected by the differences $R_1(q=0) - R_1(q_{opt})$ and $R_5(q=0) - R_5(q_{opt})$ for a given value of the phase angle ϕ. Both differences decrease for $\phi \to 90°$, thus indicating a low hyperconjugative stabilization of the C_2 form of I.

The puckering mode with $\phi = 90°$ always allocates the strongest torsion to the bond intersected by the C_2 axis but it keeps down the values of dihedral angles θ_1 and θ_2. This becomes obvious if changes of ring angles are calculated for an infinitesimal puckering of a regular pentagon according to formulas first given by Dunitz[35] (see Table VII). The analysis of the out-of-plane displacements of the pentagon further reveals that, because of $\theta_1 = \theta_5 > \theta_2 = \theta_4 > \theta_3$, the envelope form is predestined to allow for a favorable strengthening of both OO bond lengths ($R_1 = R_5 = 145.4$ pm), thus leading to an optimum hyperconjugative overall stabilization of the molecule.

Evidently, a possible interaction of the lone pair p_π(O) orbitals with σ^*_{CO} or σ^*_{CC} can be considered as neglible since both orbitals are higher in energy than σ^*_{OO}. The

TABLE V. Structural parameters of four nonsymmetrical conformations of 1,2,3-trioxolane calculated with basis *B* (distances in picometers, angles in deg).

Parameter	$\phi = 18°$	$\phi = 36°$	$\phi = 54°$	$\phi = 72°$
q	42.4	40.1	40.4	39.0
R_1	144.9	144.9	145.4	146.7
R_2	143.6	143.7	143.1	143.1
R_3	154.4	152.6	152.7	151.8
R_4	144.2	145.5	143.9	143.7
R_5	146.0	146.9	147.8	147.8
α_1	102.8	103.9	105.3	105.9
α_2	102.6	103.0	103.2	104.5
α_3	103.5	103.3	102.0	102.4
α_4	104.9	104.3	104.1	103.1
α_5	105.2	106.8	106.8	106.9
θ_1	46.7	42.0	36.0	25.3
θ_2	36.8	41.2	43.2	39.7
θ_3	13.8	25.0	34.8	39.8
θ_4	14.5	0.6	12.7	24.1
θ_5	37.7	25.8	13.5	0.3
β_1	109.6	109.5	109.7	109.9
β_2	112.4	112.2	112.6	112.3
β_3	106.8	106.8	107.0	106.5
β_4	113.6	113.5	113.7	114.0
β_5	112.3	112.8	113.1	113.8
β_6	109.5	108.5	107.8	106.8
β_7	112.8	112.4	111.9	112.0
β_8	106.5	107.2	108.5	109.4

TABLE VI. Structural parameters of four nonsymmetrical conformations of 1,2,4-trioxolane calculated with basis B (distances in picometers, angles in deg).

Parameter	$\phi = 18°$	$\phi = 36°$	$\phi = 54°$	$\phi = 72°$
q	29.3	32.3	35.2	37.6
R_1	141.3	141.7	141.7	142.2
R_2	143.3	142.6	142.5	142.3
R_3	147.4	147.2	146.8	146.7
R_4	144.4	145.0	144.8	143.8
R_5	141.5	142.0	142.3	142.8
α_1	106.7	106.7	107.2	108.2
α_2	105.4	104.7	104.0	104.0
α_3	105.1	103.9	102.9	102.0
α_4	106.5	106.3	105.1	104.1
α_5	105.8	105.9	106.0	105.1
θ_1	33.6	35.1	32.4	25.0
θ_2	26.3	33.9	38.6	38.8
θ_3	9.8	20.6	30.9	38.9
θ_4	10.2	0.3	11.5	23.7
θ_5	27.1	21.6	12.6	0.3

computed changes of the CC bond length result from different degrees of bond staggering for the conformers Ia to If. For $\phi = 0°$, CH bond eclipsing leads to a large value of R_3 (155 pm, basis B) which continuously decreases if ϕ and the torsion around the CC bond increases.

We conclude that the electronic force to pucker the trioxolane ring develops in an accumulation of negative charge in the OOO moiety and positive charge in the CH_2CH_2 bridge. Destabilizing charge repulsion and dipole–dipole interactions can be lowered by out-of-plane distortions of the planar ring. The degree and the mode of puckering are largely directed by a hyperconjugative stabilization of the nonplanar 1,2,3-trioxolane forms. The tendency for CH_2CH_2 staggering as well as the increase of bond angle strain in the puckered forms can be considered as second order effects which influence the precise values of the conformational barriers.

B. 1,2,4-Trioxolane

Experimental evidence has been given that this molecule should exist in the symmetrical twist form IIf.[10,12–14] Our calculations confirm the experimental findings at all levels of basis set sophistication (Table II.B). Also, they indicate that pseudorotation of the ring should be the preferred interconversional process hindered by a barrier of ≈3 kcal/mole. The planar form represents a local maximum of the conformational surface which lies 4–6 kcal/mole above the energy of the C_2 form.

Following the course of interpretation pursued for the primary ozonide, we explain the conformational tendencies of the ring by the electronic features of the peroxy bridge. Hydrogen peroxide is the appropriate alicyclic rotor to compare it with. The energy variation resulting from a rotation of *syn* H_2O_2 to its skewed form (7.5 kcal/mole),[22] though three times lower than the corresponding value for H_2O_3, exceeds the rotational barrier of CH_3OH (1.2 kcal/mole)[34] by more than 6 kcal/mole. Again, we consider dipole–dipole interactions due to a charge separation along the CO bonds to represent the driving force for ring puckering. A possible hyperconjugative delocalization of an electron lone pair of the peroxy bridge should provide significant stabilization of the puckered conformations. It is easy to see that this is best accomplished for $\phi = 90°$ ($\theta_3 > 40°$) while a hyperconjugative stabilization of the peroxy bridge should be absent in the envelope form ($\theta_3 = 0°$).

One piece of relevant theoretical information indicative of lone pair delocalization is provided by the dependence of the OO bond distance on ϕ. For $\phi = 0°$, R_3 is about 1 pm longer than for $\phi = 90°$. Thus, the strengthening of the OO bond turns out to be smaller for the final ozonide than for the primary ozonide which agrees with the hypothesis that a σ^*_{CO} orbital is less suitable to interact than σ^*_{OO} due to the higher energy of the former. A more detailed analysis of the structural parameters of Table VI reveals that the epoxy oxygen is also involved in the hyperconjugative stabilization mechanism. It has to be noted that $R_1(CO) < R_2(CO)$ is obtained with basis B while the CO bond lengths of I take an intermediate position. This ordering can be best explained if the discussion is confined to the two planar forms in order to exclude the hyperconjugative effect described above. As a result of the electronegativity difference between oxygen and carbon, negative charge is accumulated on all oxygen atoms incorporated into the ozonide rings. However, if two or more oxygen atoms are chained, charge repulsion will cushion the electron transfer from the CH_2 groups to the O atoms. According to their negative excess charges, the oxygen atoms have to be arranged in the following way (see Table VIII):

$$\text{O(epoxy)} > \text{O(peroxy)} \sim \text{O(trioxy, terminal)} > \text{O(trioxy, central)}.$$

TABLE VII. Ring angles α_j and θ_j resulting from infinitesimal out-of-plane displacements of a regular planar pentagon ($\alpha_0 = 108°$).[a]

Angle, deg	$\phi = 0°$ (C_s)		$\phi = 90°$ (C_2)		$\Delta(C_2 - C_s)$
	q(infinit.)	$q = 10$ pm	q(infinit.)	$q = 10$ pm	$q = 10$ pm
α_1	$\alpha_0 - 0.0103q^2$	106.97	$\alpha_0 + 0.0006q^2$	108.06	1.09
α_2	$\alpha_0 - 0.0066q^2$	107.34	$\alpha_0 - 0.0032q^2$	107.68	0.34
α_3	$\alpha_0 - 0.0004q^2$	107.96	$\alpha_0 - 0.0093q^2$	107.07	−0.89
θ_1	$0.1541q$	15.41	$0.0501q$	5.01	−10.40
θ_2	$0.0953q$	9.53	$0.1311q$	13.11	3.58
θ_3	0	0	$0.1621q$	16.21	16.21

[a]Angles are calculated by formulas first given by Dunitz, Ref. 35.

TABLE VIII. Gross populations of 1,2,3-trioxolane (I) and 1,2,4-trioxolane (II) obtained with basis sets *B* and *D*.

		Compound I		Compound II	
Atom	Orbital	Basis *B*	Basis *D*	Basis *B*	Basis *D*
(C)–O–(C)	total			8.716	8.484
	$2p_\pi$			1.933	1.918
(O)–O–(C)	total	8.381	8.252	8.385	8.258
	$2p_\pi$	1.965	1.954	1.965	1.955
(O)–O–(O)	total	8.040	8.033		
	$2p_\pi$	1.999	1.989		
C	total	6.016	6.004	5.669	5.759
	$2p_\pi$	1.155	1.100	1.163	1.106
H	1*s*	0.791	0.863	0.794	0.870

In order to get rid of some of the excess charge gained by an inductive withdrawal of electrons, the O atoms back-donate electrons from their $2p_\pi$ orbitals to the pseudo-π orbitals of the CH_2 groups. This is proved by the $2p_\pi$(O), $2p_\pi$(C), and 1*s*(H) gross orbital populations (Table VIII) which are clearly inconsistent with the trends of total charges. Thus, the epoxy oxygen possesses the lowest $2p_\pi$(O) population indicating strong back donation to the CH_2 groups. Back donation by the terminal O atoms of the OOO chain seems to be less which can be partially attributed to the lower excess charge of the O atoms in question and partially to the fact that destabilizing methylene group interactions will be enhanced by the acceptance of too much charge in the pseudo-π orbitals of the CH_2CH_2 bridge. Accordingly, R_2(CO) of compound I is longer by 2 pm than R_1(CO) of II.

If the cyclic polyoxides pucker we can expect an interplay of the π-back donation and the hyperconjugative effect, the latter involving all oxygen atoms and all ring bonds. The relative contribution of each effect to the stability of the ring is determined by the torsion of the ring bonds, i.e., the respective puckering mode. Since the maximum torsion wanders around the ring for $\phi = 0° \rightarrow 360°$, the hyperconjugative stabilization periodically changes for each bond, thus leading to the variations calculated for the bond lengths.

V. RELIABILITY OF THEORETICAL ENERGIES AND STRUCTURES

Since in previous theoretical work on 1,2,3-trioxolanes the oxygen envelope was considered as an unstable form of the ring and since our conformational energies vary considerably with the basis sets employed (Table I.B), it is useful to analyze the variation in calculated barrier values and structures in order to set our theoretical predictions on a sound basis.

Evidently, the largest changes occur for the barrier to pseudorotation of 1,2,3-trioxolane when stepping from basis *A* to basis *B* which agrees with the results of Hiberty.[9] Basis *A* tends to equalize the energies of planar and twist form while basis *B* gives low relative energies for both the twist and the envelope form. It is interesting to note that these tendencies are reinforced by an ill-chosen set of geometrical parameters. Using fixed values for the ring angles,[5,6] the planar form can become a saddlepoint (basis *A*), thus excluding pseudorotation as an energetically favored process, or the energy of the twist form can drop below the one of the envelope form (basis *B*) in an apparent confirmation of other quantum chemical calculations.

We explain these results by a complex interplay of basis set deficiencies. Referring to the experience gathered for H_2O_2,[22] H_2O_3 (Paper II) as well as other small molecules (see data of Table IX), the following statements can be made with regard to the basis sets *A*, *B*, and *C*:

(1) Basis *A* makes OO bond lengths too short by about 6 pm caused by an underestimation of charge separation in polar bonds. In addition, it has the tendency to decrease XOX angles below experimental values since a single set of *p* GTF's prefers an orthogonal arrangement of the three atoms.

(2) Basis *B*, on the other hand, leads to significant charge separations due to its split valence shell character. Yet, it does not provide sufficient overlap to counterbalance repulsion between negatively charged atoms. Consequently, OO bond lengths are predicted about 6 pm longer than those obtained with *A* or *C* which leads to an accidental agreement with spectroscopic values. The angle XOX (X=H, C, O), however, are widened beyond experimental values which is also caused by strong charge repulsion.

(3) Basis *C* and near HF basis sets predict OO bond lengths to be far too short. This results from the neglect of correlation within the HF theory, specifically left–right correlation of bond electrons, and applies to HF bond lengths in general. On the other hand, the superiority of basis *C* is revealed by its accurate description of the equilibrium dihedral angles of polyoxides[22] [and Paper II]. With regard to XOX angles basis *C* values are better than those of basis *B* but still larger than the observed angles.

With the aid of these findings as well as the data compiled in Table IX the following interpretation of basis *A* and *B* results can be given.

From reported studies on compounds containing CC or CO bonds, a reasonable description for the OCCO trapezoid of the planar form of I by both basis sets can be assumed. If the bonds of the OOO moiety are kept short (basis *A*), the angle α_1 necessarily has to open. The angle widening (111°, basis *A* vs 108°, basis *B*), however, is badly described by basis *A* which leads to an artificial destabilization of the planar ring. Angle strain at O(1) induced by the basis is lowered by ring puckering. Clearly, that puckering mode will be preferred by basis *A* that implies the strongest decrease of α_1.

In Table VII, the internal ring angles α_j of an infinitesimal puckered pentagon are listed.[35] Useful conclusions concerning the dependence of the angles α_j on the phase ϕ can be drawn if a finite puckering amplitude is adopted. Thus, we expect for the puckering mode with $\phi = 0°$: $\alpha_1 < \alpha_2 < \alpha_3$, and for $\phi = 90°$: $\alpha_1 > \alpha_2 > \alpha_3$. Since

TABLE IX. Basis set peculiarities reflected by theoretical equilibrium parameters R(OX) and α(XOX) calculated for small molecules.[a]

Parameter	Molecule	Basis *A*	Basis *B*	Basis *C*	Best[b]	Ref.
Bond lengths, pm						
R(OO)	H_2O_2(*cis*)	140.6	146.5	140.4	146.0	c,d
R(OO)	CH_3OOH(stag)	140.6	146.4	140.8	147.4	e
R(OO)	H_2O_3 (*sp*,*sp*)	140.5	146.5	139.4	147.0	f
R(OC)	CH_3OH(stag)	143.3	143.1	140.0	142.6	c,g
					(142.7)	h
R(OC)	CH_3OOH(stag)	144.5	143.0	139.5	141.8	e
Bond angles, deg						
HOH	H_2O	100.0	111.2	105.5	104.2	i,j,g
OOH	H_2O_2 (*cis*)	104.9	107.9	106.7	103.6	c,d
OOH	H_2O_3 (*sp*,*sp*)	105.1	109.2	108.1	105.3	f
COH	CH_3OH (stag)	103.8	112.5	108.9	107.3	c,g
					(108.9)	h
OOO	H_2O_3(*sp*,*sp*)	111.4	113.1	112.9	112.1	f
OOC	CH_3OOH (stag)	104.1	105.2	105.5	102.3	e
COC	$(CH_3)_2O$	109.4	115.9		(111.7)	k,l,m
COC	Oxolane(C_{2v})	110.1	113.1	111.2		n,o

[a]If possible, the conformation which comes closest to the situation of the ring compounds I and II has been used as a reference. If not otherwise noted, all geometrical parameters have been optimized.
[b]Correlation corrected values obtained either with basis *C* (CH_3OOH, H_2O_3, CH_3OH, H_2O) or *D* (H_2O_2). Numbers in parenthesis are experimental values.
[c]Basis *A*, W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, Progress Phys. Organ. Chem. **2**, 175 (1974).
[d]Reference 2.
[e]D. Cremer, unpublished results. For basis *C*, only partial optimization [R(OO), R(OC), α(OOC)] performed.
[f]Paper II.
[g]D. Cremer, unpublished results.
[h]K. Kimura and M. Kubo, J. Chem. Phys. **30**, 151 (1959).
[i]Basis *A* and basis *B*, W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, J. Am. Chem. Soc. **93**, 6377 (1971).
[j]Basis *C*, P. C. Hariharan and J. A. Pople, Mol. Phys. **27**, 209 (1974).
[k]Basis *A*, D. Cremer and J. A. Pople, unpublished results.
[l]C. E. Blom, L. P. Otto, and C. Altona, Mol. Phys. **32**, 1137 (1976).
[m]U. Blukis, P. H. Kasai, and R. Myers, J. Chem. Phys. **38**, 2753 (1963).
[n]Basis *A* and *B*, Ref. 18(b). Only α_1 optimized.
[o]D. Cremer, unpublished results. Only α_1 optimized.

all angle values will decrease with an increase of q and since this decrease will be strongest for the OOO angle of the C_s form Ia, it follows that basis *A* will overestimate the energy difference $E(C_s)-E(C_2)$ by artificially destabilizing the twist form.

The situation is reversed for basis *B*. Now, the puckering mode is preferred which warrants a relatively large OOO angle. Accordingly, the twist form is favorably described by *B* while the stabilization of the envelope form seems to be underestimated. The energy gap between the two conformations closes from 6 to 0.7 kcal/mole.

Appreciation of these basis set effects helps to understand the sometimes amazingly good results of minimal basis set calculations. For example, if the R(OO) distance of I is fixed to 147 pm, the angle effect and, accordingly, the destabilization of the twist form is diminished. A reasonable barrier to pseudorotation can be obtained with basis *A*. Such a standardization of the ring geometry, of course, demands *a priori* knowledge of suitable bond lengths and probable basis set effects. As a consequence, it may lead to an undesirable screening of the actual electronic effects which, of course, can also occur if standard geometries are used with a larger basis set like *C*.

In this connection, it is interesting to note that the puckering amplitude of conformation Ia obtained with basis *A* is larger than the one evaluated with *B*. This result suggests that theoretical puckering amplitudes do not necessarily increase with an improvement of the basis set[36]: A larger value of q has to be queried if the basis set does not provide a consistent description of all ring atoms. In any case, distortions of the ring bonds are best accounted for by a highly flexible basis, preferably one which includes polarization functions.

Both requirements, namely a consistent description of all ring atoms and a high flexibility, are met by basis *C* which is documented by the data of Table IX and the results obtained for puckered four-, five-, and six-membered rings.[37] Provided the crucial parameters q and α_1 are reoptimized with *C* and basis *B* bond lengths are used to reflect the tendencies of the true equilibrium

values, a barrier to pseudorotation of 3 kcal/mole and a barrier to planarity of 7.9 kcal/mole is calculated for the primary ozonide. The reliability of these data is confirmed in two ways, namely, first, by the barrier values obtained with the fully augmented basis *D* and, secondly, by the fairly good agreement with the predictions derived from the correlation corrected potential of H_2O_3 (Paper II). The necessity of polarization functions is self-evident. Apart from the uncertainty with regard to the bond lengths, we regard the puckering parameters computed with *C* and the conformational energies obtained with *D* as the most accurate values so far published for 1,2,3-trioxolane.

Similar considerations as for the primary ozonide apply to the RHF data of the final ozonide. Again, the tendency of basis *A* to overestimate the relative stability of the envelope is reflected by the energy values of Table II.B, although the angle effect is now less obvious. According to the data of Table VII, the puckering mode that leads to a favorable narrowing of the COC angle α_1 also opens the COO angle α_3. A partial cancellation of the two angle effects can be expected both at the level of basis *A* and that of basis *B*. Therefore, the pseudorotation barrier of II (Table II.B) seems to be less influenced by basis set effects.

Indication of the deficiencies of *A* and *B* is given by their description of the barrier to planarity. Both basis sets underestimate the stabilization of the ozonide ring which is gained by puckering. This is also reflected by the three theoretical puckering amplitudes of Table IV. We conclude that a lack of flexibility and a weakening of the angle effect due to opposed angle variations at positions 1 and 3 are responsible for the *q* values and, hence, the inversion barriers of *A* and *B*. A better quantum chemical description is provided by the augmented basis sets *C* and *D* which both predict a barrier to pseudorotation of about 3 kcal/mole and a barrier to planarity twice as large.

In Table X, theoretical and experimental geometries

TABLE X. Experimental geometries observed for 1,2,4-trioxolane (II), 3-methyl-1,2,4-trioxolane (Me-II), and 3-carbomethoxy-5-anisyl-1,2,4-trioxolane (anisyl-II-COOMe). Theoretical parameters obtained with basis *C* are given for comparison (distances in pm, angles in deg. Numbers in parentheses give uncertainties of experimental values).

Molecule	II	II	II	Me-II	Ansiyl-II-COOMe
Ref.	This work	12	14	10	13
Method	RHF/Basis C[b]	ED[c]	MW	MW	x ray
Structure	r_e	r_a	r_0	r_s	disordered[h]
Symmetry	C_2	C_2	C_2	(C_2)	(C_2)
ϕ[a]	90, 270	90, 270	90, 270	270.8	273.6
q[a]	44.7	46.4	46.1	46.1	46.2
R_1	142.6	141.4(3)[d]	143.6(6)	142.3(1.8)[d]	155.9(1.3)
R_2	143.3	141.4(3)[d]	139.5(6)	139.9(1.4)	133.8(8)
R_3	146.7	148.7(6)	147.0(1.5)	147.1[e]	147.9(1.4)
R_4				141.1(5)	140.1(1.4)
R_5				142.3(1.8)[d]	136.7(1.6)
α_1	105.8	105.9(1.1)	102.8(4)	104.6(6)	102.1(8)
α_2	105.4	105.3(8)	106.3(6)	105.6(8)	103.3(7)
α_3	100.2	99.2(7)	99.2(4)	99.7(5)	102.2(7)
α_4				99.2(3)	98.0(8)
α_5				105.7(4)	107.9(7)
θ_1	15.3	16.2(6)	16.6(4)	17.0	12.9(1.0)
θ_2	38.9	40.2(1.3)	41.3(1.0)	41.0	38.8(9)
θ_3	47.4	49.1(1.5)	50.2(1.3)	49.3	51.2(8)
θ_4				39.8	43.3(1.0)
θ_5				15.4	20.4(1.1)
CH	109.0[e]	112.6(1.1)	109.4(5)	109.1(5)[g]	
				110.8(4)	
HCH	109.5[e]	112.3[f]	112.9(5)	114.3(3)	

[a]Ring puckering coordinates calculated from experimental data with the program RING (see Ref. 32).
[b]Bond lengths calculated with basis *B*.
[c]An envelope form could not be excluded despite a slight preference of the C_2 (twist) form.
[d]Assumed to be equal.
[e]Assumed values.
[f]Uncertainty large, not given in Ref. 12.
[g]Parameters of the unsubstituted CH_2 group are given.
[h]The disorder is observed for the ozonide ring only. The relative amount of the C_2 ring structure is about 65%. The other structure roughly corresponds to an envelope form.

TABLE XI. Potential coefficients V_{kl} ($\times 10^3$) for 1,2,3-trioxolane and 1,2,4-trioxolane calculated with Eq. (2).[a]

Basis set	V_{02}	V_{04}	V_{22}	V_{24}	Minimum
		1,2,3-Trioxolane			
A	−5.27	0.00168	−2.12	0.00014	C_s
B	−5.60	0.00167	0.10	−0.00019	C_s
C	−6.38	0.00162	−0.77	−0.00001	C_s
D	−5.92	0.00149	−1.04	0.00008	C_s
		1,2,4-Trioxolane			
A	−4.64	0.00182	0.78	0.00013	C_2
B	−4.02	0.00170	0.85	0.00026	C_2
C	−5.57	0.00178	0.72	0.00020	C_2
D	−5.45	0.00175	0.58	0.00024	C_2

[a] V_{00} is taken to be the energy of the planar form.

of 1,2,4-trioxolane and two of its derivatives are compared. Calculated and observed ring puckering coordinates are in satisfactory agreement, though q seems to be still slightly underestimated by basis *C*. We emphasize that the degree and mode of puckering is hardly influenced by substituents, a result which also holds for other substituted five-membered rings.[38] Considering the fact that r_0, r_a, r_s, and r_e structures are compared, bond lengths and bond angles are in reasonable agreement. For H_2O_2, the r_0 value of R(OO) was found[22,39] to coincide with the theoretical r_e (RHF/basis *B*) value (146.4 vs 146.0 pm) both being about 1 pm longer than the true r_e value (145.2 pm, obs. vs 145.1 pm, theor). Listed OO bond lengths (Table X) are in line with this result and suggest that the true equilibrium OO distance of 1,2,4-trioxolane should be comparable to the one of H_2O_2.

Theory does not agree with experiment with regard to the ordering $R_1 < R_2$ and, in connection with this, $\alpha_1 > \alpha_2$. We have checked this inconsistency by comparing theoretical CO bond lengths of CH_3OH and CH_3OOH which

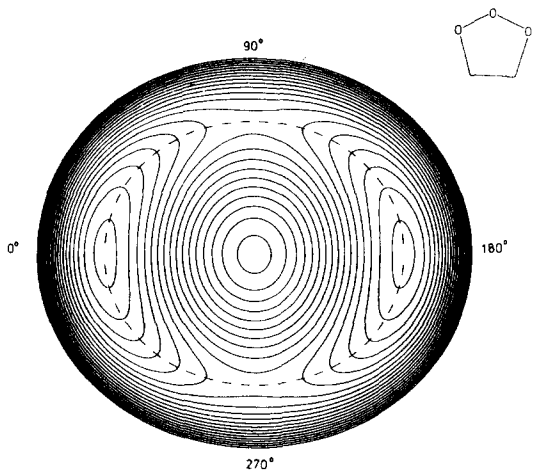

FIG. 3. Potential surface of 1,2,3-trioxolane, obtained with basis *C*. The potential is zero at the center of the (ϕ, q) diagram, the innermost contour line corresponds to −0.2 kcal/mole. The vertical spacing of two successive equipotential curves is 0.5 kcal/mole.

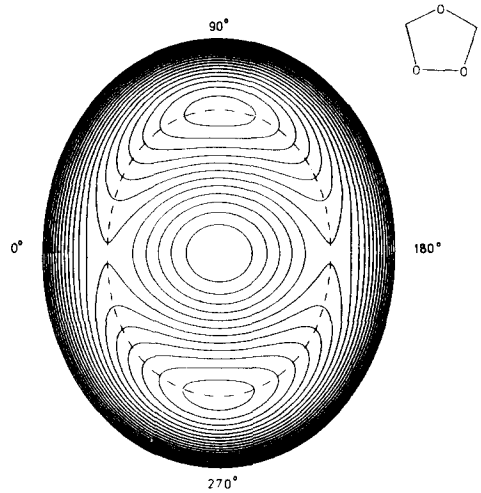

FIG. 4. Potential surface of 1,2,4-trioxolane, obtained with basis *C*. The potential is zero at the center of the (ϕ, q) diagram, the innermost contour line corresponds to −0.5 kcal/mole. The vertical spacing of two contour lines is 0.5 kcal/mole.

are also included in Table IX. Using polarization functions in the basis and correcting the RHF approach for correlation errors (Paper II), the carbon bond to the peroxy bridge (CH_3COOH) is indeed found to be 1 pm shorter than the corresponding bond to the hydroxy oxygen (CH_3OH). The Mulliken population values suggest stronger π donation from the peroxy bridge than from the hydroxy oxygen to the CH_3 group. Basis *B* and *A* fail to describe this effect adequately, thus leading to similar or reversed bond lengths. Probably, this situation also applies to compound II.

VI. FORM OF THE CONFORMATIONAL POTENTIAL

By means of the expansion (2) the pseudorotational potential $V(q, \phi)$ of both trioxolanes has been evaluated. For basis *B* results, all terms of Eq. (2) have been considered in order to test the importance of the $\cos(4\phi)$ components. These terms do not contribute to the barriers but modify the shape of the potential along the pseudorotation pathway of the ring. Thus, for example, a positive value of $(V_{42} + V_{44}q^2)$ leads to a broadening of the pseudorotation minimum and a narrowing of the corresponding maximum. Under this condition, the number

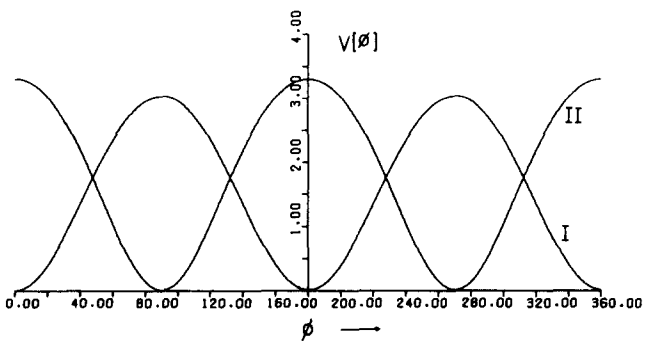

FIG. 5. Pseudorotational potential $V(\phi)$ in kcal/mole for 1,2,3-trioxolane (I) and 1,2,4-trioxolane (II) calculated with basis *C*.

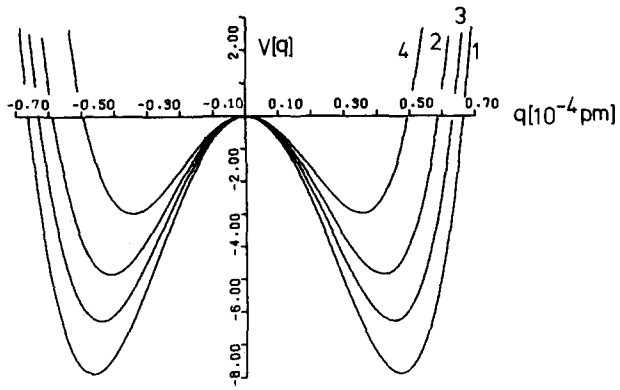

FIG. 6. Inversional potential $V(q)$ in kcal/mole for the C_s and C_2 conformer of 1,2,3-trioxolane (line 1 and 2) and for the C_2 and C_s conformer of 1,2,4-trioxolane (3,4) calculated with basis C.

of conformations with comparably low energy would be enlarged. We have found neither for the primary ozonide nor the final ozonide contributions of the V_{4l} terms to the potential to be significant. With regard to 1,2,4-trioxolane where the deficiencies of basis B are of less importance we deduce that the inclusion of the V_{0l} and V_{2l} terms in the expansion of $V(q,\phi)$ is sufficient to describe the conformational potential for small values of q.

In Table XI, the coefficients V_{kl} of the expansion (2) are summarized. Figures 3 and 4 show energy contour maps (RHF/basis C) of the potential surface of the two ozonides. The dotted lines indicate the pseudorotation paths which connect the surface minima by following the steepest ascent and descent lines to and from the saddlepoints of the conformational potential. One-dimensional sections out of the (q,ϕ) space are plotted in Figs. 5 and 6. Figure 5 gives the energy variation along the pseudorotation paths while Fig. 6 depicts the barriers to planarity for $\phi = 0°$ and $\phi = 90°$ for both the primary and final ozonide.

Basis set dependent effects discussed in the previous section are also manifested by the evaluated V_{kl} coefficients. Thus, the absolute value of V_{22} of I, i.e., the term which dominates the pseudorotational barrier, is too high for basis A and too low for B compared with the better values of C and D. Also, the steady increase of the $|V_{02}|$ values, indicative of reinforced puckering, goes parallel to the enhanced flexibility of the basis sets used. The slight reduction observed for the corresponding value obtained with basis D suggests that reoptimization of q at this level of basis set sophistication will probably enhance the puckering of the minimum conformations.

Effects resulting from the anharmonicity of the potential (terms V_{k4}) are fairly important in the region of optimum puckering. This is illustrated by the $V(q)$ curves of Fig. 6. The variation of anharmonicity effects with the phase angle is moderate inside the pseudorotation circuit. We conclude that a reasonable account on the pseudorotational surfaces of both compounds is given by our *ab initio* data for puckering amplitudes $q < 50$ pm.

VII. CONCLUSIONS

While the various semiempirical methods (EHT,[5] CNDO/2,[6] MINDO/3[7]) are rather inconclusive with regard to the most probable 1,2,3-trioxolane conformation, the *ab initio* calculations clearly predict the symmetrical envelope conformation of I to represent the conformational minimum. However, accurate conformational barriers can only be achieved if two basic requirements are fulfilled within the RHF description of the molecule.

(1) Large basis sets including polarization functions have to be employed in the calculations of the various conformers.

(2) Complete optimization of the conformational parameters is necessary. This can be achieved if a well-defined conformational model is used which facilitates the location of stationary points of the conformational surface. Optimization of the bond lengths does not necessarily lead to an improvement since minimal as well as augmented basis sets severely underestimate the OO bond length. As long as correlated wave functions cannot be used for molecules like I, a standardization of bond lengths using optimum basis B values seems to be the appropriate geometrical choice.

Our calculations indicate that dipole–dipole interactions and a hyperconjugative delocalization of oxygen lone pair electrons are the major effects which determine degree and mode of ring puckering. It is doubtful whether these electronic features are adequately described by NDO methods. Even in the case of small basis set RHF calculations, the theoretical predictions of interconversional barriers are unsatisfying, unless a fortunate choice of the geometries is made. We have shown that this results from an inconsistent description of the ring atoms by the minimal basis set A as well as the split valence shell basis B. Therefore, we emphasize that the success of those basis sets in the study of hydrocarbon compounds does not necessarily imply a similar success with regard to heterocompounds.

The agreement of our calculations with the predictions derived from the internal rotational potential of hydrogen trioxide underlines the close relationship between the conformational behavior of the geminal double rotor and the five-membered ring.

Although the quantum chemical study of 1,2,4-trioxolane turns out to be less problematic due to the topology of the ring (a peroxy bridge is opposite an epoxy bridge), similar conclusions can be drawn with regard to the necessity of polarization functions and geometry optimization. The computed equilibrium structure of the C_2 comformer of II is in reasonable agreement with experimental findings for both the parent compound II and two of its derivatives. Therefore, it seems appropriate to use the geometrical parameters of this work in a study of substituted ozonides.

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