

Theoretical determination of molecular structure and conformation. IV. Electronic effects influencing the stability of methyl substituted primary ozonides^{a),b)}

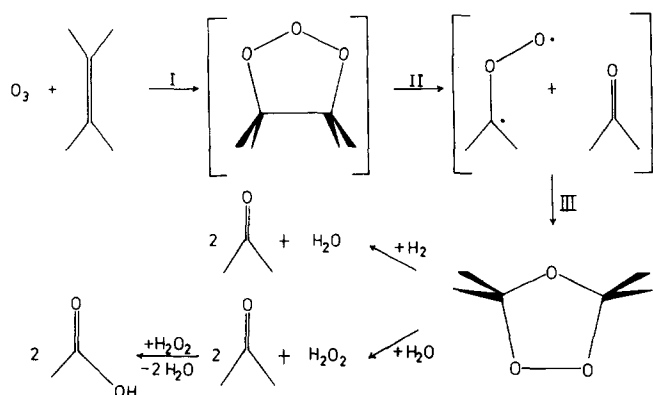
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The conformational surfaces of three methyl substituted primary ozonides (PO), namely, 4-methyl-1,2,3-trioxolane (propene PO), *cis*-4,5-dimethyl-1,2,3-trioxolane (*cis*-2-butene PO) and the corresponding *trans* PO (*trans*-2-butene PO), are studied with restricted Hartree-Fock (RHF) theory employing a split valence $[3s2p/2s]$ and an augmented split valence $[3s2p1d/2s]$ basis set. An analysis of the computed RHF energies reveals that only with polarization functions in the basis set is a reliable theoretical description of the three PO's guaranteed. In the case of propene PO and *trans*-2-butene PO, reasonable results are obtained by means of a rigid pseudorotor model based on the theoretically determined structures of various 1,2,3-trioxolane conformations. However, a flexible pseudorotor model is necessary in the case of *cis*-2-butene PO in order to achieve a realistic account of substituent-substituent interactions. The conformational surfaces of all three PO's closely resemble that of the parent PO, 1,2,3-trioxolane. Thus, the preferential interconversional process of a methyl substituted PO is pseudorotation hindered by barriers between 2.3 and 3.5 kcal/mole. In marked contrast to previous semiempirical results, the oxygen envelope (E) conformations are calculated to be the most stable puckered PO forms. This finding is most important with regard to the stereochemical aspects of the ozonolysis mechanism. The methyl groups either stabilize or destabilize the puckered PO ring depending on the position of the substituent. With the aid of the pseudorotation phase angle and a well-defined substituent orientation angle, reliable predictions with regard to the electronic effect of a methyl group can be made. It is shown that only an equatorially placed methyl group leads to a favorable orbital mixing between the π -type MO's of the ring and the substituent and a resultant lowering of the two highest occupied MO's of the PO. The puckered ring is stabilized by back-donation of electron charge to the substituent which is not possible if the substituent is axially positioned.

I. INTRODUCTION

More than two decades ago, R. Criegee proposed a three step mechanism for the reaction of ozone with alkenes in solution.¹ In its original basic form (Scheme I), it simply involves the formation of a 1,2,3-trioxolane, the primary ozonide (PO), by cycloaddition of ozone to an alkene double bond. In the second step, the primary ozonide cleaves to give an aldehyde and a peroxyethylene (carbonyl oxide or Criegee zwitterion)² which recombine to a 1,2,4-trioxolane, the final ozonide (FO), in the third step of the reaction.



While the FO can be intercepted and analyzed, only in-

direct evidence has been given for the other reaction intermediates.³ Nevertheless, the available experimental data strongly support the Criegee mechanism as the predominant pathway of the ozonolysis in solution.

One experimental finding not covered by scheme I is the stereospecificity of the reaction. Thus, it has been shown that the *cis-trans* ozonide ratios for the FO's as well as the cross ozonides resulting from unsymmetrical alkenes, depend on the alkene geometry.⁴ For this reason, Bauld, Bailey *et al.*⁵ proposed a stereochemical refinement of the Criegee mechanism which was based on two provisos, namely, first, the existence of stable nonplanar ozonide conformations and, secondly, a *syn-anti* isomerism of the peroxyethylene.² Assuming certain puckered forms of both PO's and FO's, the authors were able to rationalize a great amount of the experimentally observed *cis-trans* ratios of the intercepted FO's.

According to the Bauld-Bailey mechanism, one has to expect more *trans* FO from *trans* alkenes and more *cis* FO from *cis* alkenes which is in accord with most experimental results.⁴⁻⁶ However, the Bauld-Bailey scheme cannot be applied to the ozonolysis of small alkenes like butene or pentene. In these cases, both *cis* and *trans* alkenes tend to produce more *trans* than *cis* FO.^{4*} Experimental clues which might offer an explanation for the restriction of the Bauld-Bailey mechanism to alkenes with bulky alkyl groups are sparse and exclusively deal with the configuration and conformation of the intercepted FO.^{7,8} Therefore, attempts have been made to give a quantum chemical description of the reac-

^{a)}Papers IV-V: Presented in part, at the 13 Symposium für Theoretische Chemie, Münster, West Germany, October, 3, 1977).

^{b)}For Paper III; see the preceding paper in this issue.

tive intermediates of the ozonolysis reaction. In particular, the conformational stabilities of various alkyl substituted 1,2,3-trioxolanes have been studied by means of the semiempirical EHT⁹ and CNDO/2¹⁰ methods. The theoretical results have been used together with the spectroscopic findings on ethylene,⁷ propene and *trans*-2-butene FO⁸ in order to assess the Bauld-Bailey mechanism and to extend its application to the ozonolysis of small alkenes.^{8,11}

In Paper III of this series [see Ref. (b)], we have shown that semiempirical methods are not capable of describing the conformational features of 1,2,3-trioxolane. For example, *ab initio* calculations predict the symmetrical envelope (E) conformation as the most stable puckered ring form in marked contrast to the results of EHT,⁹ CNDO/2,¹⁰ or MINDO/3¹² calculations. The reliability of our theoretical predictions are enhanced in three ways, namely, first by an extensive optimization of geometrical parameters, second, by a thorough study of basis set effects including the role of polarization functions, and third, by an estimate of possible correlation errors using H₂O₂¹³ and H₂O₃¹⁴ as suitable reference compounds. As a result, we feel that *ab initio* calculations should offer a better chance to explore the ozonolysis mechanism of small alkenes. Therefore, we have investigated the various molecular species appearing in the ozonolysis of propene and 2-butene with the aid of *ab initio* methods. Our theoretical study is based exclusively on the Criegee mechanism of ozonolysis, since other possible reaction schemes like the aldehyde interchange mechanism¹⁵ do not seem to be as important in the ozonolysis of small alkenes.¹⁶

In this paper, we report on the conformational features of propene and 2-butene PO with emphasis on analyzing ring-substituent interactions which may play a role in the cleavage of the ozonide to aldehyde and peroxymethylene. In paper V, a similar study of the corresponding FO's of propene and 2-butene will be presented. Paper VI will deal with structure and conformation of the Criegee zwitterion. Finally, in Paper VII, the ozonolysis mechanism for small olefins will be discussed and compared with the Bauld-Bailey^{5,11} and Kuczkowski⁸ schemes.

II. NUMERICAL PROCEDURES

A. Quantum mechanical method

As in Paper III, we use restricted Hartree-Fock (RHF) theory¹⁷ employing primarily two basis sets, namely, the split valence shell [3s2p/2s] basis¹⁸ (basis B of Paper III) and the augmented split valence shell [3s2p1d/2s] basis¹⁹ (basis C of Paper III). With basis B, extensive scans of the conformational surface of the three PO's are performed while the application of basis C is limited to the calculation of PO conformations which are of special interest for the mechanism of the ozonolysis reaction. In addition, Pople's minimal STO-3G basis²⁰ (basis A of Paper III) has been used in one case to calculate the positions of the substituents.

In view of the large extent of the computations with the augmented basis C, which, for example, require the evaluation of as many as sixteen million two-electron

integrals (dimethyltrioxolane, 121 basis functions), it was necessary to establish that uncertainties in the theoretical energies resulting from roundoff errors do not exceed the energy differences discussed in this paper. Three tests have been performed for this purpose. First, we have relaxed the usual integral cutoff restriction from 10⁻⁶ to 10⁻⁷ hartree in the case of planar 3-methyl-1,2,3-trioxolane thus increasing the number of processed two-electron integrals from 7.8 to 11.2 million. The corresponding change in the total energy amounts to 7 μ hartree or 0.004 kcal/mole. Secondly, two different roundoff procedures, namely, normal rounding and a cutoff of the last significant figure, have been used in the case of dimethyl trioxolane. The resultant change in energy was less than 1 μ hartree. Finally, the usual SCF method¹⁷ has been replaced by an univariate search in the space of the molecular orbitals²¹ when calculating 1,2,3-trioxolane (see Paper III). Again the energy changed only by a few μ hartree. Therefore, we conclude that errors in the relative energies are below 0.02 kcal/mole which is comparable to the findings made by other authors in similar extensive calculations.²²

B. Conformational model

In previous work²³ (and Paper III), we have demonstrated that a mapping of the complete 3N-6 dimensional hypersurface of a N-membered ring onto a N-3 conformational subspace spanned by the ring puckering coordinates²³ facilitates the theoretical determination of stationary surface points as well as the evaluation of the conformational potential V. Thus, for the five-membered ozonide rings one can use the pseudorotation subspace that has two dimensions which are given by the puckering amplitude q and the phase angle ϕ . Every (q, ϕ) pair of the pseudorotation subspace corresponds to a specific ozonide conformation and, in the case of a substituted ozonide, to a specific orientation of the substituent relative to the mean ring plane.²⁴ However, this one to one correspondence requires an unique choice of the ring conformation with $\phi = 0^\circ$ which avoids any ambiguity with regard to the substituent positions. This has been accomplished by observing rules (1) and (2):

(1) Looking from above onto the ring, the ring atoms are numbered clockwise around the ring according to common rules of nomenclature. In this way, two faces of the ring are defined, namely the topside face (turned to the observer) and the bottomside face (turned away from the observer).

(2) If a topside or bottomside position of the ring substituents is not fixed by (1), the substituent which is attached to the ring atom with the lowest number is chosen to be a topside substituent.

In the case of the three PO's, rules (1) and (2) uniquely define one of the ten possible envelope forms of a five-membered ring as the conformation with $\phi = 0^\circ$. However, a comparison between unsubstituted and substituted PO's is facilitated if the conformation with $\phi = 0^\circ$ is chosen to be the symmetrical envelope of 1,2,3-trioxolane (see Paper III). To obtain this conformation, oxygen atom 1 has to be shifted by four places clockwise around the ring keeping the topside substituents on the topside and the bottomside substituents on the bottom-

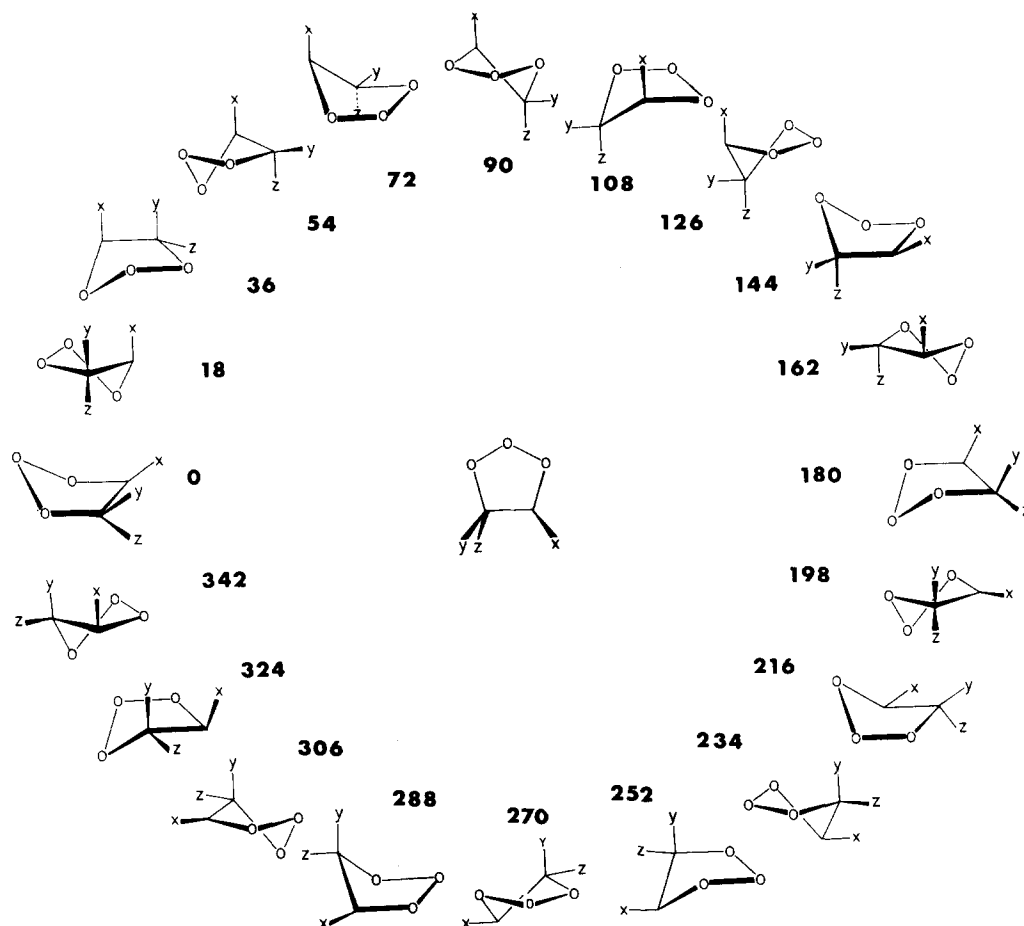


FIG. 1. Envelope and twist conformations along the pseudorotation itinerary of a substituted primary ozonide ($X=CH_3$, $Y=Z=H$: propene PO; $X=Y=CH_3$, $Z=H$: *cis*-2-butene PO; $X=Z=CH_3$, $Y=H$: *trans*-2-butene PO).

side of the ring. The corresponding shift of the phase angle ϕ amounts to 144° according to the expression $(k-1)4\pi/5$, where k represents the number of the atom at the apex of the envelope after the shift and shift values larger than 2π have to be reduced by 2π . The PO conformation with $\phi=0^\circ$ thus defined is depicted in Fig. 1. Also twenty conveniently chosen nonplanar ring conformations with $\phi=l\pi/10$, $l=0, 1, 2, \dots, 19$ have been drawn along a pseudorotation path of the substituted PO ring in order to illustrate changes in the positions of the substituents X, Y, and Z (propene PO: $X=CH_3$, $Y=Z=H$; *cis*-2-butene PO: $X=Y=CH_3$, $Z=H$; *trans*-2-butene PO: $X=Z=CH_3$, $Y=H$) for $\phi=0^\circ-360^\circ$. A mathematical description of the substituent orientations relative to the mean plane of the ring by means of the substituent orientation angle α_s has been proposed previously.²⁴ We will use this in connection with Fig. 1 when discussing the calculated conformational tendencies of the three PO's.

In all calculations, standard bond lengths [$R(CC)=154$ pm and $R(CH)=109$ pm] and bond angles ($CCH=109.5^\circ$) have been used for the methyl substituents.²⁵ Also, the conformation of the methyl group has been standardized by choosing one of its CH bonds to be *trans* to the methine hydrogen of the ring in order to allow favorable bond staggering between ring and substituent bonds. This choice of the $CHCH_3$ conformation leads to

C_5 symmetry in the case of planar *cis*-2-butene PO and C_2 symmetry in the case of the *trans* derivative. Accordingly, some of the puckered 2-butene PO conformations shown in Fig. 1 (Y or $Z=CH_3$) are the mirror images of the other. There exists a connection between chirality, puckering phase, and substituent orientation. For example, the conformations of *cis*-2-butene PO with ϕ ($\phi < 180^\circ$) and $360^\circ - \phi$ are enantiomers, each possessing a *R* and a *S* configuration at the two asymmetric C atoms of the trioxolane ring, but with reversed substituent orientations. Similarly, the conformations of *trans*-2-butene PO with ϕ ($\phi < 90^\circ$) and $180^\circ - \phi$ or with ϕ ($180^\circ < \phi < 270^\circ$) and $360^\circ - \phi$ are enantiomers. Therefore, only 12 of the 21 PO conformations shown in Fig. 1 need to be considered in the case of the 2-butene PO's.

C. Rigid and flexible pseudorotor models of a substituted PO

Ideally the puckering amplitude q of each of the PO conformations considered should be determined by energy variation. In the case of an asymmetrical ring skeleton with bond lengths taken from 1, 2, 3-trioxolane (Paper III), this requires the optimization of three parameters, namely, the puckering amplitude and two internal ring angles. In addition, eight external ring angles should be optimized in order to describe the dependence of the substituent orientations on q and ϕ accurately. This, of course, is too costly to be performed with ba-

TABLE I. Absolute and relative energies of propene and butene primary ozonide calculated with basis *B*.^a

Pseudorotation parameters		4-Methyl-1,2,3-trioxolane		4,5-Dimethyl-1,2,3-trioxolane			
ϕ , deg	q , pm	Absolute	Rel.	<i>cis</i>		<i>trans</i>	
				Absolute	Rel.	Absolute	Rel.
0	43.2	-340.97384	0	-379.94778 ^b	3.61	-379.95834	0.03
18	42.4	-340.97356	0.17	-379.94979	2.35	-379.95804	0.22
36	40.1	-340.97311	0.46	-379.95109 ^b	1.54	-379.95788	0.32
54	40.4	-340.97288	0.60	-379.95291	0.40	-379.95754	0.53
72	39.0	-340.97280	0.65	-379.95331	0.14	-379.95746	0.58
90	39.2	-340.97282	0.64	-379.95354 ^b	0	-379.95745	0.59
108	39.0	-340.97295	0.55	-379.95333	0.13		
126	40.4	-340.97320	0.41	-379.95298	0.35		
144	40.1	-340.97333	0.32	-379.95262 ^b	0.58		
162	42.4	-340.97356	0.17	-379.95182	1.08		
180	43.2	-340.97366	0.11	-379.95150 ^b	1.28		
198	42.4	-340.97367	0.11			-379.95837	0.01
216	40.1	-340.97355	0.18			-379.95839	0
234	40.4	-340.97327	0.36			-379.95800	0.24
252	39.0	-340.97297	0.54			-379.95788	0.32
270	39.2	-340.97289	0.60			-379.95783	0.35
288	39.0	-340.97297	0.54				
306	40.4	-340.97310	0.46				
324	40.1	-340.97364	0.13				
342	42.4	-340.97375	0.06				
planar	0	-340.96554	5.21	-379.94011	8.42	-379.95002	5.25

^aAbsolute energies in hartree; relative energies in kcal/mole.

^bRefined energies are shown in Table III.

sis *C* or even with basis *B*. Therefore, a standardization of the geometry of the three PO's is implemented by utilizing the structural data of 1,2,3-trioxolane (Paper III). The amplitude q and the internal ring angles have been calculated (Paper III) with basis *B* for six nonplanar forms ($\phi = 0^\circ, 18^\circ, 36^\circ, 54^\circ, 72^\circ, 90^\circ$) and with basis *C* for three nonplanar forms ($\phi = 0^\circ, 36^\circ, 90^\circ$) of the parent PO.²⁶ Since 1,2,3-trioxolane conformations with phase angles $\phi, \pi \pm \phi$, or $2\pi - \phi$ are equivalent, the basis *B* structures can be employed for 21 and the basis *C* structures for eight puckered PO forms if it is assumed that the ring conformation is not affected by the substituent. In this way, a rigid pseudorotor model of a substituted PO is defined which is used in the absence of strong steric repulsion between the atoms or atom groups attached to the ring such as in the case of propene and *trans*-2-butene PO. In order to describe the interactions between substituents positioned on the same side of the ring appropriately, partial flexibility is introduced in the rigid pseudorotor model by reoptimizing the external ring angles for each value of ϕ . This has been done for the planar and five puckered conformations of *cis*-2-butene PO employing basis *A*.

The justification of the rigid pseudorotor model is based on both experimental and theoretical observations. Calculating q and ϕ from experimentally determined structures of substituted five-membered rings, it becomes obvious that the degree and phase of puckering are only slightly affected by a single ring substituent.²⁷ For example, this is true for the substituted FO's investigated so far (see Paper III). Also, in some cases of steric crowding caused by the ring substituents,

it seems that the molecule more likely stabilizes by altering the position of the substituents than by adopting a different degree of puckering. At least, this is suggested by RHF/basis *A* calculations on the envelope (*E*) and twist (*T*) conformations of *cis*-2-butene PO with $\phi = 0^\circ, 180^\circ$, and 90° employing a fully flexible pseudorotor model of the puckered ring.²⁸ Although these observations refer to individual ring conformations, we believe that the rigid pseudorotor approach provides a reasonable description of the changes in energy during a complete pseudorotation itinerary.

III. RESULTS AND DISCUSSION

Absolute and relative energies evaluated for the three PO's with basis *B* are summarized in Table I. Results of refined calculations performed with the augmented basis *C* for selected PO conformations are shown in Table II. The RHF/basis *C* energies of *cis*-2-butene PO have been obtained by reoptimizing the substituent position with basis *A*. The corresponding values of the external angles are listed in Table III. Basis *A* and basis *B* energies of *cis*-2-butene PO are also included in Table III. By means of the computed energies, the form of the pseudorotational potential $V(\phi)$ has been determined. This is shown in Fig. 2.

A. Stability of nonplanar primary ozonide conformations

In our previous work on 1,2,3-trioxolane (Paper III), we have shown that the nonplanar ring is stabilized by delocalization of the oxygen lone pair electrons into the

TABLE II. Absolute and relative energies of propene and butene primary ozonide calculated with basis C.^a

Pseudorotation parameters		4-Methyl-1, 2, 3-trioxolane		4, 5-Dimethyl-1, 2, 3-trioxolane			
				<i>cis</i>		<i>trans</i>	
ϕ , deg	q , pm	Absolute	Rel.	Absolute	Rel.	Absolute	Rel.
0	47.0	-341.46282	0.09	-380.49941	0.88	-380.50307	0
36	44.1	-341.45969	2.05	-380.49840	1.52	-380.50014	1.84
90	41.6	-341.45774	3.28	-380.49714	2.31	-380.49754	3.47
144	44.1	-341.46055	1.51	-380.49938	0.90		
180	47.0	-341.46296	0	-380.50082	0		
216	44.1	-341.46094	1.27			-380.50126	1.14
270	41.6	-341.45831	2.92			-380.49873	2.72
324	44.1	-341.46090	1.29				
planar	0	-341.45040	7.88	-380.48725	8.75	-380.49064	7.80

^aAbsolute energies in hartree; relative energies in kcal/mole.

adjacent bonds. This effect depends on the degree and mode of ring puckering. Strongest stabilization occurs in the E forms with $\phi = 0^\circ$ or 180° while the stabilizing delocalization is only moderate in the T forms with $\phi = 90^\circ$ and 270° . However, the latter conformations are favored by increased bond staggering in the CH_2CH_2 bridge which reduces the energy gap between the E and T forms to about 3 kcal/mole (Paper III).

When discussing the methyl substituted PO's, the same arguments apply. Nevertheless, it is advantageous to redescribe the lone pair delocalization effect characteristic for polyoxides^{13,14} (and Paper III) in terms of delocalized MO's rather than localized MO's like $2p_x(\text{O})$, σ_{OO} , or σ_{CO} . In the case of planar 1, 2, 3-trioxolane, one

can distinguish between σ - and π -type MO's. The latter are formed by three lone pair $p_x(\text{O})$ AO's and two pseudo- π -orbitals of the methylene groups. Five delocalized π MO's result which, unlike the case of the aromatically stabilized cyclopentadienyl anion, are all occupied. Hence, the destabilization of planar 1, 2, 3-trioxolane can be considered to arise from the two highest occupied π MO's shown in Fig. 3. They are antibonding with regard to either CC and CO bonds (π_4) or the two OO bonds (π_5). If the ring puckers, the π MO's are able to mix with the σ MO's and, correspondingly, lose some of their antibonding, destabilizing nature. The degree and particularly the mode of puckering determines which of the two antibonding π MO's is more affected by orbital mixing. For example, the E confor-

TABLE III. Refined substituent positions obtained with basis A for *cis*-4, 5-dimethyl-1, 2, 3-trioxolane.

	$\phi = 0^\circ$	36°	90°	144°	180°	planar
A. RHF energies ^a						
Basis A	-375.76580	-375.76261	-375.75562	-375.76294	-375.76660	-375.75254
[2s1p/1s]	(0.50)	(2.50)	(6.89)	(2.30)	(0)	(8.82)
Basis B	-379.95431	-379.95504	-379.95585	-379.95585	-379.95545	-379.94630
[3s2p/2s]	(0.97)	(0.51)	(0)	(0)	(0.25)	(5.99)
B. Reoptimized external ring angles ^b						
$\beta_1(\text{OCC}_X)$	111.2	111.3	111.6	108.1	107.5	108.6
$\beta_2(\text{C}_X\text{CC})$	116.8	116.4	115.5	116.3	117.5	117.0
$\beta_3(\text{OCH})$	105.9	106.3	105.8	108.3	109.6	107.7
$\beta_4(\text{HCC})$	109.6	110.3	111.5	110.2	108.7	108.2
$\beta_5(\text{CCC}_Y)$		117.2	117.7	117.5		
$\beta_6(\text{C}_Y\text{CO})$		110.3	108.7	109.0		
$\beta_7(\text{CCH})$		108.3	108.3	108.4		
$\beta_8(\text{HCO})$		107.4	110.5	109.7		
C. Dihedral angles between external and internal ring bonds ^b						
$\tau_1(\text{C}_X\text{COO})$	97.0	84.4	88.3	124.9	154.9	127.0
$\tau_2(\text{C}_Y\text{COO})$		126.1	160.5	170.0		
$\tau_3(\text{C}_X\text{CCO})$	122.9	97.3	76.5	91.4	118.7	121.9
$\tau_4(\text{C}_Y\text{CCO})$		147.3	163.3	147.1		
$\tau_5(\text{C}_X\text{CCC}_Y)$	0	25.0	42.2	28.1	0	0

^aAbsolute energies are given in hartree; relative energies (in parentheses) in kcal/mole.

^bAll angles are given in deg. The subscripts X and Y define the position of the methyl substituent at the ring according to Fig. 1. In this and the following tables only absolute values of the dihedral angles are given.

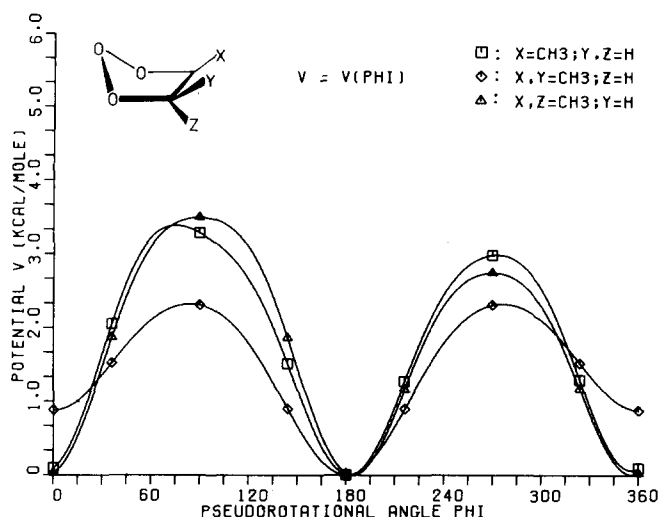


FIG. 2. Pseudorotational potential V (RHF/basis C) of propene and 2-butene PO, as a function of the puckering phase ϕ .

mations exhibit a strong torsion at the OO bonds of the ring. Hence, MO π_5 is significantly lowered in energy. It is less antibonding, thus providing stronger OO bonds and an overall stabilization of the molecule. As for MO π_4 , a moderate energy lowering can be observed resulting from somewhat weaker antibonding in the CO bonds, while its CC part is still strongly antibonding. The reverse situation applies to the T conformations of the ring ($\phi = 90^\circ$ or 270°). Now, π_4 preferentially mixes with the σ MO's due to enhanced torsion of the CH_2CH_2 bridge. Although MO π_5 is also lower in energy because of a slight reduction in the antibonding OO overlap, this lowering is far less than for the E puckered ring. The calculated orbital energies depicted in Table IV suggest that the stabilization of π_5 predominantly determines the dependence of the ring stability on the mode of ring puckering. However, the overall stabilization of the puckered trioxolane with regard to its planar form results from the total energy gain computed for π_5 and π_4 .

B. Stabilization of the planar 1,2,3-trioxolane ring by a methyl group

By utilizing the implications and consequences of the π effect described above, we will discuss in the following

TABLE IV. Stabilization of the two highest occupied MO's of 1,2,3-trioxolane due to orbital mixing caused by ring puckering.^a

ϕ , deg	Basis B					Basis C				
	Orbital energies		Stabilization			Orbital energies		Stabilization		
	π_4	π_5	π_4	π_5	total	π_4	π_5	π_4	π_5	total
0	-0.4910	-0.4605	-3.3	-11.7	-15.0	-0.4804	-0.4527	-2.8	-14.7	-17.5
18	-0.4917	-0.4580	-3.8	-10.1	-13.9					
36	-0.4928	-0.4535	-4.4	-7.3	-11.7	-0.4836	-0.4437	-4.8	-9.1	-13.9
54	-0.4929	-0.4514	-4.5	-6.0	-10.5					
72	-0.4925	-0.4500	-4.3	-5.1	-9.4					
90	-0.4923	-0.4495	-4.1	-4.8	-8.9	-0.4833	-0.4372	-4.6	-5.0	-9.6
planar	-0.4857	-0.4419	0	0	0	-0.4760	-0.4292	0	0	0

^aOrbital energies are given in hartree, individual and total stabilization energies in kcal/mole.

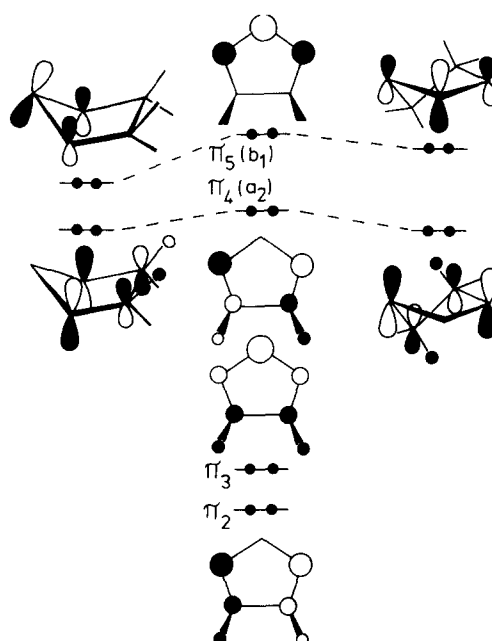


FIG. 3. Lowering of the two π -type HOMO's of 1,2,3-trioxolane due to ring puckering.

the influence of a methyl substituent on the stability of the ring. For this purpose, the two highest π -type MO's of the planar and puckered PO's are compared with the corresponding MO's of the parent PO. Possible changes of these two MO's will be elucidated by an analysis of the calculated charge distributions and the Mulliken population values.²⁹

A methyl substituent attached to the planar ring leads to a stabilization of the PO. This is revealed by the bond separation energies of Table V which have been calculated by means of the energies of Tables I and II and published energies of CH_4 , and C_2H_6 .^{30,19} In Table V, bond separation energies are also included which illustrate the effect of a methyl group in alicyclic molecules with comparative electronic structures. According to these data, the stabilizing influence of the substituent results mainly from an interaction between the orbitals of the CH_3 group and the orbitals of the polyoxide. Methylperoxide and 1,2,3-trioxolane are stabi-

TABLE V. Influence of a methyl substituent on planar 1, 2, 3-trioxolane and comparable alicyclic compounds.^a

Reaction	Specification	Bond separation energy (kcal/mole)	
		Basis B	Basis C
$\text{YC(Z)OOOCHCH}_3 + \text{CH}_4 \rightarrow \text{YC(Z)OOOCH}_2 + \text{CH}_3\text{CH}_3$	Y, Z = H	5.87	4.87
	Y = CH ₃ , Z = H		
	rig. model ^b	-0.45	
	flex. model ^b	3.43	2.62
$\text{YC(Z)OOOCHCH}_3 + \text{CH}_2\text{OOOCH}_2 \rightarrow 2 \text{CH}_2\text{OOOCHCH}_3$	Y = H, Z = CH ₃	5.77	4.74
	Y = CH ₃ , Z = H		
	rig. model ^b	-6.32	
	flex. model ^b	-2.43	-2.25
	Y = H, Z = CH ₃	-0.10	-0.12
$\text{CH}_3\text{CH}_2\text{CH}_3 + \text{CH}_4 \rightarrow \text{CH}_3\text{CH}_3^s + \text{CH}_3\text{CH}_3$		0.80	
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{CH}_3^s$	$\tau(\text{CCCO}) = 120^\circ$	0.76	0.53
$\text{CH}_3\text{CH}_2\text{OOH} + \text{CH}_4 \rightarrow \text{CH}_3\text{OOH} + \text{CH}_3\text{CH}_3^s$	$\tau(\text{CCOO}) = 120^\circ$	4.76	4.13
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + \text{CH}_3\text{CH}_3^s \rightarrow 2 \text{CH}_3\text{CH}_2\text{CH}_3$	$\tau(\text{CCCC}) = 0^\circ$	-2.24	
	$\tau(\text{CCCC}) = 120^\circ$	1.21	

^aIn order to exclude conformational effects, the conformation of the methyl substituent with regard to the adjacent ring bonds of the PO has been retained in the alicyclic rotors propane (staggered, eclipsed), propanol (CH₃CH₂ st., CH₂CH₂ ec., CCOH *trans*), ethanol (CH₃CH₂ ec., CCOH *trans*), ethylperoxide (CH₃CH₂ st., CH₂OO ec., COOH *trans*), and methylperoxide (CH₃OO ec., COOH *trans*). To balance steric effects, appropriate conformational energies of ethane have been used as indicated by the superscripts s (staggered) and e (eclipsed). Basis B energies of the alkanes have been taken from the literature: CH₄, C₂H₆, C₃H₈, Ref. 30; C₄H₁₀, Ref. 32; CH₄, C₂H₆, (Basis C), Ref. 19.

^bThe external ring angles of 1, 2, 3-trioxolane have been used in the rigid pseudorotor model, reoptimized values in the flexible pseudorotor model.

lized by CH₃ to similar extents, namely, by about 4 kcal/mole for methylperoxide and by about 5 kcal/mole for propene PO. The difference of 1 kcal/mole may be due to the favorable interaction between a CH₃ group and a CO bond found for 1-propanol.

By analysis of the MO's of propene PO, it becomes obvious that all π orbitals of the ring mix effectively with appropriate MO's of the CH₃ group. Besides the five π MO's of planar 1, 2, 3-trioxolane, additional π -type MO's result which are either OO, CO, or CC bonding, thus lowering the destabilizing effect of the two antibonding HOMO's. Also favorable for the stability of the substituted PO is the fact that electron donation by the methyl group is less than by a H atom of the methylene group as is revealed by the gross atomic charges of Table VI. Although charge separation in the CH bonds is reduced when a hydrogen augmented basis set is employed, electron donation to the ring by a methylene hydrogen is still more than twice as large as by a CH₃ group.³¹ Accordingly, the substituted PO ring does not accumulate as much negative charge as the unsubstituted one. This is further indication of the stabilizing effect of a methyl group.

If two CH₃ substituents are attached to the PO ring, then, the electronic effect of the second methyl group depends on whether both substituents are on the same side or on opposite sides of the ring. In the latter case, the stabilizing effect of the second methyl group is as high as for the first group, but a *cis* configuration

of the CH₃ groups reduces this stabilization by about 2 kcal/mole. This steric effect resembles the interactions between the CH₃ groups of butane.³² If butane conformations are chosen which correspond to the steric arrangements of the two methyl groups of planar *cis*- and *trans*-2-butene PO [$\tau(\text{C}_M\text{CCC}_M) = 0^\circ$ and 120°],³³ then, a positive interaction energy is obtained for the 120° form (see Table V), but destabilizing interactions result for the eclipsed conformation with $\tau = 0^\circ$ corresponding to *cis*-2-butene PO.

We conclude that the overall effect of a methyl group on the trioxolane ring is always stabilizing due to orbital mixing and reduced charge accumulation in the ring. However, the electronic effects of two methyl groups are additive only if methyl-methyl interactions are negligible. Then, the methyl-ring interactions represent the stability determining electronic factor.

C. The role of the substituent orientation

According to the relative energies of Tables I and II, the overall stabilization of the PO ring by a CH₃ group is either reinforced or weakened, if the ring puckers. Obviously, these changes depend on the mode of puckering and the corresponding orientation of the substituent relative to the mean plane of the ring. We define the difference Δ between the energies of the substituted and unsubstituted PO taken for the same value of ϕ and reduced by the energies of the corresponding planar forms as an appropriate measure of the positional effect of the

TABLE VI. Gross atomic populations of the ring substituents of primary ozonides calculated with Basis C.^a

ϕ , deg	X	C _X	H	Y	C _Y	Z	C _Z
A. 1,2,3-Trioxolane (X=Y=Z=H)							
0	0.1904		0.2016				
36	0.1984		0.2064	0.1967		0.1923	
90	0.1959		0.2034				
planar	0.1959						
B. 4-Methyl-1,2,3-trioxolane (X=CH ₃ , Y=Z=H)							
0	0.0452	-0.4957	0.2037	0.1898		0.1993	
36	0.0606	-0.4938	0.2088	0.1918		0.1957	
90	0.0612	-0.4939	0.2065	0.2022		0.1964	
144	0.0522	-0.4932	0.1945	0.2053		0.1974	
180	0.0474	-0.5059	0.1905	0.1998		0.1868	
216	0.0537	-0.5098	0.1983	0.1894		0.1912	
270	0.0542	-0.5064	0.1961	0.1895		0.2009	
324	0.0453	-0.4982	0.1978	0.1935		0.2074	
planar	0.0463	-0.4978	0.1966	0.1953		0.1930	
C. <i>Cis</i> -4,5-dimethyl-1,2,3-trioxolane (X=Y=CH ₃ , Z=H)							
0	0.0467	-0.4954	0.1966				
36	0.0527	-0.5008	0.2011	0.0484	-0.5007	0.1904	
90	0.0558	-0.5034	0.1976	0.0499	-0.5101	0.9111	
144	0.0568	-0.5011	0.1850	0.0455	-0.5108	0.1922	
180	0.0492	-0.5056	0.1828				
planar	0.0502	-0.4965	0.1883				
D. <i>Trans</i> -4,5-dimethyl-1,2,3-trioxolane (X=Z=CH ₃ , Y=H)							
0	0.0416	-0.4957	0.2019	0.1903		0.0453	-0.5053
36	0.0585	-0.4924	0.2080	0.1945		0.0498	-0.4924
90	0.0595	-0.4921	0.2057				
216	0.0523	-0.5094	0.1942	0.1929		0.0426	-0.4991
270	0.0518	-0.5078	0.1909				
planar	0.0436	-0.4973	0.1963				

^aPositive values indicate positively charged substituents and negative values negatively charged substituents.

substituent:

$$\Delta = (E(\text{Me-PO})_{q>0} - E(\text{Me-PO})_{q=0}) - (E(\text{PO})_{q>0} - E(\text{PO})_{q=0}). \quad (1)$$

A negative value of Δ indicates additional stabilization by the methyl group due to puckering. Accordingly, a positive value of Δ indicates a reduction in the overall stabilization of the substituent. The computed Δ energies for each of the puckered PO forms considered are listed in Tables VII-IX.

In recent studies^{8,11} the conformational features of disubstituted primary ozonides have been analyzed qualitatively in terms of *gauche-trans* interactions between substituents and ring bonds, between substituents and oxygen lone pairs, and between the substituents themselves. Giving a preference to the *trans* arrangement of ring bonds and substituent, the most stable conformation was found by counting the number of possible *gauche* and *trans* interactions.^{8,11} Certainly this is a very approximate procedure which has to be criticized for several reasons. First, the *gauche* or *trans* character of the alkyl substituent has been defined without specific knowledge of the substituent position. Secondly, the preference of a *trans* arrangement of the OCCC_s and the

OCCC_s entities³³ is a mere assumption. Even if this is true, one has to ask whether it is the dominating effect. Finally, the role of the oxygen lone pairs is by no means only repulsive. A coplanar arrangement of the CX, CY, or CZ bond and an oxygen lone pair can lead to a favorable, ring stabilizing delocalization of the latter.

Because of the fact that the bond-bond interaction approach has been extensively used to explore possible routes for the decomposition of primary ozonides^{8,11} we will investigate its justification. To aid a quantitative analysis of the interactions between CC and OO or CC and CO bonds, the rotational behavior of two appropriate alicyclic rotors, namely, ethylperoxide and 1-propanol has been investigated. The methyl-ring bond interactions in a methylated PO can be modeled, if these molecules are allowed to rotate around their central bonds while the terminal groups, CH₃ or OH, are frozen in their most stable conformations (CH₃CH₂ staggered; HOOC or HOCC *trans*).³⁴ Assuming that the conformational and electronic features of the corresponding OCCC_M and OCCC_M fragments are equivalent, an analysis of bond-bond interactions in the three PO's can be performed. Quantitatively, this is done by evaluating the dihedral angles $\tau(\text{C}_M\text{COO})$ and $\tau(\text{C}_M\text{CCO})$ for each

TABLE VII. Position and influence of the substituent in puckered conformations of 4-methyl-1, 2, 3-trioxolane. ^a

ϕ , deg	Position of X ^b	α_X , deg	Subst. effect Δ values		π effect ^c			
			B	C	total		Subst. X	
			B	C	B	C	B	C
0	<i>t-g</i> axial	26.8	-0.13	0.09	-14.1	-16.9	0.7	0.6
18	<i>t-g</i> axial	18.8	-0.03		-11.6		2.3	
36	<i>t-g</i> axial	12.7	0.11	0.68	-8.6	-10.8	3.1	3.1
54	<i>t-g</i> axial	8.2	0.09		-7.0		3.6	
72	<i>t-g</i> axial	6.4	-0.13		-5.8		3.6	
90	<i>t-g</i> axial	7.6	-0.21	0.25	-5.4	-6.3	3.5	3.3
108	<i>t-g</i> axial	11.8	-0.23		-6.2		3.2	
126	<i>t-g</i> axial	17.3	-0.20		-8.0		2.6	
144	<i>t-g</i> axial	25.0	-0.03	0.14	-10.1	-12.3	1.6	1.6
162	<i>t-g</i> inclinal	34.0	-0.03		-13.3		0.6	
180	<i>t-g</i> inclinal	43.7	-0.02	0	-15.8	-18.5	-0.8	-1.0
198	<i>t-g</i> inclinal	52.1	-0.19		-16.0		-2.1	
216	<i>t-g</i> inclinal	57.8	-0.15	-0.10	-14.2	-16.7	-2.5	-2.8
234	<i>t-g</i> equatorial	61.8	-0.05		-13.0		-2.4	
252	<i>t-g</i> equatorial	62.5	-0.22		-11.3		-1.9	
270	<i>t-g</i> equatorial	61.2	-0.25	-0.11	-10.2	-11.0	-1.3	-1.4
288	<i>t-g</i> inclinal	57.5	-0.24		-10.2		-0.8	
306	<i>t-g</i> inclinal	52.5	-0.14		-11.1		-0.5	
324	<i>t-g</i> inclinal	44.8	-0.22	-0.08	-12.2	-14.3	-0.5	-0.4
342	<i>t-g</i> inclinal	36.6	-0.14		-14.0		-0.1	

^aSubstituent effects as well as the π effects are given in kcal/mole. They are derived from the relative energies of 1, 2, 3-trioxolane (Paper III) and the π -stabilization energies of Table IV using the relevant values of the planar forms as reference energies.

^bPosition determined according to Ref. 24.

^cThe energies of the two HOMO's of propene PO are, -0.4755 and -0.4364 (basis B) and -0.4672 and -0.4248 hartree (basis C), respectively.

of the puckered PO conformations studied and determining the rotational energies of the two alicyclic molecules for these values of τ . In this way, the dependence of the angles τ on the pseudorotation angle ϕ leads to a set of energies which should reveal the stabilizing or destabilizing character of the interactions between the substituent and the ring bonds.

Unfortunately, nothing is known about the conformational tendencies of ethylperoxide and only moderate knowledge about 1-propanol has been gathered.^{35,36} Therefore, we have calculated the potential of internal rotation around the central bonds of the peroxide and the alcohol employing basis sets B and C. Standard geometries²⁵ and a rigid rotor model have been assumed. The results thus obtained are summarized in Table X.

Certainly, the assumption of rigid internal rotation leads to an overestimation of the barrier heights, especially of the *cis* barriers. However, fairly reasonable values should be obtained for dihedral angles larger than 60°, i. e., for those τ values which occur in a puckered PO. For instance, with a flexible rotor model the relative energies of ethylperoxide decrease by 0.1 to 0.3 kcal/mole if $\tau \geq 60^\circ$ while the *cis* barrier is reduced by as much as 4 kcal/mole. Evaluating the internal rotational potentials from the data of Table X, energy values representing the interaction energies be-

tween the methyl group and the ring bonds can be assigned to each of the dihedral angles τ determined for the various puckered conformations of the three PO's. These energies are summarized together with the corresponding dihedral angles τ in Tables XI-XIII.

As is shown in the next sections the description of the substituent effect in terms of bond-bond interactions does not give much of an insight into the electronic features of the methyl substituted PO's. Therefore, we carried out an alternative approach to the problem by analyzing the calculated PO MO's. The form of the two highest occupied MO's of each of the three PO's indicates that they are related to π_5 and π_4 of planar 1, 2, 3-trioxolane. The HOMO is strongly OO antibonding while the other MO is CC and CO antibonding. The energies of these MO's decrease if the ring puckers. This energy lowering depends on the phase angle ϕ , i. e., the mode of puckering as well as the position of the methyl group. In order to explain this relationship the charge distribution in the puckered PO conformations has been analyzed. According to the gross atomic populations of Table VI, an equatorially located H atom donates more charge to the ring than an axially located one. This results from an increased overlap between the 1s orbital of the more in-plane positioned H atom and the σ MO's of the ring skeleton as is illustrated by Fig. 4.

TABLE VIII. Position and influence of the substituents in puckered conformations of *cis*-4,5-dimethyl-1,2,3-trioxolane.^a

ϕ , deg	Position of Y	α_Y , deg (α_X)	Subst. effect Δ values		π effect ^b total		π effect of substituents both Y				
			B	C	B	C	B	C	B	C	
A. Standard geometries											
0	<i>t-g</i> axial	26.8		0.27		-12.5		2.5		1.8	
18	<i>t-g</i> inclinal	36.6		-1.06		-11.3		2.6		0.3	
36	<i>t-g</i> inclinal	44.8		-2.02		-9.3		2.4		-0.7	
54	<i>t-g</i> inclinal	52.5		-3.42		-8.4		2.1		-1.5	
72	<i>t-g</i> inclinal	57.5		-3.85		-7.7		1.7		-1.9	
90	<i>t-g</i> equatorial	61.2		-4.06		-7.9		1.0		-2.0	
108	<i>t-g</i> equatorial	62.5		-3.86		-9.2		0.2		-3.0	
126	<i>t-g</i> equatorial	61.8		-3.47		-11.3		-0.8		-3.4	
144	<i>t-g</i> inclinal	57.8		-2.98		-13.3		-1.6		-3.2	
162	<i>t-g</i> inclinal	52.1		-2.33		-16.0		-2.1		-2.7	
180	<i>t-g</i> inclinal	43.7		-2.06		-17.3		-2.3		-1.5	
B. Refined geometries											
0	<i>t-g</i> axial	32.5		-0.34	-0.17	-12.6	-15.6	2.5	1.9	1.8	1.3
36	<i>t-g</i> inclinal	50.9	(18.3)	-0.64	-0.49	-9.6	-12.1	2.1	1.8	-1.0	-1.3
90	<i>t-g</i> equatorial	68.2	(10.3)	-1.63	-1.36	-8.5	-9.5	0.4	0.1	-3.1	-3.2
144	<i>t-g</i> inclinal	63.4	(29.3)	-1.13	-1.11	-13.9	-16.2	-2.2	-2.3	-3.8	-3.9
180	<i>t-g</i> inclinal	49.2		-0.88	-0.87	-17.6	-20.7	-2.6	-3.2	-1.8	-2.2

^aSee comments a and b of Table VII.^bThe energies of the two HOMO's of *cis*-2-butene PO are -0.4627 and -0.4330 (basis B, standard geometry), -0.4602 and -0.4322 (basis B, reoptimized substituent orientations), and -0.4536 and -0.4191 hartree (basis C), respectively.

If an equatorially bonded H atom is replaced by a methyl group, two favorable changes in the electron structure of the ring take place. First, electron donation to the ring is significantly reduced. Secondly, one of the pseudo- π orbitals of the equatorially bonded CH₃ group is capable of overlapping with the π type MO's of the ring. Some of the charge donated to the ring through the σ MO's can be back-donated through the π -type orbit-

als, thus lowering the electron population of the two highest, mainly antibonding MO's. If the CH₃ group is axially positioned no significant π -like overlap of ring and CH₃ MO's is possible and, accordingly, no back-donation of electron charge occurs. Also, the lowering of the total ring charge due to methyl substitution of the CH₂ groups is less effective for an axially bonded H atom than for an equatorially bonded one. This is sug-

TABLE IX. Position and influence of the substituents in puckered conformations of *trans*-4,5-dimethyl-1,2,3-trioxolane.^a

ϕ , deg	Position of Z	α_Z , deg	Subst. effect Δ values		π effect ^b total		π effect of substituents both Z			
			B	C	B	C	B	C	B	C
0	<i>b-g</i> inclinal	136.3	-0.14	0.08	-14.7	-17.6	0.2	-0.1	-0.5	-0.7
18	<i>b-g</i> inclinal	146.0	-0.02		-10.9		3.0		0.7	
36	<i>b-g</i> axial	155.0	-0.07	0.55	-7.3	-9.5	4.4	4.4	1.3	1.3
54	<i>b-g</i> axial	162.7	-0.12		-5.0		5.6		2.0	
72	<i>b-g</i> axial	168.2	-0.24		-3.3		6.1		2.5	
90	<i>b-g</i> axial	172.4	-0.30	0.52	-2.7	-3.8	6.2	5.8	2.7	2.5
198	<i>b-g</i> inclinal	143.4	-0.23		-16.2		-2.3		-0.2	
216	<i>b-g</i> inclinal	135.2	-0.39	-0.15	-15.2	-17.6	-3.5	-3.7	-1.0	-0.9
234	<i>b-g</i> inclinal	127.5	-0.41		-13.9		-3.3		-0.9	
252	<i>b-g</i> inclinal	122.5	-0.50		-12.6		-3.2		-1.3	
270	<i>b-g</i> equatorial	118.8	-0.54	-0.23	-11.9	-12.6	-3.0	-3.0	-1.7	-1.6

^aSee comments a and b of Table VII.^bThe energies of the two HOMO's of planar *trans*-2-butene PO are -0.4659 and -0.4314 (basis B) and -0.4587 and -0.4207 hartree (basis C), respectively.

TABLE X. RHF energies of ethylperoxide and 1-propanol obtained for various values of the angles $\tau(\text{CCOO})$ and $\tau(\text{CCCO})$.^{a,b}

Rotational angle τ , deg	Basis B [3s2p/2s]		Basis C [3s2p1d/2s]	
	Absolute	Rel.	Absolute	Rel.
A. Ethylperoxide				
0	-228.49491	11.03 (7.05)	-228.81292	11.16
60	-228.51018	1.45 (1.34)	-228.82797	1.72
90	-228.51056	1.21 (1.16)	-228.82832	1.50
120	-228.50854	2.48 (2.20)	-228.82637	2.72
180	-228.51249	0 (0)	-228.83071	0
B. 1-Propanol				
0	-192.82213	6.02	-193.09839	6.26
60	-192.83173	0	-193.10837	0
90	-192.82854	2.00	-193.10532	1.91
120	-192.82531	3.85	-193.10209	3.94
180	-192.83145	0.17	-193.10829	0.05

^aAbsolute energies are given in hartree, relative energies in kcal/mole. Numbers in parentheses indicate the changes in relative energies if flexible rotation is assumed.

^bThe dihedral angle $\tau = 0^\circ$ is defined by a *cis* arrangement of heavy atom bonds. See text for definition of the conformations of the terminal groups.

gested by the population values of Table VI.

In order to substantiate the interplay of substituent and ring MO's two sets of data have been evaluated which provide a quantitative measure of the substituent position and the substituent effect. These are the substituent orientation angles²⁴ and the stabilization energies of the two HOMO's. The orientation angles α reveal whether the substituent is more equatorially or more

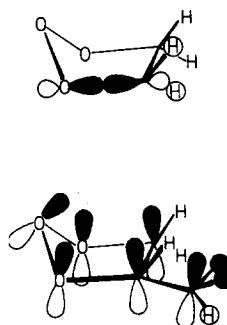


FIG. 4. Enhanced overlap between a 1s orbital of an equatorially positioned H atom and a σ MO of the ring skeleton (above). Overlap between a π -type MO of the ring and a pseudo- π orbital of an equatorially positioned methyl group (below).

axially placed, i. e., whether it is more or less capable of accepting charge back-donated by the π -like orbitals of the ring. The energetical consequence of the substituent orientation is determined by the lowering of the two PO HOMO's in the same way as is done for the Δ values, i. e., by replacing the total energies of Eq. (1) by the sum of the two orbital energies. If the π effect caused by the substituent is negative, then the role of the methyl group can be described as stabilizing, otherwise as destabilizing. The relevant values of α and the π -stabilization energies are listed in Tables VII, VIII, and IX.

Having established the two possible ways of describing substituent-ring interactions, we will discuss in the next section the conformational behavior of the three PO's in detail.

D. 4-Methyl-1,2,3-trioxolane (propene PO)

Irrespective of the mode of puckering, nonplanar forms of the monosubstituted PO are more stable than

TABLE XI. Bond-bond interaction energies (kcal/mole) calculated for puckered conformations of 4-methyl-1, 2, 3-trioxolane.^a

ϕ , deg	$\tau(\text{XCOO})$, deg	XCOO interaction energy	$\tau(\text{XCCO})$, deg	XCCO interaction energy	Total interaction energy
0	92.5	-0.9	118.4	0	-0.9
18	83.2	-1.2	104.3	-0.8	-2.0
36	78.5	-1.3	92.9	-1.9	-3.2
54	76.4	-1.3	82.7	-3.0	-4.3
72	79.7	-1.3	77.9	-3.4	-4.7
90	85.7	-1.2	75.9	-3.5	-4.7
108	95.2	-0.8	77.7	-3.4	-4.2
126	106.6	-0.3	82.2	-3.0	-3.3
144	120.0	0	90.8	-2.1	-2.1
162	134.4	-0.2	101.8	-1.0	-1.2
180	147.6	-0.9	115.3	0	-0.9
198	156.9	-1.4	129.2	-0.1	-1.5
216	161.2	-1.6	142.4	-1.0	-2.6
234	162.8	-1.7	149.7	-1.8	-3.5
252	159.6	-1.6	154.4	-2.3	-3.9
270	153.6	-1.2	156.6	-2.5	-3.7
288	144.3	-0.7	155.1	-2.4	-3.1
306	133.1	-0.2	151.6	-2.0	-2.2
324	119.9	0	142.6	-1.1	-1.1
342	106.2	-0.3	132.6	-0.3	-0.6

^aInteraction energies have been derived from the data of Table X. Reference points are the interaction energies obtained for the planar 1, 2, 3-trioxolane ring.

TABLE XII. Bond-bond interaction energies (kcal/mole) calculated for puckered conformations of *cis*-4,5-dimethyl-1,2,3-trioxolane.^a

ϕ , deg	$\tau(\text{YCOO})$, deg	YCOO interaction		YCCO interaction		Total inter-action energy		XCCY inter-action energy	
		energy	$\tau(\text{YCCO})$, deg	energy	X+Y	$\tau(\text{XCCY})$, deg	rig.	flex.	
0	92.5	-0.9	118.4	0	-1.8	0	0.	0	
18	106.2	-0.3	132.6	-0.3	-2.6	14.5	-1.6	-0.7	
36	119.9	0	142.6	-1.1	-4.3	24.7	-4.1	-1.8	
54	133.1	-0.2	151.6	-2.0	-6.3	34.0	-6.7	-3.0	
72	144.3	-0.7	155.1	-2.4	-7.8	37.3	-7.5	-3.4	
90	153.6	-1.2	156.6	-2.5	-8.4	38.8	-7.9	-3.6	
108	159.6	-1.6	154.4	-2.3	-8.1	36.9	-7.5	-3.4	
126	162.8	-1.7	149.7	-1.8	-6.8	32.7	-6.3	-2.8	
144	161.2	-1.6	142.4	-1.1	-4.8	24.5	-4.1	-1.8	
162	156.9	-1.4	129.2	-0.1	-2.7	13.6	-1.4	-0.6	
180	147.6	-0.9	115.3	0	-1.8	0	0	0	

^aSee comment in Table XI. The conformational energies of the XCCY fragment have been derived from the STO-3G results on butane, Ref. 32.

its planar conformation. Both basis *B* and basis *C* results predict the planar form to be located at a local maximum of the pseudorotational surface. Two conformational minima are found for ϕ values close to 0° or 180° , i. e., the oxygen E forms are the most stable conformations of the ring. The barriers to pseudorotation correspond to the energies of the T forms with $\phi = 90^\circ$ and 270° . This finding is in opposition to the predictions of semiempirical studies on propene PO^{9,10} but agrees with the *ab initio* results achieved for the parent PO.

Comparing the relative energies of Tables I and II, it becomes evident that the basis set effects found for 1,2,3-trioxolane (Paper III) also play a role in RFH calculations of the methyl substituted PO's. Thus, basis *B* largely underestimates the stability of the oxygen E forms due to its tendency of favoring ring conformations with a relatively large OOO angle, i. e., puckering

modes with $\phi = 90^\circ$ or 270° . On the other hand, basis *C* has been found (Paper III) to provide a consistent description of all ring atoms. It has a sufficient flexibility to describe the subtle electronic effects which stabilize the puckered ring. Therefore, we exclusively base our predictions of barriers heights and conformational stabilities on the RHF/basis *C* energies of Table II. According to them, pseudorotation of propene PO is hindered by barriers of 3.3 and 2.9 kcal/mole. Another 4 to 5 kcal/mole are necessary when the molecule tries to surmount the barrier to planarity.

Although the positional effect of the CH₃ group is small, the Δ values obtained by RHF/basis *C* calculations clearly suggest that an equatorially positioned methyl substituent ($\alpha_x \geq 60^\circ$) leads to stabilization of the ring (-0.1 kcal/mole) while an axial position ($\alpha_x < 30^\circ$) has the opposite effect [$\Delta(\phi = 36^\circ) = 0.7$ kcal/mole]. The

TABLE XIII. Bond-bond interaction energies (kcal/mole) calculated for puckered conformations of *trans*-4,5-dimethyl-1,2,3-trioxolane.^a

ϕ , deg	$\tau(\text{ZCOO})$, deg	ZCOO interaction		ZCCO interaction		Total inter-action energy		XCCZ inter-action energy	
		energy	$\tau(\text{ZCCO})$, deg	energy	X+Z	$\tau(\text{XCCZ})$, deg	rig.	flex.	
0	147.6	-0.9	115.3	0	-1.8	126.2	-0.1	-0.1	
18	134.4	-0.2	101.8	-1.0	-3.2	140.1	-1.0	-0.9	
36	120.0	0	90.8	-2.2	-5.4	151.3	-2.2	-1.9	
54	106.6	-0.3	82.2	-3.0	-7.6	160.3	-3.1	-2.8	
72	95.2	-0.8	77.7	-3.4	-8.9	164.5	-3.4	-3.1	
90	85.7	-1.2	75.9	-3.5	-9.4	166.4	-3.6	-3.2	
198	106.2	-0.3	132.6	-0.3	-2.1	112.0	-0.3	-0.2	
216	119.9	0	142.6	-1.1	-3.7	102.1	-1.0	-0.8	
234	133.1	-0.2	151.6	-2.0	-5.7	93.5	-1.7	-1.4	
252	144.3	-0.7	155.1	-2.4	-7.0	90.4	-1.8	-1.6	
270	153.6	-1.2	156.6	-2.5	-7.4	88.8	-1.9	-1.8	

^aSee comments in Tables XI and XII.

substituent effects derived from basis B energies signify the same relation between Δ and α values, but they are somewhat inconsistent for small substituent orientation angles.

Convincing evidence for the dependence of the π effect on the position of the methyl group is provided by the stabilization energies obtained for the two highest occupied MO's and listed in Table VII. The π effect of the substituent is strongly destabilizing for α values close to 0° . If the orientation angle becomes greater than 60° because of an increase in ϕ , then the π effect becomes stabilizing (negative Δ). These changes occur smoothly and parallel the changes in the Δ and α values. They hardly depend on the basis, though the basis B π -stabilization energies seem to underestimate the stabilizing effect of an equatorially positioned CH_3 group slightly.

The magnitude of the π effect, as compared to the computed Δ values, indicates that it does not solely determine the electronic influence of the substituent. In fact, one cannot expect a direct equivalence of Δ - and π -stabilization energies, since all MO's change when going from the planar to the puckered PO conformations. Provided there exists a direct relationship between total and orbital energies,³⁷ a detailed analysis of all orbitals should be performed in order to obtain quantitatively coinciding results. Nevertheless, it seems safe to conclude that the π effect is the dominant electronic factor which clearly characterizes the stabilizing or destabilizing role of the substituent.

In the next paragraph, we will investigate whether a similar result can be obtained by evaluating the interactions energies between external and internal ring bonds. According to the dihedral angles listed in Table XI, and the rotational tendencies of ethylperoxide, a favorable *trans* arrangement of bonds is achieved by the molecule for puckering modes close to $\phi = 234^\circ$. Taking planar propene PO as the appropriate reference conformation, puckered ring forms with an equatorial CH_3 group should be more stable by about 0.3 kcal/mole over those with an axial CH_3 group. This, of course, is in accord with the Δ energies of Table VII. However, if the interactions of the methyl group with the vicinal CO ring bond are included in the analysis, the picture is reversed. Now, the PO conformations with an axial CH_3 substituent should be favored, since the *gauche* conformation of 1-propanol is more stable than the *trans* form as is shown in Table X. In addition, the high *gauche-trans* barrier of 1-propanol (3.8 kcal/mole as compared to 2.5 kcal/mole for ethylperoxide) leads to a relatively large separation of the quasi-*gauche* arrangement with $\tau = 76^\circ$ ($\phi = 90^\circ$, -3.5 kcal/mole) and the quasi-*trans* arrangement with τ still 25° below the ideal value of 180° ($\phi = 270^\circ$, -2.5 kcal/mole). Even if this energy separation is somewhat exaggerated by the rigid rotor model of 1-propanol, the dilemma of predicting a stabilizing effect for the axially positioned methyl group remains. Furthermore, the results of Table XI indicate that the bond-bond interaction approach provides no distinction between the two E forms as it assigns to both the same ring-substituent interaction energy of -0.9 kcal/mole.

E. *Cis*-4,5-dimethyl-1,2,3-trioxolane (*cis*-2-butene PO)

If standard external ring angles optimized for the parent PO are employed in the case of *cis*-2-butene PO, then a complete change of the conformational behavior of the 1,2,3-trioxolane ring occurs. The energy minima are no longer found for puckering modes with $\phi = 0^\circ$ or 180° but for those with $\phi = 90^\circ$ or 270° . Also, the barriers to pseudorotation as well as to inversion are drastically increased, but still show a 5 kcal/mole advantage for pseudorotation of the ring. The changes in the conformational tendencies of the trioxolane ring are caused by substituent-substituent rather than substituent-ring interactions. This is suggested by the π -stabilization energies listed in Part A of Table VIII. The total stabilization of the two HOMO's is as usual stronger for the E forms than for the T forms. As for the individual methyl group effects, the inverted oxygen E should be more stabilized by the two substituents than the T forms at $\phi = 90^\circ$ and 270° or the E form at $\phi = 0^\circ$. Thus, no specific stabilization of the T forms is revealed. It seems that the rigid pseudorotor model leads to a wrong order of conformational stabilities due to an overestimation of the repulsive interactions between the methyl groups.

As was already noted above, the substituent-substituent interactions are best modeled by the conformational behavior of butane. This has been extensively studied by Pople and co-workers³² who demonstrated that the calculated potential of internal rotation around the central bond of butane is quite unrealistic if rigid rotation is assumed. However, substantial improvement of the theoretical potential can be gained by using a flexible rotor model in which the CCC angles are optimized for each conformation considered. In Table XII, we have listed the dihedral angles $\tau(\text{C}_M\text{CCC}_M)$ and the corresponding substituent-substituent interaction energies taken from the rigid and flexible rotor potentials of butane.³² The energy of the *cis* form of butane has been used as reference energy since its steric interactions should be comparable to those effective for planar *cis*-2-butene PO, the reference conformation for the puckered *cis*-2-butene PO forms.

When going from an E form with $\phi = 0^\circ$ or 180° to one of the T forms with $\phi = 90^\circ$ or 270° the C_MCCC_M angle opens from 0° to about 40° . In the case of butane, a 40° rotation from the *cis* towards the *gauche* form is accompanied by an energy decrease of 7.9 kcal/mole if rigid rotation is assumed, but by only 3.6 kcal/mole if flexible rotation is assumed. This means that in the latter case the energy change is comparable to those occurring in the conformational processes of ethane (2.9 kcal/mole³⁸) or propane (3.8 kcal/mole³⁹). Therefore, the conclusion can be drawn that a *cis*-2-butene PO model with flexible positions of the substituents, i. e., reoptimized external ring angles for each value of ϕ , should lead to a conformational surface similar to those of ethylene and propene PO.

In Table III, reoptimized external ring angles obtained with basis A are shown for six selected confor-

mations of *cis*-2-butene PO. Basis *A* is known to lead to a satisfactory description of structure and conformation in the case of unsubstituted alkanes.⁴⁰ Hence, it should also provide a reasonable account of the widening of the CCC angles in *cis*-2-butene PO caused by steric repulsion between the two CH₃ groups. However, the deficiencies of basis *A* are too severe (see Paper III) to allow a reasonable description of the PO ring itself. Accordingly, we refrain from interpreting basis *A* energies, but analyze the more reliable values obtained with the augmented basis *C* when using the refined external ring angles.

The relative energies of Table III clearly indicate that the form of the pseudorotational surface of *cis*-2-butene PO is more determined by the conformational tendencies of the trioxolane ring than the steric interactions between the CH₃ groups. The E forms still exhibit the lowest energies, thus suggesting that the conformational minima are still located in the vicinity of $\phi = 0^\circ$ and 180° . Also, the saddlepoints of the (q, ϕ) surface are probably close to $\phi = 90^\circ$ and 270° . The steric repulsion between the two CH₃ groups leads only to a 0.7 kcal/mole lowering of the energy of the T forms. It should also be responsible for a 1 kcal/mole increase of the barrier to planarity (8.8 kcal/mole, Table II).

Since a 0.7 kcal/mole stabilization of the T forms is of the same magnitude as the pseudorotational barrier of 1,2,3-trioxolane obtained with basis *B* (Paper III), it follows that the RHF/basis *B* energies of Table III falsely predict broad pseudorotational minima close to the location of the T forms. Nevertheless, basis *B* results are interesting for two reasons. First, they demonstrate the usefulness of the π effect which, according to the data of Table VIII, is almost independent of both the geometrical model and the degree of basis set sophistication. This independence suggests that it should be possible to obtain reasonable conformational predictions on higher alkene PO's with basis *B* by utilizing the computed order of π -stabilization energies.

Secondly, basis *B* as well as basis *C* results hint that higher *cis*-alkene PO's exist where the extrastabilization of the oxygen E is totally absorbed by repulsive substituent-substituent interactions. For these PO's, the conformational minimum will be shifted from $\phi = 0^\circ$ or 180° to $\phi = 90^\circ$ or 270° , in accord with Bailey's assumption of CC half-chair conformations for highly alkylated PO's.⁵ We are presently investigating this point.

It is interesting to compare the π effect brought about by two methyl groups (column 6 of Table VIII) with the one of a single methyl group calculated for propene PO. Deducting the appropriate values of table VII from the substituent π effects of Table VIII, the π effect of the second CH₃ group can be derived. These are also listed in Table VIII. Apart from conformations with a small value of ϕ , the second methyl group, symbolized by Y, is placed in either an inclinal or equatorial position and, therefore, leads to a stabilization of the ring. Its effect is about 1 kcal/mole stronger than the one of a single CH₃ group with the same orientation with re-

gard to the mean plane of the ring. An analysis of the charge distribution in *cis*-2-butene PO provides an explanation for this finding. According to the gross atomic charges of Table VI, the donation of electrons to the ring by a methyl group and an adjacent methine hydrogen is lower in *cis*-2-butene PO than in propene PO, thus leading to a lower electron population of the two highest occupied MO's. Probably, the existence of a positively charged substituent in the close vicinity cushions the electron donation ability of the second CH₃ substituent.

In Table XII, the dihedral angles $\tau(\text{YCOO})$ and $\tau(\text{YCCO})$ are listed together with the corresponding bond-bond interaction energies. The latter correctly predict the conformations close to $\phi = 144^\circ$ to be more stabilized by substituent-ring interactions than the corresponding forms close to $\phi = 36^\circ$. But they still fail to reveal the stabilizing effect of two inclinal CH₃ groups attached to an E puckered trioxolane ring ($\phi = 180^\circ$) as compared to the destabilizing effect of two axially arranged CH₃ groups of the E form with $\phi = 0^\circ$. In addition, the bond-bond interaction energies significantly overestimate the stabilization of the T forms. If the methyl-methyl interactions derived from the internal rotational potential of butane³² are added to the energies listed in column 6 of Table XII, the stabilization of the T forms exceeds those of the E forms by as much as 10 kcal/mole. It is this overestimation of stabilizing bond-bond interactions for the T forms which has prevented any consideration of the E conformations with $\phi = 0^\circ$ or 180° in past studies on *cis*-alkene PO's.^{5,8,11}

F. *Trans*-4,5-dimethyl-1,2,3-trioxolane (*trans*-2-butene PO)

If the steric effects of two CH₃ groups placed on opposite sites of the ring are also modeled by the conformational behavior of butane, then two extreme situations can be distinguished. In the first, the two methyl substituents are almost *trans* to each other. This is the case of a PO conformation with $\phi = 90^\circ$. In the second situation, which occurs for $\phi = 270^\circ$, the dihedral angle $\tau(\text{C}_M\text{CCC}_M)$ has decreased below 90° (Table XIII). Hence, pseudorotation from $\phi = 90^\circ$ to $\phi = 270^\circ$ leads from *trans* to *gauche* interactions between the substituents. The corresponding change of the rotational potential of butane amounts to 3.5 kcal/mole (rigid rotation) and 3.1 kcal/mole (flexible rotation), respectively,³² as is shown in Table XIII. The relatively small difference between the rigid and the flexible rotor values indicates that a rigid pseudorotor model suffices to give a reasonable account of the conformational features of *trans*-2-butene PO. In addition, the magnitude of the C_MCCC_M interaction energies of Table XIII suggests that substituent-substituent interactions should hardly cause a significant change in the conformational potential of the trioxolane ring.

The relative energies of *trans*-2-butene PO depicted in Tables I and II confirm this prediction. The conformational energies resemble those of ethylene and propene PO indicating pseudorotational minima for the two equivalent oxygen E forms with $\phi = 0^\circ$ or $\phi = 180^\circ$.

Again, the barriers to pseudorotation are determined by the energies of the T forms with $\phi = 90^\circ$ and 270° . The difference of 0.7 kcal/mole in the computed stabilities of these forms is easily rationalized by the π effect of the two methyl groups. The conformation with $\phi = 90^\circ$ is less stable than that with $\phi = 270^\circ$, since both substituents are placed axially with regard to the mean ring plane. For $\phi = 270^\circ$, the methyl groups are equatorial as is revealed by the substituent orientation angles of Table IX. Accordingly, the π effects of the methyl groups are both destabilizing if $\phi = 90^\circ$, and both stabilizing if $\phi = 270^\circ$, thus leading to the computed relative energies of 3.5 ($\phi = 90^\circ$) and 2.7 kcal/mole ($\phi = 270^\circ$). We emphasize that an analysis of the two T conformations in terms of bond-bond interactions leads to the opposite order of stabilities (Table XIII), no matter whether substituent-ring, substituent-substituent, or all possible bond-bond interactions are considered.

Since the diequatorially substituted PO is lower in energy than the diaxially substituted one, the exact positions of the pseudorotational minima are likely to be shifted to ϕ values $< 360^\circ$ and $> 180^\circ$, i. e., to ring conformations which allow the substituents to adopt a more equatorial than axial orientation. The energies of Tables I and II indicate a similar, though smaller shift in the case of propene PO. However, it is doubtful whether this effect increases for higher alkylated *trans*-PO to such an extent that the order of conformational stabilities calculated for propene and 2-butene PO is reversed. Considering the data of Table XIII, it seems that the stronger substituent-substituent interactions in conformations with $180^\circ < \phi < 360^\circ$ should prevent a shift of the conformational minimum to $\phi = 270^\circ$. Therefore, we predict that stable E forms with $\phi = 0^\circ$ or 180° are likely to exist for all *trans*-alkene PO's.

IV. COMPARISON WITH SEMIEMPIRICAL RESULTS

Two semiempirical studies of substituted PO's have been reported in the literature. The first, published by Renard and Fliszár,⁹ used the EHT method while the second, published by Rouse,¹⁰ was based on CNDO/2. Since the results of these studies have been utilized in mechanistic considerations,^{8,11} it is appropriate to discuss their findings briefly at this point.

General criticism with regard to the geometrical model of the PO ring chosen in both studies has to be raised. Both Fliszár *et al.*⁹ and Rouse¹⁰ optimized the puckering of some or all conformations depicted in Fig. 1. For each conformer, i. e., for a fixed value of ϕ , a dihedral angle was chosen which can be related to the puckering amplitude q . Holding all geometrical parameters at constant values, the dihedral angle was varied until an energy minimum was found. Since the ring skeleton possesses nine degrees of freedom and six of these are fixed by the choice of the conformation (ϕ) and the five ring bond lengths, three geometrical parameters are left to define the puckered ring completely. If only one of them, for example, a dihedral angle or q , is optimized, there remain two parameters which have to be fixed in a consistent way. *This, of course, is not possible.* For example, a standardization of the

TABLE XIV. Semiempirical conformational energies of *cis*- and *trans*-2-butene primary ozonide.^a

<i>cis</i>			<i>trans</i>		
ϕ , deg	EHT	CNDO/2	ϕ , deg	EHT	CNDO/2
0	nm	2.3	0	nm	0.9
18	16.9	2.3	18	6.6	1.2
36	12.1	2.3	36	nm	nm
54	9.9	0.7	54	6.2	1.2
72	6.9	0.7	72	5.3	nm
90	0	0.9	90	0.8	nm
108	6.7	0.5	198	5.5	0.9
126	9.6	0	216	3.5	1.1
144	11.7	1.4	234	4.3	0
162	16.4	1.4	252	3.4	0.3
180	nm	1.5	270	0	0.5
planar	19.1	2.8	planar	7.2	1.7

^aExtracted from the data of Ref. 10. nm, no minima found for this conformer.

COO angles of the PO ring^{9,10} implies that they will not change with a change in ϕ , which is not true. A freezing of the COO angle influences the optimization of the puckering parameter since both are strongly coupled. Thus, a relatively large value of the COO angle prohibits extensive puckering and favors the more planar forms while the contrary is true for a relatively small value of the COO angle. Two rigid internal ring angles represent such a severe simplification of the ring geometry that it actually does not matter whether the ring bonds are standardized in a rather crude⁹ or somewhat more realistic manner.¹⁰

In order to analyze the reported EHT and CNDO/2 energies of *cis*- and *trans*-2-butene PO we have listed them in Table XIV. They have been extracted from the results of Rouse.¹⁰ It is clear that some of the energy changes along the pseudorotation path result from the restrictions of the model. Most probably CNDO/2 as well as EHT do not describe the planar forms as saddle-points but as local maxima in (q, ϕ) space if the geometrical model of this work is used.⁴¹ Apart from these inconsistencies of the semiempirical energies, three general observations can be made. First, EHT greatly overestimates changes in conformational energies while CNDO/2 underestimates them. The latter is parallel to the tendency of the CNDO/2 calculations of making the ring more planar. For example, the puckering amplitude of the T form with $\phi = 90^\circ$ is 37 pm according to EHT while it is only half as large according to CNDO/2.⁴¹ Secondly, both methods fail to describe the E forms ($\phi = 0^\circ$ and 180°) adequately. This failure is more obvious for EHT than for CNDO/2. Finally, there exists a consistency in the results of both methods, namely in the prediction that CH₃ groups which are equatorially positioned lead to stabilization. This is in accord with the findings of our work.

Observation one and two are fairly easy to explain from what is known about typical failures of EHT and CNDO/2. Thus, Hoffmann reported in his first paper on EHT⁴² that the method strongly overestimates steric repulsion if a rigid rotor approach is used. He found

the *cis* form of butane to be less stable than the *gauche* form by about 20 kcal/mole compared to an experimental value of about 6 kcal/mole.⁴² It is clear that this discrepancy overshadows any effect resulting from the trioxolane ring. Any ring conformation which allows the CH₃ groups to move into a *gauche* arrangement will be artificially stabilized by EHT. Also, the degree of puckering will only increase if the steric repulsions between the methyl groups are decreased.

As for CNDO/2, it has been found that this method describes the conformational energies of butane reasonably, but underestimates the *cis* barrier of H₂O₂ by about 3 kcal/mole.⁴³ This has to do with the fact that a NDO method inadequately describes such a subtle electronic effect as lone pair delocalization. As a consequence, the torsion around the OO bonds of the primary ozonide is kept low by a NDO approach, thus leading, firstly, to reduced puckering and, secondly, to stable ring conformations far away from the E forms with $\phi = 0^\circ$ or 180° . A typical example for this failure of NDO methods is provided by a recent MINDO/3 calculation on 1, 2, 3-trioxolane which found the ring literally planar despite the ample parameter optimization performed for the MINDO/3 method.⁴⁴

We conclude that none of the published semiempirical calculations on PO's is capable of correctly predicting the most stable ground state conformer. Therefore, the attempts made by various authors^{8,11} to explain inconsistencies in the *cis/trans* ratios of small normal and cross ozonides by means of semiempirical EHT or CNDO/2 calculations are not convincing. A reconsideration of the ozonolysis of propene and butene should be based on the *ab initio* data of this work.⁴⁵

V. CONCLUSIONS

The main conclusions of this work may be summarized as follows:

(1) In order to obtain reliable RHF energies of methyl substituted PO's, two basic requirements have to be fulfilled, namely, first, the inclusion of polarization functions in the basis set and, second, the usage of an appropriate conformational model of the ring. Our results indicate that the rigid pseudorotor approach is sufficient as long as substituent-substituent interactions are not too strong. This is the case for propene and *trans* 2-butene PO. However, if both substituents reside on the same side of the ring as in *cis*-2-butene PO, the rigid pseudorotor model leads to a false prediction of conformational stabilities. A pseudorotor model with flexible substituent positions is necessary to obtain the correct order of conformational stabilities.

(2) Both propene and 2-butene PO preferentially adopt an E puckered ring conformation with $\phi = 0^\circ$ or 180° which is about 2.3–3.5 kcal/mole more stable than the T forms with $\phi = 90^\circ$ or 270° . The latter should be located at the saddlepoints of the conformational surface, i. e., their energies determine the barriers to pseudorotation. According to the relative energies of the planar forms, pseudorotation is more favorable by about 4–5 kcal/mole than inversion of the ring through the planar form. The calculated energies suggest that the

conformational surfaces of all three PO's resemble that of 1, 2, 3-trioxolane.

(3) Comparing the changes in the pseudorotational barriers due to methyl substitution of the PO ring, it becomes obvious that one important difference between *cis*- and *trans*-alkene PO's is likely to exist. The *trans*-alkene PO's should preferentially adopt a ground state conformation close or equal to the E forms with $\phi = 0^\circ$ or 180° . The same can be expected for the PO's of 1-alkenes. However, in the case of *cis*-alkene PO's, a shift of the conformational minima from ϕ values close to 0° and 180° to ϕ values close to 90° and 270° is foreseeable if bulky alkyl groups are attached to the PO ring. Thus, *the conformational behavior of small cis-alkene PO's like cis 2-butene PO should be different from those of higher cis-alkene PO's*. This finding casts a new light on the stereochemical implications of the ozonolysis reaction.

(4) The electronic effect of a methyl group on the PO ring is always stabilizing due to favorable mixing of the orbitals of the ring and the CH₃ group. This stabilization is enhanced or lowered in puckered ring conformations. Thus, an equatorially positioned CH₃ substituent leads to increased stabilization, while an axially positioned CH₃ reduces the stabilizing effect. This observation can be quantitatively elucidated by determining the substituent orientation angles²⁴ and the lowering of the two highest occupied MO's. This lowering is due, first, to ring puckering (π effect of the ring) and, secondly, to substituent-ring interactions (π effect of the substituents).

(5) The computed π effects have been found to be independent of both basis set limitations and restrictions of the geometrical model. Accordingly, the π effect should offer a possibility of determining the relative stabilities of higher alkene PO by a less sophisticated approach than that used in this work.

(6) A quantitative investigation of bond-bond interactions by means of appropriate alicyclic rotors reveals that this way of analyzing the conformational stabilities of PO's has to be used with great care. In the case of propene and butene PO, a bond-bond interaction analysis leads to false predictions with regard to the substituent effects and the most stable ground state conformations. Evidently, this failure is responsible for the fact that E forms have always been considered to play a rather unimportant role in the ozonolysis mechanism.^{5,8-11}

(7) An analysis of the semiempirical work on PO's reveals that neither EHT nor NDO methods should be capable of predicting the right conformational behavior of PO's.

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