

# Theoretical determination of molecular structure and conformation. V. Electronic effects influencing the stability of methyl substituted final ozonides<sup>a)</sup>

Dieter Cremer

Lehrstuhl für Theoretische Chemie, Universität Köln, D-5000 Köln 41, West Germany  
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Restricted Hartree-Fock (RHF) theory is used to explore the conformational surfaces of three methyl substituted final ozonides (FO), namely, 3-methyl-1,2,4-trioxolane (propene FO), *cis*-3,5-dimethyl-1,2,4-trioxolane (*cis*-2-butene FO) and the corresponding *trans* isomer (*trans*-2-butene FO). A split valence [3s2p/2s] basis and an augmented split valence [3s2p1d/2s] basis is employed. The interconversional processes of the FO ring are studied with a rigid pseudorotor model. Puckered ring conformations are found to be more stable than the planar forms in all three cases. Pseudorotation is hindered by barriers of 3.1 and 5.9 kcal/mole (propene FO), 1.6 and 5.4 kcal/mole (*cis*-2-butene FO), and 5.7 kcal/mole (*trans*-2-butene FO). The conformational minima are located at the twist puckered forms (OO half-chair), a result which can be rationalized in terms of lone pair delocalization or  $\sigma$ - $\pi$  orbital mixing. In agreement with spectroscopic results, the most stable FO conformation is found to possess at least one methyl substituent in an equatorial position. Thus, a favorable interaction between ring and substituent MO's is guaranteed which leads to a stabilization of the two highest occupied MO's and back-donation of charge from the ring to the substituent. The difference in the conformational behavior of primary ozonides (PO) and FO's is shown to result from the different topologies of the two trioxolane rings.

## I. INTRODUCTION

In order to elucidate the mechanism of ozonolysis, detailed knowledge about structure and conformation of substituted 1,2,4-trioxolanes, the so-called final ozonides (FO), is desirable. First steps in this direction have been undertaken by Kuczkowski and co-workers, who performed microwave studies on 1,2,4-trioxolane (ethylene FO) itself,<sup>1</sup> 3-methyl-1,2,4-trioxolane (propene FO), and *trans*-3,5-dimethyl-1,2,4-trioxolane (*trans*-2-butene FO).<sup>2</sup> Their results provided strong evidence of a stable twist (T) conformation<sup>3</sup> of the trioxolane ring which is equal or very close to a OO half-chair form. The methyl groups were found to be equatorially located at the puckered ring skeleton. The same study also attempted to determine the most stable conformation of *cis*-3,5-dimethyl-1,2,4-trioxolane (*cis*-2-butene FO). However, no spectral assignments could be made for this compound.<sup>2</sup>

In earlier work on the mechanism of ozonolysis, Bauld, Bailey, and co-workers<sup>4</sup> proposed certain puckered ozonide conformations in order to rationalize the experimentally observed *cis-trans* ratios of normal and cross FO's obtained when ozonizing *cis* or *trans* alkenes.<sup>5</sup> Their mechanistic proposal was partially based on the assumption of a stable CO twist conformation of a FO. Although the authors explicitly stated that their steric assumptions do not apply to the case of small alkene FO's like propene or 2-butene FO, the spectroscopic findings gave rise to considerable doubts with regard to the mechanistic importance of the CO twist conformation. As a consequence, the Bauld-Bailey version of the ozonolysis mechanism was reviewed in order to reconcile mechanistic suggestions with conformational results.<sup>2,6</sup>

In Paper III of this series,<sup>7</sup> we have already verified

<sup>a)</sup>For Paper IV, see the preceding paper in this issue.

the OO twist form for ethylene FO on the basis of non-empirical restricted Hartree-Fock (RHF) calculations. In addition, we have shown that pseudorotation of the trioxolane ring is as easy as internal rotation of ethane,<sup>8</sup> i. e., both interconversional processes are hindered by barriers of just 3 kcal/mole. The reported microwave data do not support a similar conclusion with regard to the conformational behavior of propene and 2-butene FO's. No effects from pseudorotation have been observed in the experimental spectra.<sup>2</sup> It seems that the flexibility of 1,2,4-trioxolane is reduced by methyl substitution. However, an unequivocal answer to the question of substituent-ring interactions or the possible importance of the CO twist form in the ozonolysis reaction can only be given if the whole conformational surface of an alkene FO is explored, a project which is difficult to accomplish by presently available experimental techniques. Therefore, this theoretical study is aimed at both scrutinizing and extending the spectroscopic findings on propene and 2-butene FO's. Another of its objectives is to investigate the underlying electronic reasons of substituent-ring interactions. If their nature can be fully understood, a further step toward a theoretical elucidation of the ozonolysis reaction of small olefins will have been made.

## II. NUMERICAL PROCEDURES

The same quantum mechanical techniques have been employed as in Paper IV [see Ref. (a)], namely, standard RHF calculations<sup>9</sup> with either the split valence [3s2p/2s] basis<sup>10</sup> (basis B) or the augmented split valence [3s2p1d/2s] basis<sup>11</sup> (basis C). In Paper III, it has been shown that due to a fortuitous cancellation of basis set errors, the deficiencies of B are less severe in the case of 1,2,4-trioxolane than in that of 1,2,3-trioxolane.<sup>7</sup> For example, the barrier to pseudorotation calculated with basis B (3.08 kcal/mole) differs by just a few tenths of a kilocalorie from the barrier values ob-

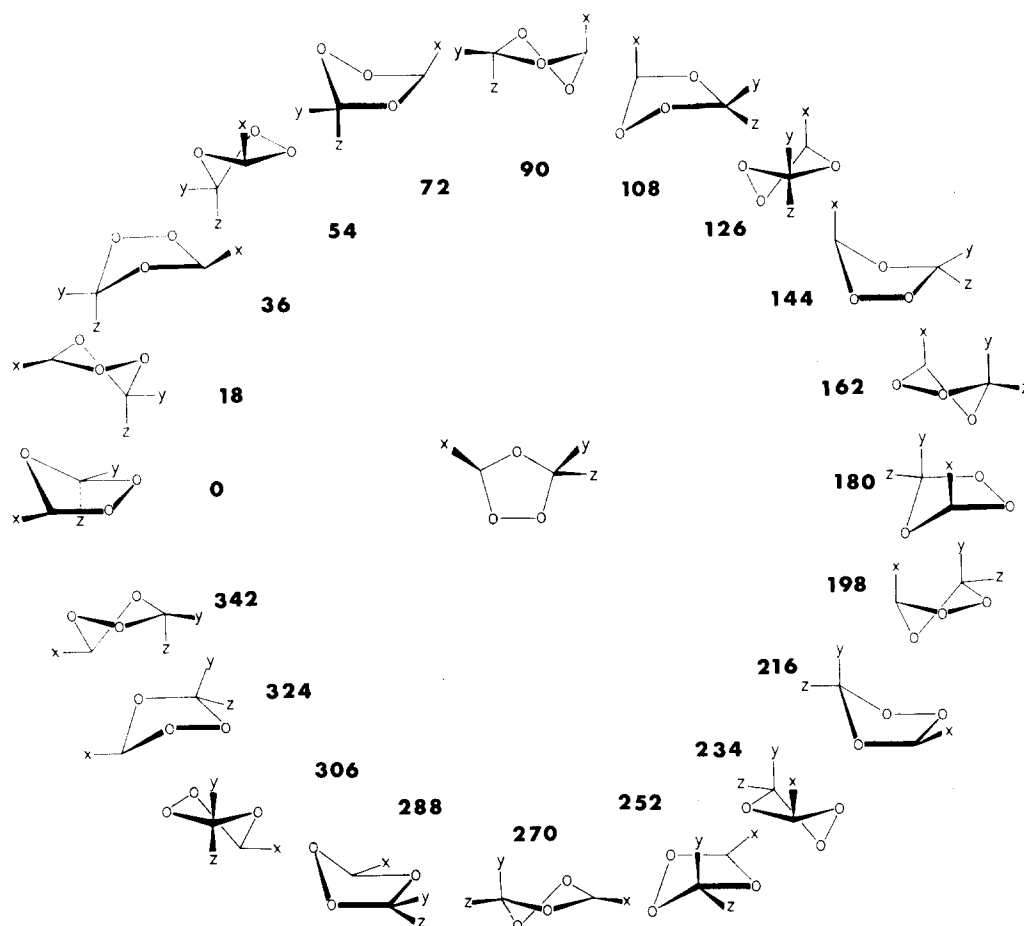


FIG. 1. Envelope and twist conformations along the pseudorotation itinerary of a substituted final ozonide ( $X=CH_3$ ,  $Y=Z=H$ : propene FO;  $X=Y=CH_3$ ,  $Z=H$ : *cis*-2-butene FO;  $X=Z=CH_3$ ,  $Y=H$ : *trans*-2-butene FO).

tained with the heavy-atom augmented basis *C* (3.30 kcal/mole) or with a fully augmented double- $\zeta$  [ $4s3p1d/2s1p$ ] basis (3.04 kcal/mole). The disadvantages of basis *B* are revealed by its poor account of the barrier to planarity and of the puckering of the ring which are both underestimated. In view of these results, we have employed basis *B* when exploring the pseudorotational modes of the three FO's. However, the actual barrier values, especially the one to planarity, have been recalculated with basis *C* in order to get reliable results and to illustrate the effect of polarization functions on the FO energies.

With one exception, namely the inverted oxygen E form<sup>3</sup> of *cis*-2-butene FO, a rigid pseudorotor model of the FO ring has been used. This is based on the theoretical structures of 1,2,4-trioxolane obtained with basis *B* or basis *C*.<sup>7</sup> The nonplanar FO conformations are characterized by the puckering amplitude  $q$  and the puckering phase  $\phi$ .<sup>12</sup> The angle  $\phi=0^\circ$  has been determined first according to rules (1) and (2) of Paper IV. Then, oxygen atom 1 has been shifted by three places clockwise around the ring in order to obtain a conformation which is equal to the symmetrical E form of the parent FO. This relocation of atom 1 corresponds to a  $72^\circ$  shift of  $\phi$  and leads to the assignment of  $\phi$  values to puckered FO forms shown in Fig. 1.

All conformations of Fig. 1 have been studied in the

case of propene FO ( $X=CH_3$ ,  $Y=Z=H$ ). As for *cis*-2-butene FO ( $X=Y=CH_3$ ,  $Z=H$ ) and *trans*-2-butene FO ( $X=Z=CH_3$ ,  $Y=H$ ),  $C_s$  and  $C_2$  symmetry has been assumed for the planar ring forms. This required that the same geometry and conformation was used for the two methyl groups. Since no attempts have been made to investigate a possible coupling between ring pseudorotation and methyl rotation, conformation and geometry of the methyl groups has been retained in the puckered forms of 2-butene FO as described in the preceding paper (see Paper IV). Thus, only one conformation of each enantiomeric pair depicted in Fig. 1 has been studied. This reduces the number of computed 2-butene FO conformations from 42 to 24.

We note that the external ring angles of 1,2,4-trioxolane have not been optimized.<sup>7</sup> Instead, the orientations of the external ring bonds have been determined by assuming local  $C_{2v}$  symmetry for a  $CH_2$  group and a tetrahedral HCH angle. These constraints have been retained when replacing a H atom by a methyl substituent.

As indicated above, a more flexible pseudorotor model was used in the case of the E form ( $\phi=180^\circ$ ) of *cis*-2-butene FO. This turned out to be necessary because of the strong steric interactions between the methyl substituents occurring in the E and related *cis*-2-butene conformations (see Fig. 1). A preliminary account of their magnitude has been gained by calculat-

TABLE I. Absolute and relative energies of propene and 2-butene final ozonide calculated with basis B.<sup>a</sup>

Pseudorotation parameters		3,5-Dimethyl-1,2,4-trioxolane					
		3-Methyl-1,2,4-trioxolane		<i>cis</i>		<i>trans</i>	
$\phi$ , deg	$\eta$ , pm	Absolute	Rel.	Absolute	Rel.	Absolute	Rel.
0	28.6	-341.05278	2.86	-380.04237	1.97	-380.03999	4.18
18	29.3	-341.05282	2.84	-380.04243	1.93	-380.03983	4.29
36	32.3	-341.05342	2.47	-380.04310	1.51	-380.04045	3.90
54	35.2	-341.05449	1.80	-380.04420	0.82	-380.04177	3.07
72	37.6	-341.05592	0.90	-380.04551	0	-380.04361	1.91
90	41.0	-341.05625	0.69	-380.04544	0.04	-380.04450	1.35
108	37.6	-341.05473	1.64	-380.04297	1.59		
126	35.2	-341.05275	2.88	-380.03742	5.08		
144	32.3	-341.05120	3.86	-380.02898	10.37		
162	29.3	-341.05040	4.36	-380.02276	14.28		
180	28.6	-341.05037	4.38	-380.02051 <sup>b</sup>	15.69		
198	29.3	-341.05088	4.06			-380.04052	3.85
216	32.3	-341.05216	3.26			-380.04187	3.01
234	35.2	-341.05398	2.11			-380.04371	1.85
252	37.6	-341.05612	0.77			-380.04573	0.58
270	41.0	-341.05735	0			-380.04666	0
288	37.6	-341.05668	0.42				
306	35.2	-341.05520	1.35				
324	32.3	-341.05386	2.19				
342	29.3	-341.05302	2.72				
planar	0	-341.05012	4.53	-380.03913	4.00	-380.03907	4.76

<sup>a</sup>Absolute energies in hartree; relative energies in kcal/mole.<sup>b</sup>See Table IX, for refined RHF/basis B energy.

ing appropriate conformations of diethylether with the minimal STO-3G basis<sup>13</sup> (basis A). This is discussed in the following section.

### III. RESULTS AND DISCUSSION

Theoretical energies obtained with basis B for the three FO's are listed in Table I. RHF/basis C energies of selected FO conformations are shown in Table II. Using the energies of Table I, the pseudorotational potential  $V$  has been drawn as a function of the phase angle  $\phi$  for each of the three compounds. These plots are depicted in Fig. 2.

#### A. Stability of nonplanar final ozonide conformations

The tendency for oxygen lone pair delocalization can be considered as the driving force of ring puckering ef-

fective in planar 1,2,4-trioxolane. This has been pointed out in Paper III.<sup>7</sup> In order to analyze the conformational features of methyl substituted 1,2,4-trioxolanes the lone pair delocalization effect is described by utilizing the computed canonical RHF MO's. Among these, the two highest occupied MO's are of special interest. These are made up by the three  $p_x(\text{O})$  AO's and two pseudo- $\pi$  orbitals of the methylene groups and possess  $a_2$  and  $b_1$  symmetry. As can be seen from Fig. 3, their form resembles those of the antibonding MO's  $\pi_4$  and  $\pi_5$  of the cyclopentadienyl anion which means that their occupation causes the destabilization of the planar trioxolane ring. If the ring puckers, the antibonding overlap between the constituent AO's of  $\pi(b_1)$  and  $\pi(a_2)$  is reduced.<sup>14</sup> In addition, effective  $\sigma$ - $\pi$  orbital mixing takes place, thus leading to a lowering of the energies of the two HOMO's and an overall stabilization of the ring.

TABLE II. Absolute and relative energies of propene and 2-butene final ozonide calculated with basis C.<sup>a</sup>

Pseudorotation parameters		3,5-Dimethyl-1,2,4-trioxolane					
		3-Methyl-1,2,4-trioxolane		<i>cis</i>		<i>trans</i>	
$\phi$ , deg	$\eta$ , pm	Absolute	Rel.	Absolute	Rel.	Absolute	Rel.
0	35.0	-341.55554	3.07	-380.60053	1.62	-380.59593	5.75
90	44.7	-341.55857	1.17	-380.60311	0	-380.60143	2.30
180	35.0	-341.55097	5.94	-380.59448 <sup>b</sup>	5.41		
270	44.7	-341.56043	0			-380.60510	0
planar	0	-341.55012	6.47	-380.59428	5.54	-380.59449	6.66

<sup>a</sup>Absolute energies are given in hartree; relative energies in kcal/mole.<sup>b</sup>Geometrical parameters are taken from the refined equilibrium structure shown in Table IX.

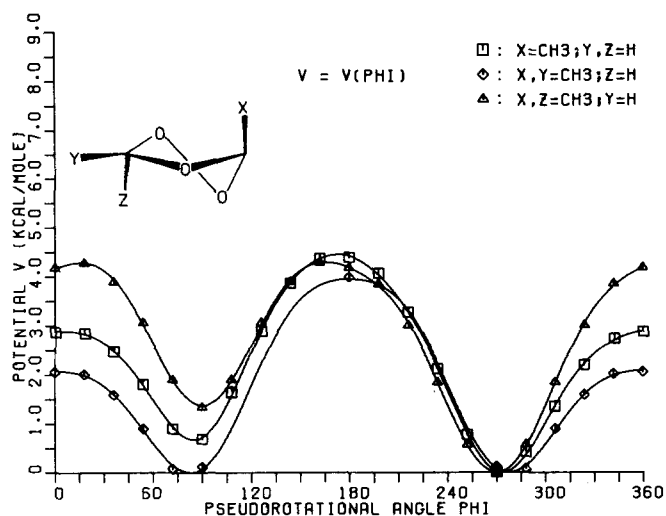


FIG. 2. Pseudorotational potential  $V(\text{RHF}, \text{basis } B)$  of propene and 2-butene FO as a function of the puckering phase  $\phi$ .

So far the MO analysis of 1,2,4-trioxolane is parallel to that of 1,2,3-trioxolane (Paper IV). However, one important difference exists which becomes obvious when analyzing the ordering of the HOMO's in the two planar trioxides. Compared with 1,2,3-trioxolane, the  $b_1$  and  $a_2$  MO have swapped their positions in 1,2,4-trioxolane, the latter orbital being now the highest in energy. Also, the energy difference between  $\pi_5$  and  $\pi_4$  has decreased from about 0.05 to 0.01 hartree as is revealed by the orbital energies listed in Table III. This results from the fact that the  $p_z(\text{O})$  AO's of the FO participate in both  $\pi$ -type MO's to a comparable extent while in the case of 1,2,3-trioxolane, the  $b_1$  MO is distinct from the  $a_2$  MO by its high  $p_z(\text{O})$  contributions. The most favorable mode of ring puckering is determined by the stabilization of the  $\pi$  MO which is strongest OO antibonding, namely  $\pi_5(b_1)$  in the case of 1,2,3-trioxolane and  $\pi_5(a_2)$  in the case of 1,2,4-trioxolane. MO  $\pi_5$  of the FO loses some of its OO antibonding character if the strongest torsion occurs in the

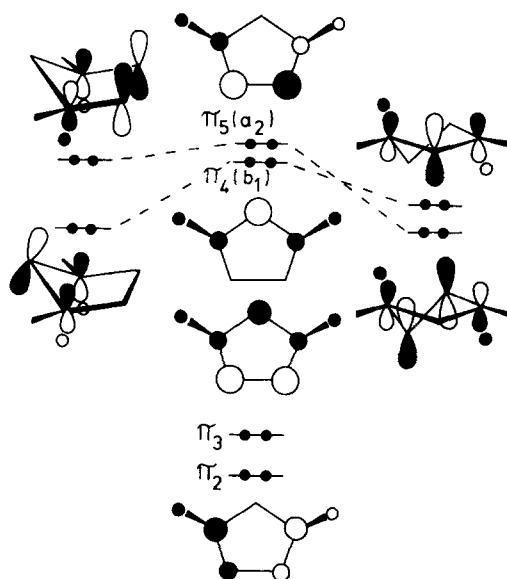


FIG. 3. Lowering of the two  $\pi$ -type HOMO's of 1,2,4-trioxolane due to ring puckering.

peroxy bridge of the ring, i.e., for a puckering mode with  $\phi = 90^\circ$  or  $270^\circ$ . Then, the  $a_2$  MO<sup>14</sup> becomes even more stable than the  $b_1$  MO<sup>14</sup> as is indicated by the orbital energies of Table III. The energy gain calculated for the  $a_2$  MO of the T form amounts to  $-15.9$  kcal/mole (see comment b of Table III) which has to be compared with an orbital lowering of  $-2.0$  kcal/mole in the E puckered ring. Although this energy difference is decreased because of a preferential stabilization of MO  $\pi_4(b_1)$  in the E form, the overall  $\pi$ -stabilization effect is dominated by the lowering of the MO  $\pi_5(a_2)$ , thus effecting the pronounced stability of the T conformations. We conclude that the topology of the ring predetermines the form and ordering of the two  $\pi$ -type HOMO's, the dependence of the  $\pi$ -stabilization effect on the phase angle  $\phi$  and, correspondingly, the preferential mode of ring puckering.

TABLE III. Stabilization of the two highest occupied MO's of 1,2,4-trioxolane due to orbital mixing caused by ring puckering.<sup>a</sup>

$\phi$ , deg	Basis B					Basis C				
	Orbital energies <sup>b</sup>		Stabilization			Orbital energies <sup>b</sup>		Stabilization		
	$\pi_4$	$\pi_5$	$\pi_4$	$\pi_5$	total	$\pi_4$	$\pi_5$	$\pi_4$	$\pi_5$	total
0	-0.4680	<u>-0.4495</u>	-7.4	-1.8	-9.2	-0.4658	<u>-0.4389</u>	-11.2	-2.0	-13.2
18	-0.4679	<u>-0.4502</u>	-7.3	-2.2	-9.5					
36	-0.4681	<u>-0.4523</u>	-7.5	-3.5	-11.0					
54	-0.4670	<u>-0.4550</u>	-6.8	-5.2	-12.0					
72	<u>-0.4656</u>	-0.4574	-5.9	-6.7	-12.6					
90	<u>-0.4678</u>	-0.4587	-7.3	-7.5	-14.8	<u>-0.4610</u>	-0.4507	-8.2	-9.4	-17.6
planar	-0.4562	<u>-0.4467</u>	0	0	0	-0.4479	<u>-0.4357</u>	0	0	0

<sup>a</sup>Orbital energies are given in hartree; individual and total stabilization energies in kcal/mole.

<sup>b</sup>The MO which is predominantly OO antibonding, i.e., the  $a_2$  symmetrical MO of the planar ring, has been underlined. Thus, the change in the ordering of the orbitals is indicated. If this change is taken into consideration, stabilization energies of  $-1.7$  and  $-13.2$  kcal/mole (basis B) and of  $-1.7$  and  $-15.9$  kcal/mole (basis C), respectively, result for  $\phi = 90^\circ$ .

TABLE IV. Influence of a methyl substituent on planar 1,2,4-trioxolane, dimethylether, and methylperoxide.<sup>a</sup>

Reaction	Specification	Bond separation energy (kcal/mole)	
		Basis B	Basis C
$\overline{\text{OC(H)(CH}_3\text{)OC(Y)(Z)O}} + \text{CH}_4 \rightarrow \overline{\text{OC(H}_2\text{)OC(Y)(Z)O}} + \text{CH}_3\text{CH}_3$	Y, Z = H	8.67	7.39
	Y = CH <sub>3</sub> , Z = H	8.61	7.20
	Y = H, Z = CH <sub>3</sub>	8.57	7.33
$\overline{\text{OC(H)(CH}_3\text{)OC(Y)(Z)O}} + \overline{\text{OC(H}_2\text{)OC(H}_2\text{)O}} \rightarrow 2 \overline{\text{OC(H)(CH}_3\text{)OC(H}_2\text{)O}}$	Y = CH <sub>3</sub> , Z = H	-0.06	-0.18
	Y = H, Z = CH <sub>3</sub>	-0.09	-0.05
$\text{CH}_3\text{CH}_2\text{OCH}_3 + \text{CH}_4 \rightarrow \text{CH}_3\text{OCH}_3^{\text{e,e}} + \text{C H}_3\text{C H}_3^{\text{s}}$	$\tau(\text{CCOC}) = 120^\circ$	4.93	4.43
$\text{CH}_3\text{CH}_2\text{OOH} + \text{CH}_4 \rightarrow \text{CH}_3\text{OOH}^{\text{e}} + \text{CH}_3\text{CH}_3^{\text{s}}$	$\tau(\text{CCOO}) = 120^\circ$	4.76	4.13

<sup>a</sup>The conformation of the C<sub>M</sub>COC and C<sub>M</sub>COO fragments of the planar propene and 2-butene FO's has been retained in the alicyclic rotors methylethylether (CH<sub>3</sub>CH<sub>2</sub> staggered, CH<sub>2</sub>OCH<sub>3</sub> eclipsed, eclipsed) and ethylperoxide (CH<sub>3</sub>CH<sub>2</sub> st., CH<sub>2</sub>OO ec., COOH *trans*). To balance steric effects, appropriate conformations of ethane, dimethylether, and methylperoxide are used. These are indicated by the superscripts s (staggered) and e (eclipsed). Basis B energies have been taken from the literature: CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, Ref. 22; (basis C, Ref. 11); CH<sub>3</sub>OCH<sub>3</sub>, Ref. 23.

### B. Stabilization of the planar 1,2,4-trioxolane ring by a methyl group

In Table IV, the bond separation energies of two formal reactions involving the planar FO's are listed. The values obtained for the first reaction suggest that the influence of the methyl group leads to about 7–8 kcal/mole stabilization of the FO which is about 3 kcal/mole higher than the stabilization energy computed for a primary ozonide (see Paper IV). The atomic charges of Table V reveal that the methyl group donates about 0.14 *e* less to the ring than a hydrogen atom does. This, of course, lowers the population of the two π-type HOMO's and leads to a stabilization of the ring. The stability of the ring is also favored by the fact that the CH<sub>3</sub> and ring orbitals mix, thus yielding additional π-type MO's which are less OO and CO antibonding than π<sub>4</sub> and π<sub>5</sub>. Similar effects can also be observed for dimethylether and ethylperoxide. For example, the stabilization of methylperoxide due to a CH<sub>3</sub> group is about 4 kcal/mole and that of dimethylether about 4.5 kcal/mole as is shown by the data of Table IV. The net effect of a methyl group in either propene or 2-butene FO can be roughly considered as the sum of the individual stabilization energies of an ether and a peroxy unit.

The bond separation energies of the second formal reaction of Table IV reveal that there is no important 1,3-interaction between the methyl groups of planar 2-butene FO. The stabilizing effect of a second methyl group is as high as that of the first one. No difference in the stabilities of planar *cis* or *trans* 2-butene FO is indicated by the RHF energies.

### C. The role of the substituent orientation

In order to analyze the effect of a CH<sub>3</sub> substituent in a puckered FO conformation, three sets of data have been evaluated and listed in Tables VI–VIII. The first set comprises the energy differences Δ defined in Paper IV and derived from the data of Tables I and II. The Δ values provide a direct answer to the question of whether the stabilization effect of the methyl group increases or

decreases in a given puckered ring conformation defined by *q* and *φ*. The second set of data consists of the substituent orientation angles α<sub>x</sub>, α<sub>y</sub>, and α<sub>z</sub><sup>15</sup> evaluated for each nonplanar conformation of Fig. 1. They indicate whether a substituent is more axially or more equatorially positioned with regard to the mean plane of the ring. Finally, the stabilization energies of the two HOMO's have been tabulated. By means of the data

TABLE V. Gross atomic populations of the ring substituents of final ozonides calculated with basis C.<sup>a</sup>

φ, deg	X	C <sub>X</sub>	H	Y	Z
A. 1,2,4-Trioxolane (X = Y = Z = H)					
0	0.2075		0.1711		
90	0.1790		0.1937		
planar	0.1812				
B. 3-Methyl-1,2,4-trioxolane (X = CH <sub>3</sub> , Y = Z = H)					
0	0.0586	-0.5067	0.1682	0.2054	0.1695
90	0.0497	-0.4866	0.1982	0.1925	0.1791
180	0.0458	-0.4907	0.2101	0.1703	0.2082
270	0.0466	-0.5133	0.1772	0.1768	0.1919
planar	0.0446	-0.4925	0.1828	0.1799	0.1800
C. <i>Cis</i> -3,5-dimethyl-1,2,4-trioxolane (X = Y = CH <sub>3</sub> , Z = H)					
0	0.0558	-0.5059	0.1669		
90	0.0464	-0.4866	0.1964	0.0453 <sup>b</sup>	0.1774
180	0.0383	-0.5037	0.2025		
planar	0.0428	-0.4914	0.1816		
D. <i>Trans</i> -3,5-dimethyl-1,2,4-trioxolane (X = Z = CH <sub>3</sub> , Y = H)					
0	0.0585	-0.5034	0.1677	0.2084	0.0429 <sup>c</sup>
90	0.0491	-0.4862	0.1979		
270	0.0438	-0.5109	0.1750		
planar	0.0424	-0.4926	0.1815		

<sup>a</sup>Positive values indicate positively charged substituents and negative values negatively charged substituents.

<sup>b</sup>The charge at the C atom of the methyl group is -0.5104.

<sup>c</sup>The charge at the C atom of the methyl group is -0.4916.

TABLE VI. Position and influence of the substituent in puckered conformations of 3-methyl-1,2,4-trioxolane.<sup>a</sup>

$\phi$ , deg	Position of X <sup>b</sup>	$\alpha_X$ , deg	Subst. effect $\Delta$ values		$\pi$ effect <sup>c</sup> total		Subst. X	
			B	C	B	C	B	C
0	<i>t-g</i> inclinal	57.6	-0.45	-0.42	-10.2	-14.7	-1.0	-1.5
18	<i>t-g</i> inclinal	48.7	-0.08		-10.1		-0.6	
36	<i>t-g</i> inclinal	43.3	-0.21		-11.2		-0.2	
54	<i>t-g</i> inclinal	35.9	-0.05		-11.5		0.5	
72	<i>t-g</i> axial	27.2	0.06		-11.3		1.3	
90	<i>t-g</i> axial	17.9	0.46	0.98	-12.2	-14.8	2.6	2.8
108	<i>t-g</i> axial	12.5	0.80		-9.5		3.1	
126	<i>t-g</i> axial	9.5	1.03		-8.7		3.3	
144	<i>t-g</i> axial	10.1	1.18		-8.0		3.0	
162	<i>t-g</i> axial	13.6	1.44		-6.7		2.8	
180	<i>t-g</i> axial	13.7	1.07	2.45	-6.8	-10.0	2.4	3.2
198	<i>t-g</i> axial	22.4	1.14		-7.5		2.0	
216	<i>t-g</i> axial	28.1	0.58		-9.7		1.3	
234	<i>t-g</i> inclinal	35.7	0.26		-11.5		0.5	
252	<i>t-g</i> inclinal	44.5	-0.07		-13.0		-0.4	
270	<i>t-g</i> inclinal	54.0	-0.23	-0.19	-15.9	-18.8	-1.1	-1.2
288	<i>t-g</i> inclinal	58.8	-0.42		-13.9		-1.3	
306	<i>t-g</i> equatorial	61.3	-0.50		-13.4		-1.4	
324	<i>t-g</i> equatorial	60.4	-0.49		-12.4		-1.4	
342	<i>t-g</i> inclinal	57.0	-0.20		-10.7		-1.2	

<sup>a</sup>Substituent effects as well as the  $\pi$  effects are given in kcal/mole. They are derived from the relative energies of 1,2,4-trioxolane<sup>7</sup> and the  $\pi$  stabilization energies of Table III using the relevant values of the planar forms as reference energies.

<sup>b</sup>Position determined according to Ref. 15.

<sup>c</sup>The energies of the two HOMO's of planar propene FO are -0.4477 and -0.4386 (basis B) and -0.4399 and -0.4294 hartree (basis C), respectively.

in Table III, substituent dependent  $\pi$  effects can be deduced which are characteristic for orbital mixing between methyl and trioxolane MO's and for the distribution of charge between substituent and ring.

Charge donation to the ring requires an effective overlap of the methyl  $\sigma$  MO's with those of the ring. It

is best accomplished if the substituent is equatorially positioned (Paper IV). Then a withdrawal of  $\sigma$  electrons by both the ether and the peroxy oxygen atoms takes place as is illustrated by the hydrogen and methyl charges listed in Table V. However, if the substituent possesses suitably oriented pseudo- $\pi$  orbitals, some of the charge can be back-donated to the substituent. This

TABLE VII. Position and influence of the substituents in puckered conformations of *cis*-3,5-dimethyl-1,2,4-trioxolane.<sup>a</sup>

$\phi$ , deg	Position of Y	$\alpha_Y$ , deg	Subst. effect $\Delta$ values		$\pi$ effect <sup>b</sup> total		$\pi$ effect of substituents both Y			
			B	C	B	C	B	C	B	C
0	<i>t-g</i> inclinal	57.6	-0.81	-0.94	-11.0	-15.4	-1.8	-2.2	-0.8	-0.7
18	<i>t-g</i> inclinal	57.0	-0.46		-11.2		-1.7		-1.1	
36	<i>t-g</i> equatorial	60.4	-0.64		-12.6		-1.6		-1.4	
54	<i>t-g</i> equatorial	61.3	-0.50		-13.0		-1.0		-1.5	
72	<i>t-g</i> inclinal	58.8	-0.31		-12.7		-0.1		-1.4	
90	<i>t-g</i> inclinal	54.0	0.34	0.74	-13.5	-16.1	1.3	1.5	-1.3	-1.3
108	<i>t-g</i> inclinal	44.5	1.28		-10.1		2.5		-0.6	
126	<i>t-g</i> inclinal	35.7	3.76		-8.8		3.2		-0.1	
144	<i>t-g</i> axial	28.1	8.22		-7.7		3.3		0.3	
162	<i>t-g</i> axial	22.4	11.89		-6.3		3.2		0.4	
180	<i>t-g</i> axial	13.6	12.91	7.51	-6.1	-10.7	3.1	2.5	0.7	-0.7
				2.85 <sup>c</sup>		-1.6 <sup>c</sup>		11.6 <sup>c</sup>		8.0 <sup>c</sup>

<sup>a</sup>See comments a and b of Table VI.

<sup>b</sup>The energies of the two HOMO's of planar *cis*-2-butene FO are -0.4377 and -0.4339 (basis B) and -0.4315 and -0.4253 hartree (basis C), respectively.

<sup>c</sup>Flexible pseudorotor model, see Table IX.

TABLE VIII. Position and influence of the substituents in puckered conformations of *trans*-3,5-dimethyl-1,2,4-trioxolane.<sup>a</sup>

$\phi$ , deg	Position of Z	$\alpha_Z$ , deg	Subst. effect $\Delta$ values		$\pi$ effect <sup>b</sup> total		$\pi$ effect of substituents both Z			
			B	C	B	C	B	C	B	C
0	<i>b-g</i> axial	166.3	0.64	2.07	-8.0	-11.6	1.0	1.6	2.0	3.1
18	<i>b-g</i> axial	166.4	1.14		-7.6		1.9		2.5	
36	<i>b-g</i> axial	169.9	0.99		-8.4		2.6		2.8	
54	<i>b-g</i> axial	170.5	0.99		-8.6		3.4		2.9	
72	<i>b-g</i> axial	167.5	0.84		-8.5		4.1		2.8	
90	<i>b-g</i> axial	162.1	0.89	1.92	-10.1	-12.5	4.7	5.1	2.1	2.3
198	<i>b-g</i> inclinal	123.0	0.70		-8.9		0.6		1.4	
216	<i>b-g</i> equatorial	119.6	0.10		-11.0		0		-1.3	
234	<i>b-g</i> equatorial	118.7	-0.23		-13.2		-1.2		-1.7	
252	<i>b-g</i> inclinal	121.2	-0.49		-14.4		-1.8		-1.4	
270	<i>b-g</i> inclinal	126.0	-0.46	-0.38	-17.1	-20.4	-2.3	-2.8	-1.2	-1.6

<sup>a</sup>See comments a and b of Table VI.

<sup>b</sup>The energies of the two HOMO's of planar *trans*-2-butene FO are -0.4368 and -0.4340 (basis B) and -0.4306 and -0.4254 hartree (basis C), respectively.

is possible for an equatorially oriented CH<sub>3</sub> group but not for an axially oriented one. Some of the methyl charges of Table V disclose this effect. An even better indication of the  $\pi$  effect is given by the charge distributions at the C atoms of the methyl groups or the  $\pi$ -stabilization energies listed in Tables VI-VIII.

We have also investigated the question of whether a conformational analysis in terms of bond-bond interactions is appropriate in the case of a FO. For this purpose, the potential of internal rotation around the CC bond of methylethylether has been calculated with basis sets B and C.<sup>16</sup> Then the interaction energies of substituent and ring bonds have been estimated for each conformation of Fig. 1 by utilizing the evaluated internal rotational potentials of methylethylether and ethylperoxide (Paper IV) as well as the dihedral angles  $\tau(C_MCO)$  and  $\tau(C_MCOO)$ <sup>17</sup> of the puckered FO forms. The attempt to predict relative conformational stabilities from interaction energies was only partially successful, for example in the case of the T forms with  $\phi = 90^\circ$  or  $270^\circ$ . However, in general the bond-bond interaction approach does not lead to reasonable predictions, an observation which has also been made in the case of the PO's (see Paper IV). Therefore, we refrain from a detailed discussion of the interaction energies in the following.

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

According to the relative energies of Tables I and II, a methyl group has a stronger impact on the conformational flexibility of a FO than of a PO (see the Tables I and II of the preceding Paper IV). Nevertheless, the gross features of the  $(q, \phi)$  surface of propene FO still resemble those of the ethylene FO surface. For example, the conformational minima are located close to  $\phi = 90^\circ$  and  $270^\circ$  where the latter value determines the position of the global minimum. The local maximum corresponds to the energy of the planar form which is 6.5 kcal/mole (basis C) less stable than the T puckered

form with  $\phi = 270^\circ$ . This has to be compared to a value of 6.3 kcal/mole (basis C) evaluated for ethylene FO.<sup>7</sup> The saddlepoints of the  $(q, \phi)$  surface are located at  $\phi = 0^\circ$  and  $\phi = 180^\circ$ , i. e., the relative energies of the E puckered conformations determine the pseudorotational barriers. Pseudorotation of the ring from  $\phi = 270^\circ$  to  $\phi = 90^\circ$  is hindered by a barrier of about 3.1 kcal/mole which is similar to the barrier height evaluated for ethylene FO.<sup>7</sup> However, a  $\phi = 90^\circ$  to  $\phi = 270^\circ$  interconversion of the FO ring is almost as difficult as inversion through the planar ring. The barrier has increase to 5.9 kcal/mole, partially because of unfavorable substituent-ring interactions.

Clearly, the data of Table VI confirm the expected relationship between substituent orientation and  $\pi$  effect. According to the computed orientation angles, the methyl group is axially oriented for  $72^\circ \leq \phi \leq 216^\circ$  while it is almost equatorial for  $\phi$  values close to  $0^\circ$  or  $360^\circ$ . The corresponding  $\pi$  values signify a strong destabilization of the puckered ring by an axial methyl group and a slight stabilization of about 0.5 kcal/mole by an equatorial group. Obviously, it is the influence of an axially positioned substituent which causes the high pseudorotational barrier at  $\phi = 180^\circ$ . The calculated  $\pi$  effects support this view. They are positive in the range  $54^\circ \leq \phi \leq 234^\circ$ , i. e., the range of small  $\alpha_x$  values. The lowest substituent orientation angle ( $\phi = 126^\circ$ ,  $\alpha = 9.5^\circ$ ) leads to the highest destabilizing  $\pi$  effect of the methyl group. On the other hand, the conformations with an equatorially positioned CH<sub>3</sub> group ( $\alpha_x \geq 60^\circ$ ,  $306^\circ \leq \phi \leq 324^\circ$ ) are characterized by relatively large negative  $\pi$ -stabilization energies which is indicative of favorable  $\sigma$ - $\pi$  orbital mixing and  $\pi$  back-donation from the ring to the substituent.

In Paper IV, it has already been demonstrated that a direct equivalence between  $\Delta$  values and  $\pi$  effect cannot be expected. Comparing the two sets of data evaluated for propene PO (Table VII, Paper IV) and the corresponding FO it becomes obvious that the  $\pi$  ef-

fects of both compounds are similar while the  $\Delta$  values of the FO are considerably larger than those of the PO. A similar observation made for *cis*-2-butene PO was indicative of an artificial exaggeration of substituent-substituent interactions caused by the application of the rigid pseudorotor model. Since the position of the atoms and atom groups attached to the FO ring has been determined in an even more approximate way, substituent-substituent interactions may be overestimated in an undue manner. Their actual importance can be predicted with the aid of the substituent orientation angles. If they are close to  $0^\circ$  for a pair of topside substituents (or close to  $180^\circ$  for a pair of bottomside substituents), strong 1,3-interactions have to be expected since both substituents stand perpendicular to the mean plane of the ring, probably approaching each other up to the range of van der Waals repulsion.

By means of Table VII, where the substituent orientation angles of the group Y are listed (Y=H, propene FO), a case with almost parallel external ring bonds can be found. It occurs for the inverted E form which, if disubstituted, possesses a pair of axially oriented substituents pointing almost at the same direction. Hence, steric 1,3-interactions will be strongest for  $\phi = 180^\circ$ . Their importance will decline if  $\phi$  changes to either  $90^\circ$  or  $270^\circ$ . Although the repulsion between the  $\text{CH}_3$  group and the H atom placed in position Y of the trioxolane ring (see Fig. 1) should not be very strong, it may influence the high  $\Delta$  value because of the rigid pseudorotor model employed. Probably the second pseudorotational barrier ( $\phi = 90^\circ$  to  $270^\circ$ ) is slightly exaggerated, since the molecule is able to avoid steric repulsions by altering the substituent orientations.<sup>18</sup>

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

The situation of two methyl groups interacting strongly across the ring applies to *cis*-2-butene FO. According to the energies of Table I, the E conformation with  $\phi = 180^\circ$  is destabilized by 15.7 kcal/mole with regard to the T puckered forms. The  $\pi$ -stabilization energies of Table VII reveal no unusual substituent-ring interactions for this conformation. Therefore, its large destabilization seems to result predominantly from 1,3-steric repulsion in a rigid pseudorotor model. The closest  $\text{H}\cdots\text{H}$  contact across the ring is just 141 pm which is far inside the region of van der Waals repulsion. Certainly, such a narrow contact is avoided in a more realistic model of the ring.

To relieve steric repulsion, the methyl groups can either bend outward or rotate. Also, the degree of ring puckering can be reduced. Each of the possible relaxation mechanisms will be cushioned at some point, as they ultimately lead to unfavorable molecular structures. Strong bending of the  $\text{CH}_3$  groups enhances bond angle strain, rotation causes additional torsional strain, and a reduction of ring puckering leads to  $\pi$  destabilization.

The effectiveness of the various relaxation processes can be estimated by choosing appropriate model compounds and studying each of the molecular changes separately. For example, from the rotational potential of methylethylether it can be predicted that the energy gain

due to methyl rotation in the *cis*-2-butene conformation with  $\phi = 180^\circ$  should be low. A  $60^\circ$  rotation of the C bonded  $\text{CH}_3$  group requires about 3.7 kcal/mole (RHF/basis B, standard geometry), thus effecting an energy loss of 7–8 kcal/mole if both  $\text{CH}_3$  groups of the puckered FO rotate.

In order to give an estimate of the bending effect, two diethylether conformations have been investigated, one with a dihedral angle  $\tau(\text{C}_M\text{COC})$  of  $90^\circ$  taken from the *cis*-2-butene conformation at  $\phi = 180^\circ$  and one with  $\tau(\text{C}_M\text{COC}) = 160^\circ$  taken from the conformation with  $\phi = 0^\circ$ . The COC angle has been adjusted to the one of the FO ring while all other structural parameters have been kept at standard values.<sup>19</sup> With the minimal STO-3G basis (basis A), the  $90^\circ$  conformation of diethylether is found to be 17.6 kcal/mole above the one with  $\tau = 160^\circ$  which is somewhat larger than the energy difference  $E(\phi = 0^\circ) - E(\phi = 180^\circ)$  (13.7 kcal/mole) computed for *cis*-2-butene FO. If the  $\text{C}_M\text{CO}$  angle is optimized, the energy of the  $90^\circ$  form decreases by 9.4 kcal/mole. As is shown in Table IX, this energy gain is 8.8 kcal/mole larger than the one calculated for the  $160^\circ$  conformation. If a pseudorotor model with flexible substituent orientations is employed, we conclude that the relative energy of the inverted E form of *cis*-2-butene FO can be reduced below 10 kcal/mole, but most probably not below the energy of the planar form. To lower the destabilizing interactions between the  $\text{CH}_3$  groups further, a reduction of the degree of puckering seems unavoidable. This is also suggested by a diethylether model with a flexible COC angle (see Table IX). In the conformation with  $\tau(\text{C}_M\text{COC}) = 90^\circ$  the COC angle widens to  $114.3^\circ$  while it is about  $111.5^\circ$  for  $\tau(\text{C}_M\text{COC}) = 160^\circ$ . The computed energy gain with regard to a standard geometry model is 17.3 in the first and 4.0 kcal/mole in the second conformation. Translated to *cis*-2-butene FO, this means that a COC angle widening, necessarily connected with a reduction of  $q$  and supported by an outward bending of the methyl groups, diminishes 1,3-steric repulsions to such an extent that puckered conformations at  $\phi = 180^\circ$  become comparable in energy or even more stable than the planar form.

This prediction is confirmed by an actual optimization of the E form applying a flexible pseudorotor model ( $q$ , COC, and external ring angles are varied under the constraint of  $C_s$  symmetry). With basis B, the reoptimized E form ( $\phi = 180^\circ$ ) is found to possess an energy about 12 kcal/mole (Table IX) lower than the one calculated for the rigid pseudorotor model. The degree of puckering has decreased to 15.5 pm which allows a widening of the COC angle to  $111.7^\circ$ . Using the parameters of Table IX in a RHF/basis C calculation, the inverted E form turns out to be 0.1 kcal/mole more stable than the planar ring.

The RHF results for *cis*-2-butene FO can be interpreted as follows: Electronic effects caused by the substituents have a larger impact on ring geometry and conformational flexibility of *cis*-alkene FO's than of the corresponding PO's. Two reasons are responsible for their influence. First, the variation of steric interactions during a complete pseudorotation itinerary is



TABLE IX. 1,3-Steric interactions between two methyl groups in  $\beta$  position to an ether oxygen. Comparison of energetical and structural changes possible in two geometrical models of diethylether and *cis*-2-butene final ozonide.<sup>a-c</sup>

	$\tau(\text{C}_M\text{COC}) = 90^\circ$		$\tau(\text{C}_M\text{COC}) = 160^\circ$	
	Flexible subst. orientations	Flexible pseudorotor	Flexible subst. orientations	Flexible pseudorotor
A. Diethylether <sup>d</sup>				
Energy	-229.27861	-229.29115	-229.29243	-229.29796
Energy gain <sup>f</sup>	9.4	17.3	0.6	4.0
Rel. energy	12.2	4.3	3.4	0
$\beta_1(\text{C}_M\text{CO})$	117.2	115.1	109.1	108.4
$\beta_2(\text{C}_M\text{CH})$	107.6	108.7	109.0	109.6
$\beta_3(\text{HCO})$	109.2	108.6	111.3	111.1
$\beta_4(\text{HCH})$	105.5	107.0	107.1	107.1
$\alpha(\text{COC})$	(103.0) <sup>g</sup>	114.3	(103.0) <sup>g</sup>	111.5
B. <i>Cis</i> -2-butene FO, $\phi = 180^\circ$ <sup>e</sup>				
Energy	-380.03440	-380.03926		
Energy gain <sup>f</sup>	8.7	11.8		
$\beta_1(\text{C}_M\text{CO}_E)$ <sup>h</sup>	115.2	113.2		
$\beta_2(\text{C}_M\text{CO}_P)$	112.2	111.5		
$\beta_3(\text{HCO}_E)$	106.8	(106.8)		
$\beta_4(\text{HCO}_P)$	107.4	(107.4)		
$\eta$	(28.6)	15.5 <sup>i</sup>		
$\alpha(\text{CO}_E\text{C})$	(106.9)	111.7 <sup>i</sup>		

<sup>a</sup>Absolute energies are given in hartree, relative energies in kcal/mole, bond angles in deg, and the puckering amplitude  $\eta$  in pm.

<sup>b</sup>In the geometrical model with flexible substituent orientations, all bond angles of the methylene group have been optimized; in the flexible pseudorotor model, the puckering amplitude  $\eta$  and the COC angle have also been included in the optimization of *cis*-butene FO.

The resulting changes have been modeled with a diethylether conformation with a variable COC angle.

<sup>c</sup>Angle or puckering amplitude values in parentheses have been retained during optimization.

<sup>d</sup>Results have been obtained with basis A, Ref. 13.

<sup>e</sup>Results have been obtained with basis B.

<sup>f</sup>The energy gain is measured against the energies of rigid conformational models of diethylether (stand. geometry) and of *cis*-2-butene FO (puckering amplitude, internal, and external ring angles are taken from 1,2,4-trioxolane, Ref. 7).

<sup>g</sup>The angle value is taken from the basis A structure of the E form of 1,2,4-trioxolane, Ref. 7.

<sup>h</sup>The distinction between an ether or an peroxy oxygen is indicated by the subscripts E and P.

<sup>i</sup>With basis C, the puckering amplitude is found to be 18.5 pm for an estimated value of  $\alpha(\text{CO}_E\text{C})$  of 108.6°.

larger in the case of a FO than a PO. For example, methyl-methyl interactions in *cis*-2-butene PO change by about 3.6 kcal/mole for  $\phi = 0^\circ$  to  $90^\circ$  (Table XII of Paper IV,  $\text{C}_4\text{H}_8$ , flexible rotor model) while the corresponding interactions in *cis*-2-butene FO increase by as much as 8.8 kcal/mole for  $\phi = 0^\circ$  to  $180^\circ$  (Table IX,  $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$  with flexible substituent orientations). Secondly, ring-substituent interactions are destabilizing for both methyl groups of the inverted E form of *cis*-2-butene FO while they are stabilizing for the equatorial methyl group and destabilizing for the axial methyl group of the T puckered PO ( $\phi = 90^\circ$  or  $270^\circ$ ) (see Paper IV). Since the energies of these conformations determine the pseudorotational barriers of the two *cis*-2-butene ozonides, the dimethyl substituted FO loses some of the flexibility of the parent FO in contrast to the en-

hanced flexibility of the corresponding PO.

Nevertheless, puckered conformations should exist for all values of  $\phi$ , i.e., pseudorotation of *cis*-2-butene FO is still the energetically favored interconversional process. The  $\pi$  effects of the substituents listed in Table VII show the usual dependence on the substituent orientation angle  $\alpha$ . As in the case of *cis*-2-butene PO, they are rather independent of basis set deficiencies (rigidity of basis B) or geometrical effects (enhanced steric repulsion due to a rigid pseudorotor model). The magnitude of the  $\pi$  effect is comparable with that found for PO's. This suggests that all  $\Delta$  values will be reduced somewhat if the orientation of the CH and  $\text{CC}_M$  bonds is correctly determined by optimization of the external ring angles.

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

Unlike the *cis* derivative, *trans*-2-butene FO does not exhibit puckered conformations with strong methyl-methyl interactions. Accordingly, the energies calculated with the rigid pseudorotor model do not lead to unusual  $\Delta$  values as is indicated by Table VIII. All modes of ring puckering stabilize the planar form. The computed conformational stabilities resemble those of propene FO. For example, the E forms ( $\phi = 0^\circ$  or  $180^\circ$ ) are less stable by 5.7 kcal/mole than the T form at  $\phi = 270^\circ$ , which is comparable to the 5.9 kcal/mole difference obtained for propene FO conformations with  $\phi = 180^\circ$  and  $\phi = 270^\circ$ . In both cases, the change from  $\phi = 270^\circ$  to  $\phi = 180^\circ$  brings one methyl group from a stabilizing inclinal position to a destabilizing axial one. This is disclosed by the  $\Delta$  energies, the substituent orientation angles, and the computed  $\pi$ -stabilization energies of Tables VI and VIII.

The difference between the two T forms with  $\phi = 270^\circ$  and  $90^\circ$  increases to 2.3 kcal/mole when a second methyl group is attached to the bottom side of the FO ring. The destabilization of the T form with  $\phi = 90^\circ$  is mainly due to the combined  $\pi$  effects of two axially oriented substituents (Table VIII). The basis *B* energies listed in Table I and plotted in Fig. 2 indicate that this destabilization causes a shift of the position of the pseudorotational barriers to  $\phi = 18^\circ$  and  $162^\circ$ . The conformations with these  $\phi$  values should be even more destabilized than the E forms because of their more positive  $\Delta$  values.

The relatively high pseudorotational barriers as well as the destabilization of the conformations in the  $0^\circ$ – $180^\circ$  region of  $\phi$  indicate that the flexibility of *trans*-2-butene FO ring is considerably reduced. In higher *trans*-alkene FO's, pseudorotation and inversion through the planar form may become competitive. Then the planar form could be located at a saddlepoint rather than a local maximum of the pseudorotational surface.

### IV. COMPARISON WITH EXPERIMENTAL AND OTHER THEORETICAL RESULTS

As far as the most stable conformation of either propene or *trans*-2-butene FO is concerned, the *ab initio* results verify the spectroscopic findings of Kuczkowski *et al.*<sup>2</sup> In both cases, the OO half-chair form with almost equatorially oriented methyl substituents ( $\phi = 270^\circ$ ) is found to be located at the global minimum of the ( $q, \phi$ ) surface. In Table X of Paper III,<sup>7</sup> we have already compared experimental and theoretical puckering amplitude (46.1 pm, exp vs 44.7 pm, theor), phase angle ( $270.8^\circ$ , exp vs  $270^\circ$ , theor), bond angles and bond lengths of propene FO. They are in reasonable agreement. The theoretical dipole moments obtained with basis *C* (1.54 D, propene FO and 1.63 D, *trans*-2-butene FO) are about 0.3 D larger than the spectroscopic values of 1.29 and 1.34 D.<sup>2</sup> This discrepancy is of the same order of magnitude as that found for ethylene FO (1.09 D, exp vs 1.41 theor).

In contrast to the experimental observation of just one stable FO conformation,<sup>20</sup> the theoretical calculations

TABLE X. CNDO/2 energies of propene and 2-butene final ozonide.<sup>a</sup>

$\phi$ , deg	Propene FO	2-Butene FO	
		<i>cis</i>	<i>trans</i>
0	nm	3.1	nm
18	3.8	1.4	>4.7
90	1.7	0	3.1
162	nm	nm	
180	nm	nm	
198	nm		4.3
270	0		0
342	2.9		
planar	4.6	3.6	5.2

<sup>a</sup>Extracted from the data of Ref. 21; nm, no minima found for this conformation.

suggest the existence of a second stable conformation of propene and *trans*-2-butene FO, namely, the T form with  $\phi = 90^\circ$  possessing one or two axially oriented  $\text{CH}_3$  groups. This form should be about 1 (propene FO) or 2 kcal/mole (*trans*-2-butene FO) less stable than the experimentally observed T conformation. Since all T conformations are locked in relatively deep energy wells of the ( $q, \phi$ ) surface, it is understandable that no effects from pseudorotation have been observed at low temperatures.<sup>2</sup>

One semiempirical study of methyl substituted FO's has been reported in the literature.<sup>21</sup> It was based on the CNDO/2 method and used a severely constrained five-membered ring model with one rather than three variable parameters. We have already discussed the consequences of such a model in Paper IV. Also, it has been outlined in Paper IV that CNDO/2 calculations tend to underestimate the stability of a puckered trioxolane due to an inadequate description of the lone pair delocalization effect. While the deficiencies of both the geometrical model and the NDO method lead to poor conformational energies in the case of a PO, the semiempirical results on substituted FO's are significantly better as is shown by the data of Table X which have been extracted from the work of Rouse.<sup>21</sup> Obviously, the conformational minima and the energy changes arising from an equatorially or axially placed methyl group can be correctly predicted with CNDO/2. The seeming improvement of semiempirical results is comparable to that obtained for basis *B* in the case of a FO. While the deficiencies of basis *B* prohibit a reliable description of 1,2,3-trioxolane, they seem to have less severe consequences if the OOO entity is split into an ether and peroxide unit. We have shown that this results from a fortuitous cancellation of basis set errors, possibly because of a favorable arrangement of O atoms in the FO ring.<sup>7</sup> Evidently, a similar cancellation of theoretical errors leads to an accidental agreement of experimental and CNDO/2 results with regard to the conformational minima of the studied FO's. However, the deficiencies of a NDO treatment of cyclic polyoxides become obvious when comparing the relative energies of the planar or the E puckered conformations (Table X). The low relative energy of the former confirms that the actual stabil-

ity of the T forms is largely underestimated by the CNDO/2 method. This conclusion also applies to the E puckered conformations which, according to Table X, should lie even above the planar forms. Probably, both the constraint of the geometrical model and the inadequacy of the CNDO/2 method cause these erroneous predictions.

## V. CONCLUSIONS

The electronic features of methyl substituted FO's closely resemble those of the corresponding PO's. Thus, in both cases, the tendency of lone pair delocalization is the driving force of ring puckering. It is responsible for the fact that without exception nonplanar ozonide forms have been found to be more stable than the planar conformations. Pseudorotation is the favorable interconversional process for all ozonides considered in Papers IV and V.

The stabilization due to ring puckering can be favorably described by the lowering of the two  $\pi$ -type HOMO's resulting from  $\sigma$ - $\pi$  orbital mixing and the corresponding reduction of their antibonding nature. This  $\pi$  effect turns out to be a valuable tool when explaining the stabilization effect of a methyl group and its reinforcement or weakening due to an altered substituent orientation in a puckered ozonide conformation. With the aid of the orientation angles, a stabilizing influence can be predicted for the equatorially located methyl groups and a destabilizing influence for the axially located groups.

The differences in the conformational behavior of the PO's and FO's arise from the different topologies of the two rings. Thus, the  $\pi(a_2)$  MO of planar 1,2,4-trioxolane determines the most favorable mode of ring puckering while this role is adopted by the  $\pi(b_1)$  MO in the case of 1,2,3-trioxolane. As a consequence, the T forms at  $\phi = 270^\circ$  or  $90^\circ$  are the most stable FO conformations, not the E forms as in the case of the PO's.

Substituent-substituent interactions are more important for FO's than for PO's which also results from the different topologies of the two ozonide rings. We have shown that the variation of these interactions during a pseudorotational itinerary, not their actual magnitude is responsible for the height of the pseudorotational barriers.

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- <sup>17</sup>The subscript M is used to distinguish between the C atom of a methyl group and those of the trioxolane ring.
- <sup>18</sup>According to model calculations based on a methylether conformation with  $\tau(C_MCO) = 90^\circ$  ( $\phi = 180^\circ$ ,  $\tau_{PO}(C_MCO) = 81.8^\circ$ ) relaxation of the  $C_MCO$  angle leads to a relative energy gain of 0.7 kcal/mole. See Ref. 16.
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