

Methoxyethenes: Structures and Conformations

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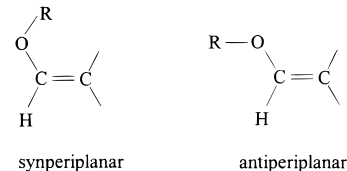
Received December 21, 1998

Abstract: The geometric structures and conformational properties of 1,1-dimethoxyethene (1,1-DME), (Z)-1,2-dimethoxyethene (Z-1,2-DME), and tetramethoxyethene (TME) have been determined by gas electron diffraction (GED) and quantumchemical calculations (HF/3-21G, HF/6-31G*, and MP2/6-31G*). Additional theoretical calculations have been performed for (E)-1,2-dimethoxyethene and trimethoxyethene. The calculations predict three or more possible conformations for these compounds in the energy range below about 2 kcal mol⁻¹. For 1,1-DME, the GED experiment results in a mixture of two conformers. The main form (61(7)%) possesses C_{2v} symmetry, with both methoxy groups synperiplanar to the C=C double bond ($\phi_{1,2}(\text{C}=\text{C}-\text{O}-\text{C}) = 0^\circ$). In the second conformer, one methoxy group is oriented synperiplanar and the other one anticlinal ($\phi_2 = 131(7)^\circ$). For Z-1,2-DME and TME, only one conformation was observed in the GED analyses. Z-1,2-DME possesses a structure with syn- and antiperiplanar ($\phi_2 = 152(6)^\circ$) methoxy groups (C₁ symmetry). In TME, all groups are oriented anticlinal, alternatingly above–below–above–below the molecular plane (D₂ symmetry). This compound is twisted around the C=C bond by 14(3)°. The MP2 calculations reproduce the conformational properties of these methoxyethenes perfectly, whereas the HF/3-21G approximation leads to incorrect results. The MP2/6-31G* method predicts for the preferred conformation of (E)-1,2-dimethoxyethene a structure with C_{2h} symmetry and both methoxy groups synperiplanar to the C=C bond. For trimethoxyethene, eight minima were detected on the energy surface. In the ground-state structure, two groups are oriented anticlinal and one synperiplanar.

Introduction

Microwave spectroscopy¹ and theoretical calculations^{2–4} result in a synperiplanar⁵ structure for the unstable vinyl alcohol, H₂C=C(H)OH (Chart 1), with the O–H bond eclipsing the C=C double bond and $\phi(\text{C}=\text{C}-\text{O}-\text{H}) = 0^\circ$. In addition to this synperiplanar form, the theoretical calculations predict a stable antiperiplanar conformation (Chart 1) with $\phi(\text{C}=\text{C}-\text{O}-\text{H}) = 180^\circ$, which is higher in energy by 1.6–3.0 kcal mol⁻¹. Similarly, a synperiplanar ground-state structure with $\phi(\text{C}=\text{C}-\text{O}-\text{C}) = 0^\circ$ was derived for methyl vinyl ether (methoxyethene), CH₃OC(H)=CH₂, by microwave spectroscopy,⁶ gas electron diffraction (GED),^{2,7–9} and theoretical calculations.^{4,9–11} For the high-energy conformer of methoxyethene, structures with dihedral angles $\phi(\text{C}=\text{C}-\text{O}-\text{C})$ from 80° to 180° were derived in various experimental studies (see ref 4 for a review). High-resolution mid-infrared spectra were interpreted in terms of a pseudoplanar anti structure with a flat double-minimum potential

Chart 1



and minima at $\pm 160^\circ$.¹⁰ Furthermore, a GED study at 200 °C nozzle temperature leads to about 30% contribution of the high-energy conformer with $\phi > 150^\circ$. Various ab initio calculations predict for this high-energy form also an antiperiplanar structure with a flat double-minimum potential and with minima between $\pm 150^\circ$ and $\pm 168^\circ$.^{4,9–11} Thus, the most convincing experiments and theoretical calculations result in an antiperiplanar structure for the high-energy conformer. In contrast to these two experimental studies and to the calculations, Raman spectra were interpreted in terms of an anticlinal structure ($\phi(\text{C}=\text{C}-\text{O}-\text{C}) = 138^\circ$) and a high barrier of 1.74(16) kcal mol⁻¹ for the antiperiplanar form.¹² From vibrational spectra, an enthalpy difference between anti- and synperiplanar conformers of 1.70(9)¹² and 1.15(25)¹³ kcal mol⁻¹, respectively, were obtained. Theoretical calculations predict slightly higher energy differences of 2.0–3.3 kcal mol⁻¹.

Syn- and antiperiplanar structures of vinyl alcohol and methoxyethene are stabilized by conjugation between the oxygen π lone pair and the C=C π bond, $n_{\pi}(\text{O}) \rightarrow \pi^*(\text{C}=\text{C})$. However, it is difficult to give a convincing and self-evident explanation

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(5) Synperiplanar (sp) describes structures with dihedral angles $\phi = 0 \pm 30^\circ$, synclinal (sc) with $\phi = 60 \pm 30^\circ$, anticlinal (ac) with $\phi = 120 \pm 30^\circ$, and antiperiplanar (ap) with $\phi = 180 \pm 30^\circ$.

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for the preference of the synperiplanar conformation relative to the antiperiplanar structure. The general observation, that single bonds (O–H or O–Me) rather eclipse a double bond (C=C) than another single bond (C–H), can be explained by viewing the double bond as a pair of two bent single bonds (banana bonds), as proposed by Pauling.¹⁴ In this simple picture, the O–R bond staggers the two bent bonds in the synperiplanar orientation, and this arrangement is favored over the eclipsed orientation of O–R and C–H in the antiperiplanar conformation. A natural bond orbital (NBO) analysis for vinyl alcohol did not lead to an evident explanation in terms of orbital interactions. The largest difference is predicted for $n_{\pi}(\text{O}) \rightarrow \pi^*(\text{C}=\text{C})$ conjugation, which favors the synperiplanar form by about 3 kcal mol⁻¹ relative to the antiperiplanar structure. Intuitively, however, this conjugation should be equal or nearly equal in both planar structures.

Compounds in which the synperiplanar conformation is destabilized by strong steric interactions, such as *tert*-butyl vinyl ether, *t*BuOC(H)=CH₂, or (*Z*)-methyl 1-propenyl ether, (*Z*)-MeOC(H)=C(H)Me, adopt nearly planar anti structures with $\phi(\text{C}=\text{C}-\text{O}-\text{C}) = 167(5)^{\circ}$ and $161(5)^{\circ}$, respectively.¹⁵ Again, these structures are favored by conjugation between the oxygen lone pair and the π bond. Fluorination of the vinyl group, however, leads to nearly perpendicular orientation of the O–C(sp³) bond in methyl trifluorovinyl ether ($\phi(\text{C}=\text{C}-\text{O}-\text{C}) = 111(4)^{\circ}$) and in perfluoromethyl vinyl ether ($\phi(\text{C}=\text{C}-\text{O}-\text{C}) = 104(2)^{\circ}$).¹⁶ Since steric interactions cannot be responsible for destabilizing planar syn or anti structures in these compounds, we have to assume that conjugation is no longer effective in the fluorinated species. This is plausible, since strong $n(\text{F}) \rightarrow \pi^*(\text{C}=\text{C})$ interactions prevent the $n_{\pi}(\text{O}) \rightarrow \pi^*(\text{C}=\text{C})$ conjugation.

In the present study, we are interested in the effect of two or more neighboring methoxy groups on the structural and conformational properties of methoxy ethenes. We report structure determinations by GED and ab initio calculations for 1,1-dimethoxyethene (1,1-DME), (*Z*)-1,2-dimethoxyethene (*Z*-1,2-DME), and tetramethoxyethene (TME). The conformational properties of 1,1-DME and *Z*-1,2-DME have been studied previously by various theoretical methods.^{17–21} Molecular mechanics and ab initio methods (STO 3G and HF/3-21G) result in different predictions for the most stable conformers of these two compounds. Vibrational spectra for the *Z*-1,2-DME were interpreted in terms of a mixture of two conformers, one of which possesses a planar structure.²² For steric reasons, both methoxy groups can be oriented antiperiplanar or one antiperiplanar and the other one synperiplanar. To our knowledge, no experimental or theoretical study concerning the conformation of TME has been reported in the literature. HF/3-21G calculations for tetrahydroxyethene, C₂(OH)₄, result in a structure with C₂ symmetry. Two hydroxy groups on one carbon atom adopt synperiplanar orientations, and the two hydroxy

groups on the other carbon atom adopt anticlinal orientations.²³ It is not known whether other stable conformations exist for this model compound.

Ab Initio Calculations

Geometry optimizations for the three methoxy ethenes were performed with the HF/3-21G, HF/6-31G*, and MP2/6-31G* methods, using the GAUSSIAN 94 program system.²⁴ For completeness, HF/3-21 and MP2/6-31G* calculations were performed also for the remaining members of this series, (*E*)-1,2-dimethoxyethene and trimethoxyethene. Different starting geometries were chosen to ensure that all possible minima on the energy surface were detected. The various conformations are described qualitatively by the orientation of the methoxy groups, synperiplanar (sp), synclinal (sc), anticlinal (ac), or antiperiplanar (ap),⁵ and quantitatively by the dihedral angles $\phi_i(\text{C}=\text{C}-\text{O}-\text{C})$. All stable conformers and their relative energies are summarized in Tables 1, 3, 5, 7, and 8. The calculated geometric parameters (HF/3-21G and MP2/6-31G*) for the preferred conformations are included in the tables for the respective experimental results (Tables 2, 4, and 6). The bond lengths obtained with the HF/6-31G* approximation are generally shorter than those obtained with the other two methods, and bond and dihedral angles are close to the MP2 results. Vibrational frequencies were calculated with the HF/6-31G* method for those conformers which were observed in the GED analysis. The Cartesian force constants were transformed to symmetry force fields, scaled with 0.90, and vibrational amplitudes were obtained with the program ASYM40.²⁵ The calculated vibrational amplitudes are given together with the experimental values as Supporting Information.

Gas Electron Diffraction

Radial distribution functions (RDFs) were calculated by Fourier transformation of the molecular intensities. An artificial damping function, $\exp(-\gamma s^2)$, with $\gamma = 0.0019 \text{ \AA}^2$, was applied to the intensities. Preliminary structural parameters and conformational compositions, which were derived from analyses of the RDFs, were refined by least-squares fitting of the molecular intensities. Differences between closely spaced distances and some parameters which describe the positions of hydrogen atoms and which are poorly determined in the GED experiment were constrained to the respective MP2 values. Furthermore, local C_{3v} symmetry and staggered orientation were assumed for methyl groups with a possible tilt angle between the C₃ axis and the O–C bond direction. In all cases, this tilt is toward the oxygen lone pairs.

1,1-Dimethoxyethene. Each of the three applied computational methods predicts three minima on the energy surface (Chart 2 and Table 1). According to the HF/3-21G approximation, the (sp,ap) form, with one methoxy group synperiplanar ($\phi_1 = 0^{\circ}$) and the other one antiperiplanar ($\phi_2 = 180^{\circ}$), is the most stable structure. HF/6-31G* and MP2/6-31G* methods, however, predict the (sp,sp) conformer to be lowest in energy.

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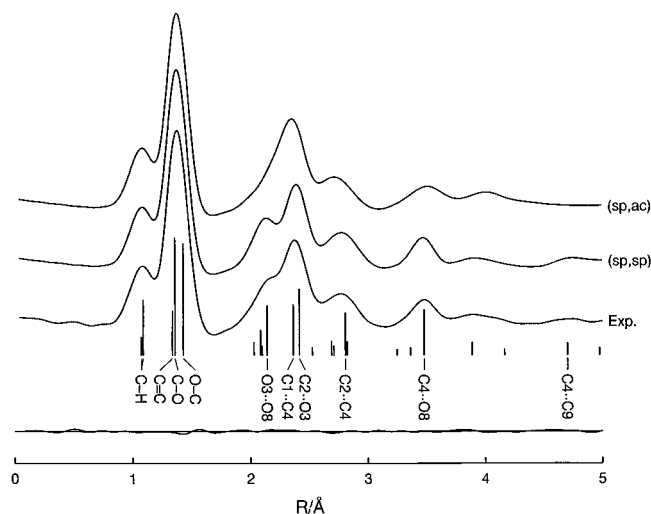
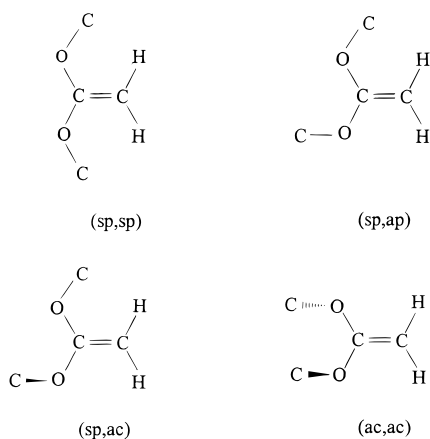


Figure 1. Calculated and experimental RDFs for 1,1-dimethoxyethene and difference curve for mixture of 61% (sp,sp) and 39% (sp,ac) conformers. Important interatomic distances are shown by vertical bars.

Table 1. Calculated Conformations and Relative Energies (kcal mol⁻¹) of 1,1-Dimethoxyethene

conformer	HF/3-21G		HF/6-31G*		MP2/6-31G*	
	(ϕ_1, ϕ_2)	ΔE^a	(ϕ_1, ϕ_2)	ΔE	(ϕ_1, ϕ_2)	ΔE
C_{2v} (sp,sp)	(0, 0)	0.00	(0, 0)	0.00	(0, 0)	0.00
C_s (sp,ap)	(0, 180)	-0.85	not stable		not stable	
C_1 (sp,ac)	not stable		(3, 145)	0.66	(-4, 142)	0.76
C_2 (ac,ac)	(118, 118)	1.19	(119, 119)	2.54	(122, 122)	2.62

Chart 2



According to these two methods, the (sp,ap) structure does not correspond to a minimum, but a similar (sp,ac) conformer, with one methoxy group oriented out of the ethene plane ($\phi_2 \approx 140^\circ$), corresponds to the second stable structure. The calculated energy of the (sp,ac) conformer is about 0.7 kcal mol⁻¹ above that of the (sp,sp) ground-state structure. All three methods result in a stable (ac,ac) structure, about 2.0–2.6 kcal mol⁻¹ above the most stable form.

Analysis of the experimental RDF (Figure 1) reveals that the (sp,sp) form is the main conformer, but the fit of the experimental GED intensities improved greatly if about 40% of an (sp,ac) form were added (Figure 2). In the least-squares analyses, the difference between the O–C and C–O bond lengths in the (sp,sp) conformer, $\Delta(\text{CO}) = (\text{O}–\text{C}(\text{sp}^3)) - (\text{C}(\text{sp}^2)–\text{O})$, was constrained to the MP2 value with an estimated uncertainty of ± 0.01 Å. Refinement of this difference caused several large correlations (>0.90) between geometric parameters. In the final

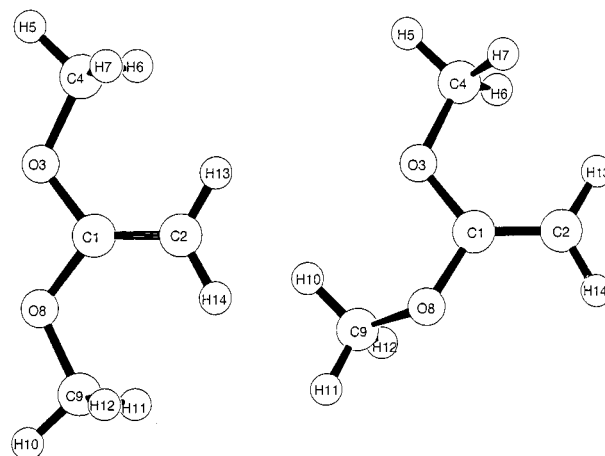


Figure 2. Molecular models and atom numbering for (sp,sp) (left) and (sp,ac) conformers (right) of 1,1-dimethoxyethene.

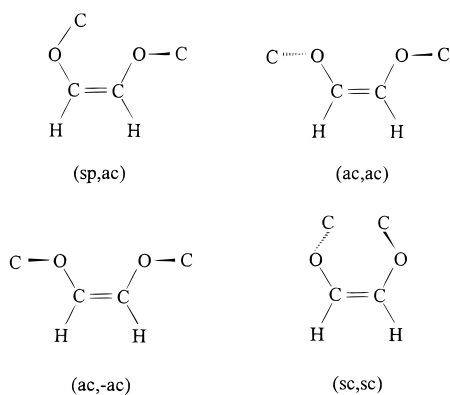
Table 2. Experimental and Theoretical Results for 1,1-Dimethoxyethene: Geometric Parameters of the (sp,sp) Conformer^a

	GED	HF/3-21G	MP2/6-31G*
C=C	1.333(5) (p_1)	1.323	1.346
(C–O) _{mean} ^b	1.390(2) (p_2)	1.395	1.391
$\Delta(\text{CO})$ ^b	0.070[10] ^c	0.085	0.070
C(sp ²)–O	1.355(6)	1.353	1.356
O–C(sp ³)	1.425(6)	1.438	1.426
(C–H) _{mean}	1.082(4) (p_3)	1.075	1.081
C=C–O	127.8(3) (p_4)	126.5	127.1
C–O–C	116.3(5) (p_5)	120.2	115.8
H–C–H	108.5(9) (p_6)	109.8	109.8
C=C–H	121.4 ^d	121.5	121.4
tilt (CH ₃)	3.7 ^d	3.6	3.7
$\phi_{1,2}$ (sp,sp)	0.0 ^d	0.0	0.0
% (sp,ac)	39(7)	<i>e</i>	36 ^f
ϕ_1 (sp,ac)	-4.2 ^d	<i>e</i>	-4.2
ϕ_2 (sp,ac)	131(8)	<i>e</i>	142

^a r_a parameters are given in angstroms and degrees. Experimental uncertainties are 3σ values and include possible systematic errors due to constraints. For molecular model, see Figure 2. ^b $(\text{C}–\text{O})_{\text{mean}} = 1/2[(\text{O}–\text{C}(\text{sp}^3)) + (\text{C}(\text{sp}^2)–\text{O})]$; $\Delta(\text{CO}) = [(\text{O}–\text{C}(\text{sp}^3)) - (\text{C}(\text{sp}^2)–\text{O})]$. ^c Not refined, but varied within the estimated uncertainty given in square brackets. ^d Not refined. ^e Not a stable structure according to this method. ^f Estimated from ΔE .

least-squares analysis, six geometric parameters and four vibrational amplitudes for the (sp,sp) conformer were refined. For the (sp,ac) form, only the dihedral angle ϕ_2 for the anticlinal methoxy group was refined. The dihedral angle for the syn-periplanar group was set to the calculated value ($\phi_1 = -4^\circ$). All other geometric parameters were tied to those of the (sp,sp) form with the calculated (MP2) differences. The vibrational amplitudes for the (sp,ac) conformer were set to the theoretical values. No correlation coefficient had a value larger than $|0.6|$. The final results for the main conformer are collected in Table 2. Vibrational amplitudes are listed in Table 1 of the Supporting Information. The conformational composition of 61(7)% (sp,sp) and 39(7)% (sp,ac) corresponds to a difference in the free enthalpy of $\Delta G^\circ = 0.27(13)$ kcal mol⁻¹. If we neglect different entropy contributions from rotations and vibrations and take into account the different multiplicities of both structures (2 for (sp,sp) and 4 for (sp,ac)), we obtain $\Delta H^\circ = 0.69(13)$ kcal mol⁻¹. This value is in excellent agreement with the energy differences derived by the HF/6-31G* (0.66 kcal mol⁻¹) and MP2/6-31G* methods (0.76 kcal mol⁻¹). The HF/3-21G approximation, which predicts an (sp,ap) structure to be most stable, gives a wrong result.

Chart 3

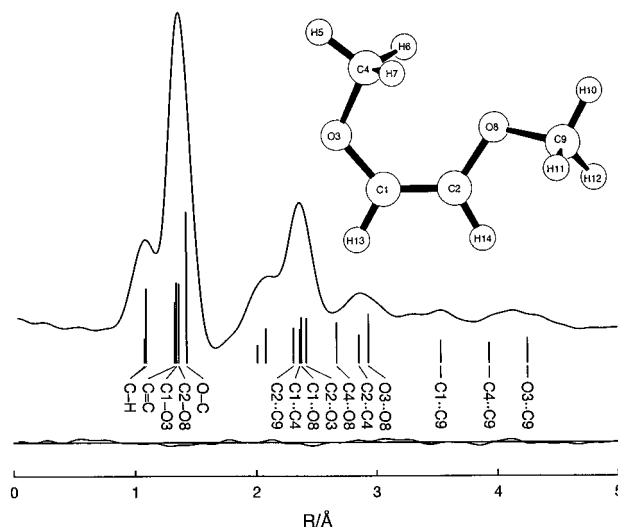
**Table 3.** Calculated Conformations and Relative Energies (kcal mol⁻¹) of (Z)-1,2-Dimethoxyethene

conformer	HF/3-21G		HF/6-31G*		MP2/6-31G*	
	(ϕ_1, ϕ_2)	ΔE	(ϕ_1, ϕ_2)	ΔE	(ϕ_1, ϕ_2)	ΔE
C ₁ (sp,ac)	(2, 123)	0.00	(-2, 132)	0.00	(9, 134)	0.00
C _s (ac,-ac)	(128, -128)	5.05	(142, -142)	0.79	(146, -146)	1.67
C ₂ (ac,ac)	not stable		(134, 134)	0.60	(142, 142)	1.70
C ₂ (sc,sc)	(66, 66)	0.97	not stable		(60, 60)	1.98

(Z)-1,2-Dimethoxyethene. The HF methods predict for this compound three stable structures (Chart 3 and Table 3), whereas four minima exist according to the MP2 method.

All three computational methods result in an (sp,ac) ground-state structure which possesses one synperiplanar ($\phi_1 \approx 0^\circ$) and one anticlinical methoxy group (ϕ_2 between 123° and 134°). According to HF/6-31G* and MP2/6-31G* calculations, structures with both methoxy groups in anticlinical orientation, both groups either on opposite sides of the ethene plane (ac,ac) or on the same side (ac,-ac), possess very similar relative energies, about 0.70 (HF/6-31G*) or 1.70 kcal mol⁻¹ (MP2/6-31G*). The HF/3-21G approximation predicts a much higher relative energy (5.05 kcal mol⁻¹) for the (ac,-ac) conformer, and the (ac,ac) form does not correspond to a minimum according to this method. Z-1,2-DME is the first alkoxy ethene for which a structure with synclinal orientation of methoxy groups occurs. No such orientation was predicted by theoretical calculations for methyl vinyl ether, *tert*-butyl vinyl ether, (Z)-methyl 1-propenyl ether, or 1,1-DME. The (sc,sc) conformation of Z-1,2-DME is calculated to lie about 1 (HF/3-21G) or 2 kcal mol⁻¹ (MP2/6-31G*) above the ground-state structure.

The experimental RDF (Figure 3) is reproduced very well with an (sp,ap) or (sp,ac) structure with $\phi_2 \approx 150^\circ$. No further improvement could be obtained by adding contributions larger than 5% of any other conformer given in Table 3. The (sp,ap) or (sp,ac) conformer possesses C₁ symmetry, and the two C(sp²)-O and O-C(sp³) distances are different. According to the calculations, however, the O-C(sp³) bond lengths of the synperiplanar (O3-C4) and anticlinical methoxy groups (O8-C9) differ by only 0.000–0.005 Å. Therefore, these two bond lengths were set equal in the experimental analysis. The C-O/O-C bond lengths were described by the mean value of C-O and O-C distances, (C-O)_{mean} = $\frac{1}{4}[(C1-O3) + (C2-O8) + 2(O-C)]$, the difference between the two C(sp²)-O bonds, $\Delta 1(CO) = (C2-O8) - (C1-O3)$, and the difference between the O-C(sp³) bond and the mean value of the C(sp²)-O bonds, $\Delta 2(CO) = (O-C) - \frac{1}{2}[(C1-O3) + (C2-O8)]$. In the least-squares refinement, $\Delta 1(CO)$, the difference between the two C=C-O angles, $\Delta(CCO) = (C2=C1-O3) - (C1=C2-O8)$, and the difference between the two C-O-C angles, $\Delta(COC)$

**Figure 3.** Experimental RDF for (Z)-1,2-dimethoxyethene and difference curve. Important interatomic distances are shown by vertical bars.**Table 4.** Experimental and Calculated Geometric Parameters of the (sp,ap)/(sp,ac) Conformer of (Z)-1,2-Dimethoxyethene^a

	GED	HF/3-21G	MP2/6-31G*
C=C	1.332(12) (p_1)	1.314	1.344
(C-O) _{mean} ^b	1.391(2) (p_2)	1.373	1.401
$\Delta 1(CO)$ ^b	0.020[10] ^c	0.029	0.020
$\Delta 2(CO)$ ^b	0.076(12) (p_3)	0.064	0.062
C1-O3	1.343(7)	1.366	1.361
C2-O8	1.363(7)	1.395	1.380
O3-C4 ^b	1.429(7)	1.445	1.432
O8-C9 ^b	1.429(7)	1.445	1.427
(C-H) _{mean}	1.089(5) (p_4)	1.078	1.092
(C=C-O) _{mean}	126.3(7) (p_5)	127.6	128.6
$\Delta(CCO)$ ^d	6.0[10] ^c	6.0	6.0
C2=C1-O3	129.3 (9)	130.6	131.6
C1=C2-O8	123.3 (9)	124.6	125.6
(C-O-C) _{mean}	114.4 (14) (p_6)	117.9	114.6
$\Delta(COC)$ ^e	5.5[10] ^c	6.1	5.5
C1-O3-C4	117.2(15)	120.9	117.3
C2-O8-C9	111.7(15)	114.8	111.8
H-C-H	110.3(16) (p_7)	109.9	109.9
C=C-H	118.1 ^f	119.0	118.1
tilt (CH ₃)	4.3 ^f	3.5	4.3
ϕ_1 (C=C-O-C4)	-8.5 ^f	1.7	-8.5
ϕ_2 (C=C-O-C9)	152(6) (p_8)	123.1	133.9

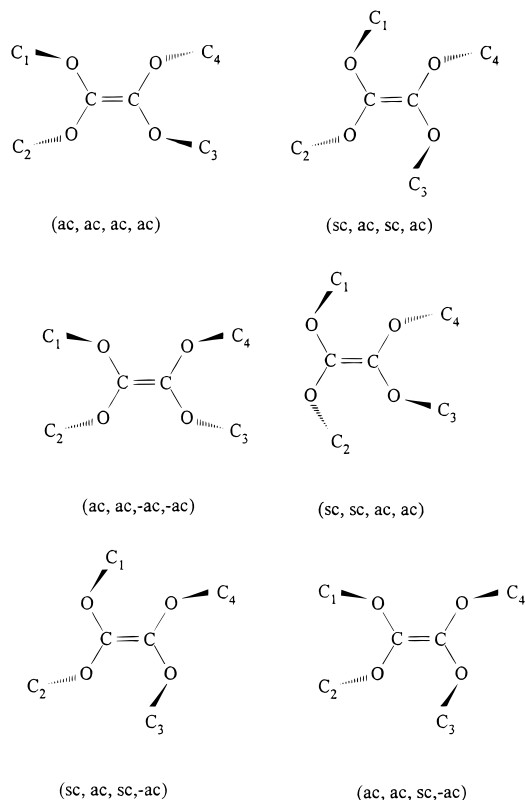
^a See footnote of Table 2. For atom numbering, see Figure 3. ^b (C-O)_{mean} = $\frac{1}{4}[(C1-O3) + (C2-O8) + 2(O-C)]$; $\Delta 1(CO) = (C2-O8) - (C1-O3)$; $\Delta 2(CO) = (O-C) - \frac{1}{2}[(C1-O3) + (C2-O8)]$; (O3-C4) = (O8-C9). ^c Not refined, but varied within the estimated uncertainty given in square brackets. ^d $\Delta(CCO) = (C2=C1-O3) - (C1=C2-O8)$. ^e $\Delta(COC) = (C1-O3-C4) - (C2-O8-C9)$. ^f Not refined.

= (C1-O3-C4) - (C2-O8-C9), were set to the respective MP2 values. Uncertainties of ± 0.01 Å and $\pm 1^\circ$ were estimated. Eight geometric parameters and six vibrational amplitudes were refined simultaneously, and the following correlation coefficients had values larger than |0.6|: $p_1/p_2 = 0.80$, $p_1/l_1 = -0.83$, and $p_5/l_2 = 0.86$. The final results are listed in Table 4. Vibrational amplitudes are listed in Table 2 of the Supporting Information.

Tetramethoxyethene. Four minima on the energy surface are predicted by the low-level HF/3-21G approximation and three minima by the higher level methods (see Chart 4 and Table 5). The structures obtained with the low- and high-level methods differ strongly; only the (ac,ac,-ac,-ac) conformer is predicted by all three methods to be a stable structure. According to the HF/6-31G* and MP2/6-31G* methods, the most stable conformer, (ac,ac,ac,ac), possesses D₂ symmetry, with all methoxy

Table 5. Calculated Conformations and Relative Energies (kcal mol⁻¹) of Tetramethoxyethene

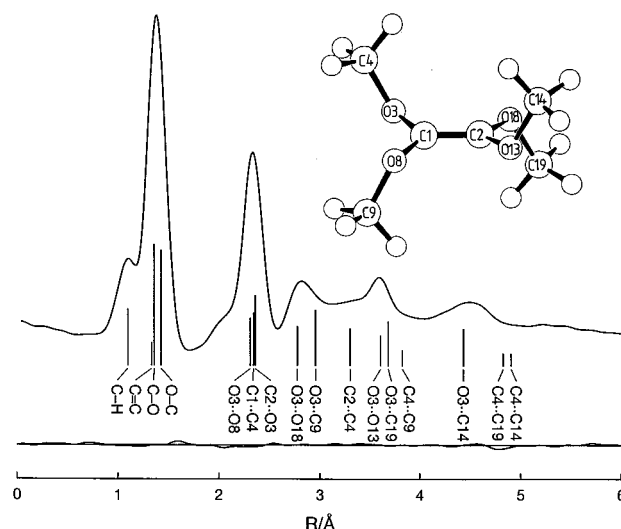
conformer	HF/3-21G		HF/6-31G*		MP2/6-31G*	
	($\phi_1, \phi_2, \phi_3, \phi_4$) ^a	ΔE	($\phi_1, \phi_2, \phi_3, \phi_4$)	ΔE	($\phi_1, \phi_2, \phi_3, \phi_4$)	ΔE
<i>D</i> ₂ (ac,ac,ac,ac)	not stable		(110, 110, 110, 110)	0.00	(113, 113, 113, 113)	0.00
<i>C</i> ₂ (sc,ac,sc,ac)	(70, 120, 70, 120)	0.00	not stable		not stable	
<i>C</i> _{2h} (ac,ac,-ac,-ac)	(113, 113, -113, -113)	2.96	(115, 115, -115, -115)	1.62	(117, 117, -117, -117)	1.46
<i>C</i> ₂ (sc,sc,ac,ac)	(72, 72, 107, 107)	0.69	not stable		not stable	
<i>C</i> ₁ (sc,ac,sc,-ac)	(48, 120, 47, -139)	2.17	not stable		not stable	
<i>C</i> ₁ (ac,ac,sc,-ac)	not stable		(111, 112, 50, -127)	3.12	(113, 113, 48, -127)	2.27

^a For numbering of dihedral angles, see Chart 4.**Chart 4**

groups oriented anticlinal and alternatingly above–below–above–below the ethene plane. This structure does not correspond to a minimum on the energy surface of the HF/3-21G approximation, but to a transition state between two equivalent (sc,ac,sc,ac) structures with *C*₂ symmetry. In this conformer, opposite methoxy groups are oriented synclinal or anticlinal, respectively, and again alternatingly above–below–above–below the plane. All three methods predict one conformer with all methoxy groups in anticlinal positions and with both groups on one side of the C=C bond above and those on the other side below the plane, (ac, ac,-ac,-ac).

The RDF of this compound (Figure 4) is very well reproduced with an (ac,ac,ac,ac) conformer. *D*₂ symmetry with a possible twist around the C=C double bond was assumed in the least-squares refinement. The C=C bond length was constrained to 1.335 Å, with an estimated uncertainty of ±0.005 Å. Nine geometric parameters and nine vibrational amplitudes were refined simultaneously, and the following correlation coefficients had values larger than |0.6|: $p_1/p_2 = -0.77$, $p_1/p_5 = -0.74$, $p_1/l_2 = 0.82$, and $p_2/l_2 = -0.88$. The results are collected in Table 6. Vibrational amplitudes are listed in Table 3 of the Supporting Information.

(*E*)-1,2-Dimethoxyethene and Trimethoxyethene. No experimental structure determinations have been performed for

**Figure 4.** Experimental RDF for tetramethoxyethene and difference curve. Important interatomic distances are shown by vertical bars.**Table 6.** Experimental and Calculated Geometric Parameters for (ac,ac,ac,ac) Conformer of Tetramethoxyethene^a

	GED	HF/6-31G*	MP2/6-31G*
C=C	1.335[5] (p_1)	1.318	1.343
C(sp ²)-O	1.361(4) (p_2)	1.349	1.367
O-C(sp ³)	1.430(5) (p_3)	1.410	1.431
C-H	1.099(4) (p_4)	1.083	1.092
C=C-O	121.5(3) (p_5)	122.0	121.4
C-O-C	115.8(7) (p_6)	115.1	112.0
H-C-H	109.7(8) (p_7)	109.5	109.9
tilt (CH ₃)	2.3(22) (p_8)	2.7	2.9
ϕ (C=C-O-C)	108.5(12) (p_9)	109.8	113.2
τ (C=C) ^c	13.5(30)	9.1	13.2

^a See footnote of Table 2. For atom numbering, see Figure 4. ^b Not refined. ^c The torsion around the C=C bond is such that the distances between methyl carbon atoms of cis-standing methoxy groups (i.e., C4...C19 and C9...C14) increase.

Table 7. Calculated Conformations and Relative Energies (kcal mol⁻¹) of (*E*)-1,2-Dimethoxyethene

conformer	HF/3-21G		MP2/6-31G*	
	(ϕ_1, ϕ_2)	ΔE	(ϕ_1, ϕ_2)	ΔE
<i>C</i> _{2h} (sp,sp)	(0, 0)	0.00	(0, 0)	0.00
<i>C</i> ₁ (sp,ac)	(0, 114)	0.45	(2, 126)	0.58
<i>C</i> ₂ (ac,ac)	(130, 130)	2.00	(139, 139)	1.85
<i>C</i> _i (ac,-ac)	(123, -123)	1.66	(134, -134)	2.04

these two compounds. Both applied theoretical methods, HF/3-21G* and MP2/6-31G*, result in four stable structures for (*E*)-1,2-dimethoxyethene (see Table 7). The dihedral angles and relative energies predicted by the two methods are very similar. The conformational properties of trimethoxyethene are rather complex. A large variety of different conformations are feasible. We have used all “reasonable” starting geometries in the

Table 8. Calculated Conformations and Relative Energies (kcal mol⁻¹) of Trimethoxyethene

conformer	HF/3-21G		MP2/6-31G*	
	(ϕ_1, ϕ_2, ϕ_3) ^a	ΔE	(ϕ_1, ϕ_2, ϕ_3)	ΔE
(ac,ac,sp)	(111, 118, 4)	0.00	(115, 122, -15)	0.00
(ac,sp,-ac)	(139, -19, -111)	-0.11	(127, -29, -117)	0.38
(ac,ac,ac)	not stable		(122, 114, 127)	0.46
(ac,sc,sc)	(132, 67, 78)	0.01	not stable	
(ac,sp,ac)	not stable		(128, -27, 131)	0.57
(ac,sc,ac)	(139, 33, 110)	0.34	not stable	
(ac,ac,sc)	not stable		(121, 114, 80)	0.66
(sp,ac,sc)	(-2, 129, 67)	1.59	(-5, 123, 83)	0.99
(sp,sc,sc)	not stable		(3, 76, 82)	1.19
(sp,ac,-sc)	(5, 140, -33)	2.27	(-4, 130, -42)	1.80
(sp,sc,ac)	(8, 38, 102)	2.28	not stable	

^a Dihedral angles are numbered analogous to those in Chart 4.

structure optimizations, but we do not claim that we have detected all minima on the energy surface. Seven (HF/3-21G) or eight (MP2/6-31G*) minima were obtained, all of which possess C_1 symmetry (Table 8). The structures and their relative energies obtained with the two computational methods differ appreciably. In the ground-state structure derived with the MP2 method, two methoxy groups on one carbon are oriented anticlinal, while the group on the other carbon is synperiplanar. Five more conformations are predicted within an energy range of only 1 kcal mol⁻¹.

Discussion

Theoretical calculations predict for all methoxyethenes of the present study three or more possible conformations within an energy range below about 2 kcal mol⁻¹. The type of conformers and their relative energies depend on the computational method. Thereby, the size of the basis set (3-21G vs 6-31G*) has a larger effect than inclusion of electron correlation (HF vs MP2). In the experimental GED investigation, only one conformer was observed in the case of (*Z*)-1,2-DME and TME, and a mixture of two conformers was determined for 1,1-DME. In the GED experiments, contributions from other conformers which are smaller than about 10% cannot be observed. The experimentally determined conformational properties are perfectly reproduced by the MP2/6-31G* calculations. This method predicts for (*Z*)-1,2-DME and TME contributions from other conformers which are smaller than 10%, in agreement with the GED analyses. The calculated relative energy, $\Delta E = E(\text{sp,ac}) - E(\text{sp,sp})$ of 0.76 kcal mol⁻¹, for 1,1-DME is in perfect agreement with the experimental ΔH^0 value of 0.69(13) kcal mol⁻¹. Since the MP2 results for these three methoxyethenes reproduce the experiments so well, we can expect that the calculated ground-state structures and conformational properties of (*E*)-1,2-dimethoxyethene and of trimethoxyethene which were derived with this method are reliable. Ground-state structures of the three experimentally studied methoxyethenes are also predicted correctly by the HF/6-31G* method. In the case of (*Z*)-1,2-DME, however, this method suggests considerable contributions from (ac,ac) and (ac,-ac) conformers with relative energies of 0.60 and 0.79 kcal mol⁻¹. No such contributions were observed in the experiment. The HF/3-21G approximation predicts wrong ground-state structures for 1,1-DME and for TME.

The structures of the most stable conformer of the dimethoxyethenes follow directly from the conformational properties of methoxyethene, where the synperiplanar orientation is favored over a nearly planar anti orientation. Thus, for 1,1-DME and (*E*)-1,2-dimethoxyethene, we expect the preference of structures

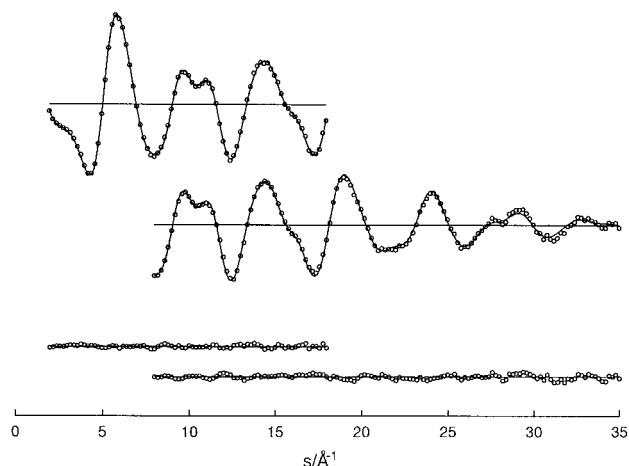


Figure 5. Experimental (O) and calculated (—) molecular intensities for 1,1-dimethoxyethene and differences.

with both methoxy groups in synperiplanar position, and this is confirmed by the GED experiment and/or MP2 calculations. In the case of (*Z*)-1,2-DME, a structure with both dimethoxy groups in synperiplanar orientation is sterically impossible; thus, we expect a structure with one syn- and one antiperiplanar methoxy group. Again, this is confirmed by the GED experiment, where the orientation of the second group with $\phi_2 = 152(6)^\circ$ is just on the borderline between antiperiplanar (ϕ between 180° and 150°) and anticlinal (ϕ between 150° and 90°). The MP2 calculations predict for this group anticlinal orientation with $\phi = 134^\circ$. In the comparison between calculated (equilibrium) values and experimental (vibrationally averaged) values, systematic differences have to be taken into account. For dihedral angles, large amplitude torsional vibrations can cause differences of up to 10° or more.

If we transfer the conformational properties of the dimethoxyethenes, we expect for TME a structure in which two adjacent or two opposite methoxy groups are oriented synperiplanar and the other groups anticlinal. An (sp,sp,ac,ac) conformation has been predicted by theoretical calculations for tetrahydroxyethene,²³ but it does not correspond to a stable structure of TME. The experimentally observed ground-state structure possesses anticlinal orientation of all methoxy groups in accordance with HF/6-31G* and MP2/6-31G* results. The molecule is twisted around the C=C double bond by $14(3)^\circ$. The direction of the twist is such that the distances between methyl groups of cis-standing methoxy groups are increased. Such torsion around the C=C bond, but about twice as large ($28(2)^\circ$), has been observed previously for tetrakis(dimethylamino)ethene.²⁶ Since strong steric repulsion between the methyl groups can be excluded in both compounds, the twist around the C=C double bond is due to repulsion between oxygen or nitrogen lone pairs. The same type of structure with D_2 symmetry and (ac,ac,ac,ac) orientations, which is preferred by TME, has been observed also for gaseous tetrakis(trifluoromethylthio)ethene, $(\text{CF}_3)_2\text{C}=\text{C}(\text{SCF}_3)_2$.²⁷ All SCF_3 groups are oriented perpendicular to the molecular plane with $\phi = 90.9(11)^\circ$. An X-ray diffraction analysis of this compound, however, results in an (ac,ac,-ac,-ac) structure with C_i symmetry and dihedral angles of 117° and 127° .²⁸ The conformational change between gaseous and

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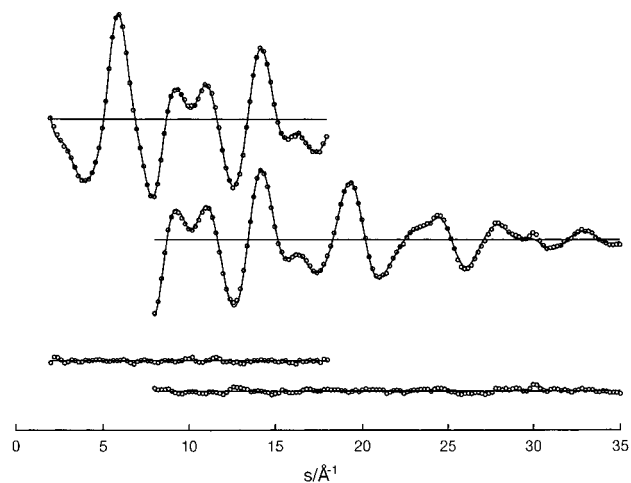


Figure 6. Experimental (○) and calculated (—) molecular intensities for tetramethoxyethene and differences.

solid phases has to be attributed to intermolecular interactions (packing effects). Similarly, an (ac,ac,−ac,−ac) conformation with $\phi \approx 135^\circ$ has been determined for crystalline tetramethylthioethene, and we can assume that the preferred conformation in the gas phase would again be an (ac,ac,ac,ac) structure.²⁹

Bond lengths and bond angles in this series of compounds are close to what is expected. The C=C distances, which either are not well determined in the experiment or had to be fixed (TME), are equal to that in ethene (1.337(2) Å).³⁰ The C(sp²)–O bond lengths are slightly shorter in synperiplanar than in anticlinal methoxy groups, but the differences are smaller than the experimental uncertainties. This trend is expected, since conjugation $n_{\pi}(\text{O}) \rightarrow \pi^*(\text{C}=\text{C})$ is more effective for synperiplanar orientation. All O–C(sp³) bond lengths are equal within their experimental uncertainties. The C=C–O and O–C–O angles show the effect of intramolecular strain. These angles are larger in synperiplanar than in antiperiplanar or anticlinal methoxy groups. Considering experimental uncertainties and systematic differences, experimental bond lengths and angles agree very well with the MP2 values. The largest discrepancy occurs for the O–C–O angle in TME (115.8(7)° vs 112.0°). Both HF methods predict this angle around 115°.

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Experimental Section

A sample of (Z)-1,2-DME has been prepared by Prof. E. Taskinen, University of Turku, Finland, by pyrolysis of 1,1,2-trimethoxyethane. The resulting mixture of (Z)- and (E)-isomers was separated by GC, and the purity of the (Z)-isomer was 99.8%. 1,1-DME was synthesized by elimination of HCl from commercial 2-chloro-1,1-dimethoxyethane.³¹ TME was prepared according to the method described in ref 32. The purity of the two latter samples was checked by ¹H and ¹³C NMR spectroscopy. No impurities were detected.

The electron diffraction intensities were recorded with a Gasdiffraktograph KD-G2³³ at 25- and 50-cm nozzle-to-plate distances and with an accelerating voltage of about 60 kV. The sample reservoirs were kept at 0 (1,1-DME), 10 ((Z)-1,2-DME), and 25 °C (TME), respectively. The inlet system and nozzle (0.3 mm diameter) were at room temperature for the two dimethoxyethenes. For TME, a nozzle with a diameter of 0.6 mm was used, and the nozzle was heated to 35 °C. The camera pressure never exceeded 10^{−5} Torr during the exposure. The photographic plates (Kodak Electron Image Plates 18 × 13 cm) were analyzed by the usual methods,³⁴ and averaged molecular intensities for 1,1-DME and for TME in the scattering ranges 2–18 and 8–35 Å^{−1}, in steps of $\Delta s = 0.2 \text{ \AA}^{-1}$, are shown in Figures 5 and 6 ($s = (4\pi/\lambda) \sin \theta/2$, where λ is the electron wavelength and θ is the scattering angle). Intensities for (Z)-1,2-DME are very similar to those for 1,1-DME and are not shown.

Acknowledgment. We express our thanks to Prof. E. Taskinen, University of Turku, Finland, for a sample of (Z)-1,2-DME and to Dr. L. Subramanian, Institut für Organische Chemie, Universität Tübingen, for the syntheses of 1,1-DME and TME. This work has been supported by the Deutsche Forschungsgemeinschaft.

Supporting Information Available: Tables listing interatomic distances and vibrational amplitudes for 1,1-dimethoxyethene, (Z)-1,2-dimethoxyethene, and tetramethoxyethene (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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