

# Gas-Phase Structures and Conformational Properties of *tert*-Butyl Vinyl Ether and (*Z*)-Methyl 1-Propenyl Ether

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**Abstract:** The gas-phase structures of *tert*-butyl vinyl ether, *t*-BuOC(H)=CH<sub>2</sub> (*t*-BVE), and (*Z*)-methyl 1-propenyl ether, MeOC(H)=C(H)Me (*Z*-MPE), have been studied by gas electron diffraction and ab initio calculations (HF/3-21G and MP2/6-31G\*). For both compounds only a single conformer with a slightly nonplanar anti structure of the C=C–O–C skeleton was observed. The vibrationally averaged dihedral angles  $\phi(\text{C}=\text{C}-\text{O}-\text{C})$  are 167(5)° (*t*-BVE) and 161(5)° (*Z*-MPE), respectively. The experimental scattering intensities are fitted slightly better with dynamic models and double minimum potentials for the internal rotation around the O–C(sp<sup>2</sup>) bonds. The dihedral angles of the equilibrium structures  $\phi_e(\text{C}=\text{C}-\text{O}-\text{C})$  are 170(5)° for *t*-BVE and 161(8)° for *Z*-MPE. The potential barriers at the exactly planar anti conformation ( $\phi(\text{C}=\text{C}-\text{O}-\text{C})=180^\circ$ ) are  $V_0 = 0.15(10)$  and  $0.20(10)$  kcal mol<sup>-1</sup>, respectively. The experimental results are reproduced very well by MP2/6-31G\* calculations ( $\phi_e = 169.0^\circ$  and  $154.2^\circ$  and  $V_0 = 0.12$  and  $0.11$  kcal mol<sup>-1</sup> for *t*-BVE and *Z*-MPE, respectively). The HF/3-21G method, however, predicts a planar structure ( $\phi_e = 180^\circ$ ) for *t*-BVE and an anticlinal structure ( $\phi_e = 138.7^\circ$ ) for *Z*-MPE.

## Introduction

Microwave spectroscopy (MW) demonstrated that the smallest enol, the unstable vinyl alcohol, H<sub>2</sub>C=C(H)OH, prefers a synperiplanar structure with the O–H bond eclipsing the C=C double bond ( $\phi(\text{C}=\text{C}-\text{O}-\text{H}) = 0^\circ$ ).<sup>1,2</sup> This experimental result is reproduced correctly by theoretical calculations which predict in addition to the syn conformer the existence of a second stable form with antiperiplanar<sup>3</sup> orientation of the O–H bond ( $\phi(\text{C}=\text{C}-\text{O}-\text{H}) = 180^\circ$ ), which is 1.6–3.0 kcal mol<sup>-1</sup> higher in energy.<sup>4–6</sup> Similarly, a synperiplanar structure with  $\phi(\text{C}=\text{C}-\text{O}-\text{C}) = 0^\circ$  was determined for methyl vinyl ether (methoxyethene), CH<sub>3</sub>OC(H)=CH<sub>2</sub>, by MW<sup>7,8</sup> and gas electron diffraction (GED).<sup>4,9–11</sup> Various experimental studies (see ref 6 for a review) have led to different results for the high-energy conformer of this compound with  $\phi(\text{C}=\text{C}-\text{O}-\text{C})$  from 80° to 180°. From Raman spectra an anticlinal structure with a dihedral angle of 138° and a high barrier for the antiperiplanar form (1.74(16) kcal mol<sup>-1</sup>) were derived.<sup>12</sup> High-resolution mid-infrared spectra, however, were interpreted in terms of a pseudoplanar anti structure with a very flat double-minimum potential and minima at  $\phi = \pm 160^\circ$ .<sup>13</sup> In a GED investigation with a sample temperature of 200 °C a contribution of ca. 30%

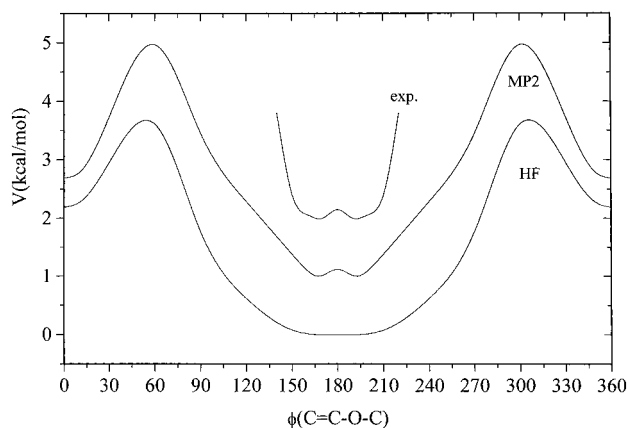
of a conformer with  $\phi > 150^\circ$  was observed.<sup>4</sup> The results of the two latter experiments are in good agreement with ab initio calculations at various levels which predict for the high energy conformer a flat double minimum potential with  $\phi_e$  between 150° and 168° and barriers at  $\phi = 180^\circ$  of 0.03–0.17 kcal mol<sup>-1</sup>.<sup>6,11,13,14</sup> The predicted energy differences between the syn and anti forms vary from 2.0 to 3.3 kcal mol<sup>-1</sup>. These values are higher than enthalpy differences derived from vibrational spectra, 1.70(9)<sup>12</sup> and 1.15(25) kcal mol<sup>-1,15</sup> respectively. Only conformers with synperiplanar C=C–O–C skeletons ( $\phi = 0^\circ$ ) were observed in a MW study of ethyl vinyl ether,<sup>16,17</sup> and in a GED investigation of methyl 2-propenyl ether (2-methoxy-1-propene), MeOC(Me)=CH<sub>2</sub>.<sup>18</sup>

To obtain more precise structural information about the high-energy form of such alkyl vinyl ethers, we have determined the structures of *tert*-butyl vinyl ether, *t*-BuOC(H)=CH<sub>2</sub> (*t*-BVE), and of (*Z*)-methyl 1-propenyl ether ((*Z*)-1-methoxypropene), MeOC(H)=C(H)Me (*Z*-MPE), by GED. For both compounds the synperiplanar forms are highly unfavorable due to steric interactions between the *tert*-butyl and vinyl groups and between the two methyl groups, respectively. Therefore, anticlinal or antiperiplanar structures are expected to be predominant. The experimental structure analyses were supplemented by ab initio calculations.

From <sup>1</sup>H NMR spectra of alkyl vinyl ethers ROC(H)=CH<sub>2</sub> it was concluded that the contribution of the resonance form R–O<sup>+</sup>=C(H)–C<sup>-</sup>H<sub>2</sub>, which stabilizes syn- and antiperiplanar structures, is greatest in methyl vinyl ether and least in *t*-BVE. From these data it was concluded that the methyl derivative prefers the synperiplanar conformation and the *tert*-butyl

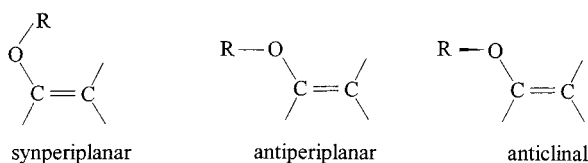
- (1) Saito, S. *Chem. Phys. Lett.* **1976**, *42*, 399.
- (2) Rodler, M.; Bauder, A. *J. Am. Chem. Soc.* **1984**, *106*, 4025.
- (3) Antiperiplanar describes structures with dihedral angles of 180 ± 30° and anticlinal with dihedral angles of 120 ± 30°.
- (4) Samdal, S.; Seip, H. M. *J. Mol. Struct.* **1975**, *28*, 193.
- (5) Bouma, W. J.; Radom, L. *J. Mol. Struct.* **1978**, *43*, 267.
- (6) Nobes, R. H.; Radom, L.; Allinger, N. L. *J. Mol. Struct.* **1981**, *85*, 185.
- (7) Cahill, P.; Gold, P.; Owen, N. L. *J. Chem. Phys.* **1968**, *48*, 1620.
- (8) Fujitake, M.; Hayashi, M. *J. Mol. Struct.* **1985**, *127*, 21.
- (9) Owen, N. L.; Seip, H. M. *Chem. Phys. Lett.* **1970**, *5*, 162.
- (10) van den Enden, L.; Geise, H. J. *J. Mol. Struct.* **1983**, *97*, 139.
- (11) Pykhout, W.; van Nuffel, P.; van Alsenoy, C.; van den Enden, L.; Geise, H. J. *J. Mol. Struct.* **1983**, *102*, 333.
- (12) Sullivan, J. F.; Dickson, T. J.; Durig, J. R. *Spectrochim. Acta, Part A* **1986**, *42*, 113.

- (13) Gallinella, E.; Cadioli, B. *J. Mol. Struct.* **1991**, *249*, 343.
- (14) Ignatiev, I. S. *J. Mol. Struct.* **1991**, *246*, 279.
- (15) Owen, N. L.; Sheppard, N. *Trans. Faraday Soc.* **1964**, *60*, 634.
- (16) Hayashi, M.; Inada, N. *J. Mol. Spectrosc.* **1994**, *165*, 195.
- (17) Owen, N. L.; Sorensen, G. O. *J. Phys. Chem.* **1979**, *83*, 1483.
- (18) Schei, S. H. *Acta Chem. Scand. Ser. A* **1983**, *37*, 153.



**Figure 1.** Calculated (HF/3-21G and MP2/6-31G\*) and experimental potential curves for internal rotation around the O-C(sp<sup>2</sup>) bond in *tert*-butyl vinyl ether. The MP2 and experimental curves are shifted by 1.0 and 2.0 kcal mol<sup>-1</sup>, respectively.

### Chart 1



compound a gauche (anticlinial) form.<sup>19,20</sup> Infrared spectra for Z-MPE indicate the presence of a single conformer.<sup>21</sup> MM2 calculations predict a gauche structure for this compound (no dihedral angle is given),<sup>22</sup> and ab initio calculations result in an antiperiplanar skeleton with a very flat double-minimum potential and  $\phi_e$  between 151° and 157°.<sup>23</sup>

### Ab Initio Calculations

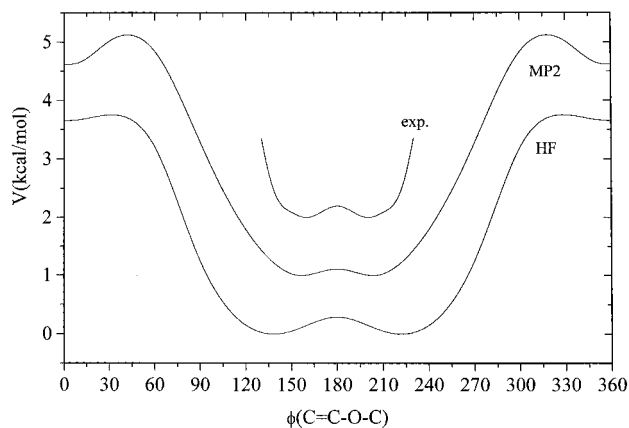
The geometries of *t*-BVE and Z-MPE were optimized for dihedral angles  $\phi(\text{C}=\text{C}-\text{O}-\text{C})$  between 0° and 180° in steps of 30° with the HF/3-21G and MP2/6-31G\* approximations. The structures were fully optimized at the minima of the potential curves. The potential curves for internal rotation around the C(sp<sup>2</sup>)-O bonds are shown in Figures 1 and 2 and the geometric parameters for the minima are included in Tables 1 and 3. The HF/3-21G method predicts for the low-energy conformer of *t*-BVE an exactly planar anti structure with  $\phi_e = 180^\circ$ . The same result is obtained with a larger basis set (HF/6-31G\*, not shown in Figure 1). According to the MP2/6-31G\* approximation, however, the C=C-O-C skeleton possesses a slightly nonplanar structure with  $\phi_e = 169.0^\circ$  and a flat double-minimum potential in the anti region. Both methods predict in addition to the antiperiplanar structure a stable synperiplanar form with  $\phi_e = 0^\circ$ , which is 2.2 or 1.7 kcal mol<sup>-1</sup> higher in energy. In the case of Z-MPE both methods result for the ground state conformer in nonplanar structures with  $\phi_e = 138.7^\circ$  (anticlinial) and 154.2° (antiperiplanar), respectively. Shallow minima are obtained for the synperiplanar conformation which are ca. 3.6 kcal mol<sup>-1</sup> higher in energy. The vibrational amplitudes for the ground-state structures of both compounds were calculated from ab initio force constants. In the case of *t*-BVE the vibrational properties at room temperature are not well represented by a flat double minimum potential, which is approximated by a harmonic function (MP2/6-31G\* result). A more realistic description is obtained with a single minimum potential at  $\phi = 180^\circ$  (HF/3-21G result) and, therefore, the HF/3-21G frequencies

(19) Hatada, K.; Takeshita, M.; Yuki, H. *Tetrahedron Lett.* **1968**, *44*, 4621.

(20) Alfonin, A. V.; Kholko, M. Ya.; Komelkova, V. I.; Shafeev, M. A.; Nedolya, N. A. *Zh. Org. Khim.* **1991**, *27*, 161 (Russian)

(21) Charles, S. W.; Cullen, F. C.; Owen, N. L. *J. Mol. Struct.* **1973**, *18*, 183.

(22) Dodziuk, H.; von Voithenberg, H.; Allinger, N. L. *Tetrahedron* **1982**, *38*, 2811.



**Figure 2.** Calculated (HF/3-21G and MP2/6-31G\*) and experimental potential curves for internal rotation around the O-C(sp<sup>2</sup>) bond in (Z)-methyl 1-propenyl ether. The MP2 and experimental curves are shifted by 1.0 and 2.0 kcal mol<sup>-1</sup>, respectively.

**Table 1.** Experimental and Theoretical Structural Parameters for *tert*-Butyl Vinyl Ether (*t*-Bve)

	GED (rigid) <sup>a</sup>		HF/ 3-21G <sup>b</sup>	MP2/ 6-31G* <sup>b</sup>
C=C	1.322(9)	$p_1$	1.316	1.336
(O-C) <sub>mean</sub>	1.406(3)	$p_2$	1.397	1.409
$\Delta\text{OC} = (\text{O}-\text{C}3) - (\text{O}-\text{C}1)$	0.077(17)	$p_3$	0.078	0.085
O-C1	1.368(10)		1.358	1.366
O-C3	1.445(10)		1.436	1.451
C-C	1.529(2)	$p_4$	1.536	1.522
(C-H) <sub>methyl</sub>	1.100(3) <sup>c</sup>	$p_5$	1.083	1.093
(C-H) <sub>vinyl</sub>	1.090(3) <sup>c</sup>		1.071	1.084
C=O	122.9(15)	$p_6$	122.0	121.4
C-O-C	117.5(11)	$p_7$	118.3	117.8
C-C-C	111.6(7)	$p_8$	110.4	111.0
tilt ( <i>t</i> -Bu) <sup>d</sup>	5.1(4)	$p_9$	5.2	4.9
H-C-H	109.1(8)	$p_{10}$	108.7	108.7
C=C-H	121.0 <sup>e</sup>		120.9	121.0
$\phi(\text{C}=\text{C}-\text{O}-\text{C})$	166.6(46)	$p_{11}$	180.0	169.0

<sup>a</sup>  $r_a$  values in Å and deg; error limits are 3 $\sigma$  values; for atom numbering see Figure 3. <sup>b</sup> Mean values are given for parameters which are not unique. <sup>c</sup> Difference fixed to 0.01 Å. <sup>d</sup> Tilt angle between the C<sub>3</sub> axis of the *tert*-butyl group and the O-C3 bond direction. <sup>e</sup> Not refined.

were used for this compound. For Z-MPE both calculational methods predict double minima potentials and vibrational amplitudes were derived from M2/6-31G\* frequencies. The Cartesian force constants were transformed to symmetry force constants. The HF/3-21G values were multiplied with a scaling factor of 0.85, except the torsional force constants for the O-C(sp<sup>2</sup>) and O-C(sp<sup>3</sup>) bonds. Unscaled MP2 force constants were used for Z-MPE. Vibrational amplitudes were derived with the program ASYM40,<sup>24</sup> and the ab initio calculations were performed with the program system GAUSSIAN 94.<sup>25</sup>

### Structure Analyses

The radial distribution functions (Figures 3 and 4) were calculated by Fourier transformation of the molecular intensities with an artificial damping function  $\exp(\gamma s^2)$ ,  $\gamma = 0.0019 \text{ \AA}^2$ . For both compounds these curves can be reproduced satisfactorily only with antiperiplanar structures and dihedral angles  $\phi(\text{C}=\text{C}-\text{O}-\text{C})$  around 160°. The geometric parameters were refined by least-squares fitting of the molecular intensities. The intensities were multiplied with a diagonal weight matrix and known complex scattering factors were used.<sup>26</sup> For the two O-C bond lengths, O-C(sp<sup>2</sup>) and O-C(sp<sup>3</sup>), the mean value and the difference  $\Delta\text{OC} = (\text{O}-\text{C}(\text{sp}^2)) - (\text{O}-\text{C}(\text{sp}^3))$  were chosen as independent parameters. All CH<sub>3</sub> groups were assumed to possess C<sub>3v</sub>

(23) Cadioli, B.; Gallinella, E. *J. Mol. Struct.* **1990**, *216*, 261.

(24) Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc.* **1993**, *160*, 117.

**Table 2.** Interatomic Distances and Vibrational Amplitudes for tert-Butyl Vinyl Ether (without Nonbonded Distances Involving Hydrogen)<sup>a</sup>

distance	amplitudes			
	GED, rigid		HF/3-21G <sup>b</sup>	
C-H	1.09–1.10	0.083(3)	$l_1$	0.078
C=C	1.32	0.041 <sup>c</sup>		0.041
O-C1	1.37	0.048 <sup>c</sup>		0.046
O-C3	1.45			
C-C	1.53	0.051(4)	$l_2$	0.054
C2...O	2.37	0.062 <sup>c</sup>		0.059
C1...C3	2.40			
O...C	2.31–2.43	0.063(11)	$l_3$	0.073
C <sub>m</sub> ...C <sub>m</sub>	2.53			
C1...C5	2.92	0.132(19)	$l_4$	0.140
C1...C4	3.61	0.062(10)	$l_5$	0.072
C2...C3	3.64			
C2...C5	4.09	0.0194(49)	$l_6$	0.0321
C2...C6	4.20			
C2...C4	4.68	0.122(28)	$l_7$	0.088

<sup>a</sup> Values in Å; error limits are 3σ values, for atom numbering see Figure 3. <sup>b</sup> Mean values are given for amplitudes which are not unique. <sup>c</sup> Not refined.

**Table 3.** Experimental and Theoretical Structural Parameters for (Z)-Methyl 1-Propenyl Ether (Z-MPE)

	GED (rigid) <sup>a</sup>		HF/ 3-21G <sup>b</sup>	MP2/ 6-31G* <sup>b</sup>
C=C	1.340(3)	$p_1$	1.313	1.339
(O-C) <sub>mean</sub>	1.395(3)	$p_2$	1.414	1.400
ΔOC = (O-C3) - (O-C1)	0.051[10] <sup>c</sup>		0.053	0.051
O-C1	1.370(6)		1.388	1.375
O-C3	1.421(6)		1.441	1.426
C2-C4	1.518(3)	$p_3$	1.506	1.498
(C-H) <sub>methyl</sub>	1.101(3) <sup>d</sup>	$p_4$	1.081	1.092
(C-H) <sub>vinyl</sub>	1.091(3) <sup>d</sup>		1.071	1.083
C=C-O	120.1(8)	$p_5$	122.4	122.2
C-O-C	117.2(13)	$p_6$	116.1	113.3
C=C-C	124.6(6)	$p_7$	123.8	124.5
(H-C-H) <sub>mean</sub>	109.9(8)	$p_8$	108.9	108.7
C=C-H1	122.4 <sup>e</sup>		122.3	122.4
C=C-H2	116.8 <sup>e</sup>		118.2	116.8
tilt (OCH <sub>3</sub> )	3.3 <sup>e</sup>		3.2	3.3
tilt (CCH <sub>3</sub> )	0.7 <sup>e</sup>		0.5	0.7
φ(C=C-O-C)	161.2(45)	$p_9$	138.7	154.2

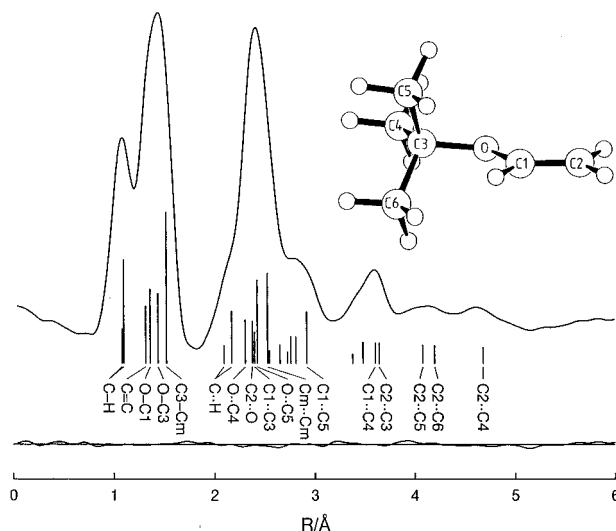
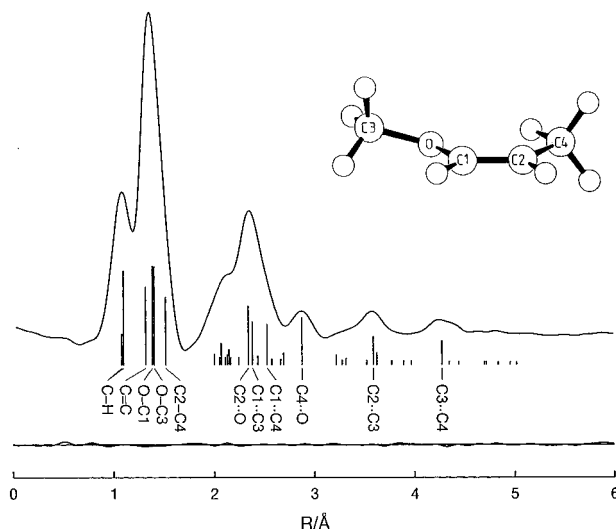
<sup>a</sup>  $r_a$  values in Å and deg; error limits are 3σ values; for atom numbering see Figure 4. <sup>b</sup> Mean values are given for parameters which are not unique. <sup>c</sup> Not refined, but varied within the estimated uncertainty given in brackets. <sup>d</sup> Difference fixed to 0.01 Å. <sup>e</sup> Tilt angle between the C<sub>3</sub> axis of the tert-butyl group and the O-C3 bond direction. <sup>e</sup> Not refined.

symmetry. The difference between C(sp<sup>3</sup>)-H and C(sp<sup>2</sup>)-H bond lengths was fixed to 0.010 Å, and all C=C-H angles were set to calculated values. Vibrational amplitudes were collected in groups according to their distances. Amplitudes which could not be refined because of high correlations or which were poorly determined in the GED analyses were set to the ab initio values.

**tert-Butyl Vinyl Ether (t-BVE).** In addition to the above assumptions the tert-butyl group was constrained to C<sub>3v</sub> symmetry with a possible tilt angle between the C<sub>3</sub> axis and the O-C(sp<sup>3</sup>) bond. With these assumptions eleven geometric parameters  $p_i$  and twelve vibrational

(25) GAUSSIAN 94 (Revision B.1), Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 1995.

(26) Haase, J. Z. *Naturforsch.* **1970**, 25 A, 936.

**Figure 3.** Experimental radial distribution function and difference curve for tert-butyl vinyl ether. The positions of important interatomic distances are indicated by vertical bars.**Figure 4.** Experimental radial distribution function and difference curve for (Z)-methyl 1-propenyl ether. The positions of important interatomic distances are indicated by vertical bars.

amplitudes  $l_k$  were refined simultaneously. The following correlation coefficients had values larger than |0.6|:  $p_1/p_3 = 0.92$ ,  $p_1/p_4 = -0.64$ ,  $p_3/p_4 = -0.74$ ,  $p_6/p_8 = -0.76$ ,  $p_1/l_2 = 0.78$ ,  $p_2/l_2 = 0.66$ ,  $p_3/l_2 = 0.91$ ,  $p_4/l_2 = -0.69$ , and  $p_8/l_3 = 0.85$ . The results of this least-squares refinement are listed in Tables 1 (geometric parameters) and 2 (vibrational amplitudes). This analysis, which is based on a rigid model with small amplitude vibrations, results in a structure with a slightly nonplanar C=C-O-C skeleton and a dihedral angle  $\phi = 167(5)^\circ$ .

This vibrationally averaged value can be interpreted either in terms of a planar equilibrium structure with a large amplitude torsional vibration around the O-C(sp<sup>2</sup>) bond or in terms of a nonplanar equilibrium structure. The former case corresponds to a flat single-minimum potential with  $\phi_e = 180^\circ$ , the latter case to a double-minimum potential with a slightly nonplanar equilibrium structure. It was attempted to distinguish between these two possibilities by applying a dynamic model with different potential functions. The molecular intensities were calculated as a superposition of structures with  $\phi$  varying from 180° to 120°, in steps of 10°. The intensities of the individual structures were weighted by a Boltzmann factor  $\exp(-V/RT)$ . Single-minimum potentials were represented by a quadratic function  $V = k\theta^2$  ( $\theta = 180 - \phi$ ) and double-minimum potentials by the expression  $V = V_0[1 - (\theta/\theta_c)^2]^2$ .  $V_0$  is the barrier at the planar structure ( $\phi = 180^\circ$ ) and  $\theta_c$  corresponds to the equilibrium structure

with  $\phi_e = 180 - \theta_e$ . The constants  $k$ ,  $V_0$ , and  $\theta_e$  which describe the potential functions could not be determined in the least-squares analyses. Refinements with different fixed values were performed and the quality of the fit was judged by  $R_{50}$ , which is the agreement factor for the long nozzle-to-plate data. A better fit was obtained with a double-minimum potential ( $R_{50} = 3.26\%$ ) than with a single-minimum potential ( $R_{50} = 3.54\%$ ). The optimized potential parameters are  $V_0 = 0.15(10)$  kcal mol<sup>-1</sup> and  $\phi_e = 170(5)^\circ$ . The agreement factor for the dynamic model with a double-minimum potential ( $R_{50} = 3.26\%$ ) is slightly lower than that for the rigid model ( $R_{50} = 3.48\%$ ).

**(Z)-Methyl 1-Propenyl Ether (Z-MPE).** In addition to the constraints described in the general section of Structure Analyses, the tilt angles for the two methyl groups were set to the MP2/6-31G\* values. Furthermore, the difference  $\Delta\text{CO}$  was constrained to the theoretical result with an estimated uncertainty of  $\pm 0.01$  Å. Nine geometric parameters  $p_i$  and nine vibrational amplitudes  $l_k$  were refined simultaneously. The following correlation coefficients had values larger than |0.6|:  $p_5/p_6 = -0.86$ ,  $p_5/p_7 = -0.66$ ,  $p_6/p_7 = 0.60$ ,  $p_2/l_2 = -0.83$ ,  $p_5/l_3 = 0.75$ ,  $p_6/l_3 = -0.76$  and  $p_6/l_8 = 0.67$ . The results of this analysis which are based on a rigid model are summarized in Tables 3 (geometric parameters) and 4 (vibrational amplitudes).

Analyses with a dynamic model were performed analogous to those described for *t*-BVE. The best fit of the experimental intensities was obtained for a double-minimum potential with  $V_0 = 0.20(10)$  kcal mol<sup>-1</sup> and  $\phi_e = 161(8)^\circ$ . The agreement factors for the rigid ( $R_{50} = 2.84\%$ ) and dynamic model ( $R_{50} = 2.82\%$ ) are nearly identical.

## Discussion

For *t*-BVE and Z-MPE only the anti forms are observed and the GED analyses result in slightly nonplanar anti structures with  $\phi(\text{C}=\text{C}-\text{O}-\text{C}) = 167(5)$  and  $161(5)^\circ$ , respectively. The electron diffraction intensities are fitted slightly better with dynamic models and double-minimum potentials which are characterized by  $\phi_e = 170(5)^\circ$  and  $V_0 = 0.15(10)$  kcal mol<sup>-1</sup> for *t*-BVE and by  $\phi_e = 161(8)^\circ$  and  $V_0 = 0.20(10)$  kcal mol<sup>-1</sup> for Z-MPE. Bond lengths and bond angles derived with the dynamic models are nearly identical to those derived with rigid models. Differences are much smaller than the respective standard deviations. The dihedral angles obtained with rigid models ( $\phi$ ) and with dynamic models ( $\phi_e$ ) agree with each other within their experimental error limits which are  $3\sigma$  values. The values for  $\phi_e$  and  $V_0$  are well reproduced by the MP2/6-31G\* approximation ( $\phi_e = 169.0^\circ$  and  $154.2^\circ$ ,  $V_0 = 0.12$  and  $0.11$  kcal mol<sup>-1</sup>, respectively). The experimental values, however, are in contrast to the results of the HF/3-21G calculations which predict a planar equilibrium structure for *t*-BVE ( $\phi_e = 180^\circ$ ) and an anticlinal conformation ( $\phi_e = 138.7^\circ$ ) for Z-MPE. Both ab initio methods reproduce the bond lengths and bond angles satisfactorily, i.e., to within  $\pm 0.03$  Å and  $\pm 3^\circ$ , respectively, except for the O-C-O angle in Z-MPE. The MP2 value is ca.  $4^\circ$  smaller than the experimental result.

The conformational properties of alkyl vinyl ethers of the type  $\text{ROC}(\text{H})=\text{CH}_2$  are primarily determined by conjugation between the oxygen lone pair and the vinyl  $\pi$  bond ( $n_\pi(\text{O}) \rightarrow \pi^*(\text{C}=\text{C})$ ). This interaction can also be expressed by the resonance form  $\text{R}-\text{O}^+=\text{C}(\text{H})-\text{C}^-\text{H}_2$ . Intuitively, this interaction is expected to stabilize planar syn and anti structures equally well. No such straightforward explanation can be given for the preference of the syn structure over the anti form in vinyl alcohol, methyl vinyl ether, and ethyl vinyl ether. Attractive interactions between hydrogen orbitals of the substituent R and the  $\pi$  system have been suggested as a possible explanation.<sup>27</sup> Alternatively, the generalized anomeric effect, i.e., interactions between the  $n_\sigma(\text{O})$  and  $\sigma^*(\text{C}=\text{C})$  orbitals, could explain the preference of the syn structure.

**Table 4.** Interatomic Distances and Vibrational Amplitudes for (Z)-Methyl 1-Propenyl Ether (without Nonbonded Distances Involving Hydrogen)<sup>a</sup>

	distance	amplitudes		
		GED, rigid		MP2/6-31G* <sup>b</sup>
C-H	1.09-1.10	0.077(3)	$l_1$	0.076
C=C	1.34	0.036(5)	$l_2$	0.041
O-C	1.37-1.42	0.047 <sup>c</sup>		0.046
C2-C4	1.52			0.048
C2...O	2.35	0.063(6)	$l_3$	0.057
C1...C3	2.38			0.066
C1...C4	2.53			0.063
C4...O	2.89	0.106(9)	$l_4$	0.107
C2...C3	3.60	0.094(12)	$l_5$	0.110
C3...C4	4.32	0.122(17)	$l_6$	0.188

<sup>a</sup> Values in Å; error limits are  $3\sigma$  values; for atom numbering see Figure 4. <sup>b</sup> Mean values are given for amplitudes which are not unique. <sup>c</sup> Not refined.

To confirm this simple bonding model, a natural bond orbital (NBO) analysis<sup>28</sup> was performed for vinyl ether,  $\text{H}_2\text{C}=\text{C}(\text{H})-\text{OH}$ . The geometries of the syn and anti forms were optimized at the HF/6-31G\* level. At this approximation, the anti conformer is 2.2 kcal mol<sup>-1</sup> higher in energy. As expected, conjugation  $n_\pi(\text{O}) \rightarrow \pi^*(\text{C}=\text{C})$  is by far the strongest interaction between donor and acceptor NBO's. In contrast to chemical intuition, this stabilization energy is predicted to be larger (43.8 kcal mol<sup>-1</sup>) for the syn conformer than for the anti form (40.5 kcal mol<sup>-1</sup>). Additional stabilization of the syn form is due to the anomeric effect  $n_\sigma(\text{O}) \rightarrow \sigma^*(\text{C}=\text{C})$ , which is stronger by 1.4 kcal mol<sup>-1</sup> than the interaction  $n_\sigma(\text{O}) \rightarrow \sigma^*(\text{C}-\text{H})$  in the anti conformer.

In the anti form of vinyl or propenyl ethers, repulsion between the two eclipsing single bonds (O-R and C-H) favors nonplanar structures. Due to competition between this repulsion and conjugation slightly nonplanar structures are expected for the anti conformer. This model rationalizes the experimental structures for *t*-BVE and Z-MPE, for which the syn conformation is unfavorable due to steric repulsions. These structures support very strongly experimental and theoretical studies for the high-energy anti conformer of methyl vinyl ether, which result also in a slightly nonplanar anti form with a very low barrier at  $\phi = 180^\circ$ . The interpretation of Raman spectra by Sullivan et al.,<sup>12</sup> which led to a high barrier at  $\phi = 180^\circ$  ( $V_0 = 1.70(9)$  kcal mol<sup>-1</sup>), is in contrast to most other experimental and theoretical studies for methyl vinyl ether and is very unlikely in view of the present results.

Table 5 compares skeletal geometric parameters of vinyl and propenyl ethers which possess syn- or antiperiplanar structures and which have been studied in the gas phase. No complete structure determination for the high-energy anti conformer of methyl vinyl ether has been reported. The dihedral angle given in the table has been derived from high-resolution mid-infrared spectra and is in perfect agreement with a GED study and theoretical calculations. The anti forms of the three compounds possess slightly nonplanar C=C-O-C skeletons with dihedral angles between  $160^\circ$  and  $170^\circ$ . No systematic trends can be observed for the C=C bond lengths. The O-C(sp<sup>2</sup>) bonds are ca. 0.02 Å shorter in the syn conformers than in the anti forms. According to the NBO analysis for vinyl alcohol, this difference is due to a stronger conjugative interaction  $n_\pi(\text{O}) \rightarrow \pi^*(\text{C}=\text{C})$  in the syn form and due to the anomeric effect  $n_\sigma(\text{O}) \rightarrow \sigma^*(\text{C}=\text{C})$ . The O-C(sp<sup>3</sup>) bond lengths in the ethers are very similar (ca. 1.42 Å), except for the *tert*-butyl ether, which possesses a longer

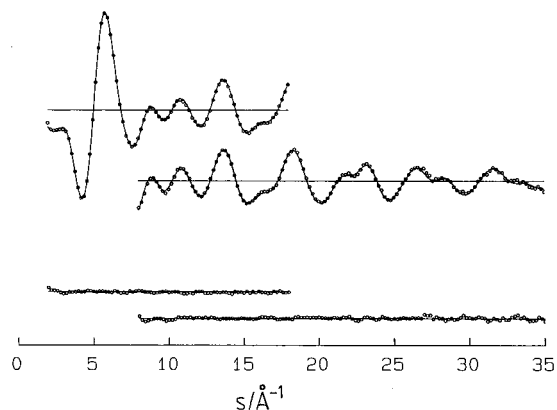
(27) Bernardi, F.; Epiotis, N. D.; Yates, R. L.; Schlegel, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 2385.

(28) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev. (Washington, D.C.)* **1988**, *88*, 899.

**Table 5.** Skeletal Parameters of Some Vinyl and Propenyl Ethers with Syn- or Antiperiplanar conformations

	C=C	O-C(sp <sup>2</sup> )	O-C(sp <sup>3</sup> )	C=C-O	C-O-C	C=C-O-C
MeOC(H)=CH <sub>2</sub> (syn) <sup>a</sup>	1.339(1)	1.350(1)	1.420(1)	128.0(1)	116.1(1)	0.0
EtOC(H)=CH <sub>2</sub> (syn) <sup>b</sup>	1.343(4)	1.348(6)	1.415(4)	128.3(3)	115.6(3)	0.0
MeOC(Me)=CH <sub>2</sub> (syn) <sup>c</sup>	1.330(7)	1.353(5)	1.416(5)	125.8(7)	116.0(11)	0.0
MeOC(H)=CH <sub>2</sub> (anti) <sup>d</sup>						~160
<i>t</i> -BuOC(H)=CH <sub>2</sub> (anti) <sup>e</sup>	1.322(9)	1.368(10)	1.445(10)	122.9(15)	117.5(11)	167(5)
MeOC(H)=C(H)Me (anti) <sup>e</sup>	1.340(3)	1.370(6)	1.421(6)	120.1(8)	117.2(13)	161(5)

<sup>a</sup> *r*<sub>s</sub> structure, ref 8. <sup>b</sup> *r*<sub>0</sub> structure, ref 16. <sup>c</sup> *r*<sub>a</sub> structure, ref 18. <sup>d</sup> Reference 13. <sup>e</sup> *r*<sub>a</sub> structure, this work.

**Figure 5.** Experimental (dots) and calculated (full line) molecular intensities and differences for *tert*-butyl vinyl ether.

bond of 1.445(10) Å. A similar lengthening of O-C bonds has been observed between Me<sub>2</sub>O (1.415(1) Å)<sup>29</sup> and (*t*-Bu)<sub>2</sub>O (1.436(4) Å).<sup>30</sup> The C=C-O angles are larger (126–128°) in the syn structures than those in the anti forms (120–123°). Only small variations occur for the C-O-C angles.

### Experimental Section

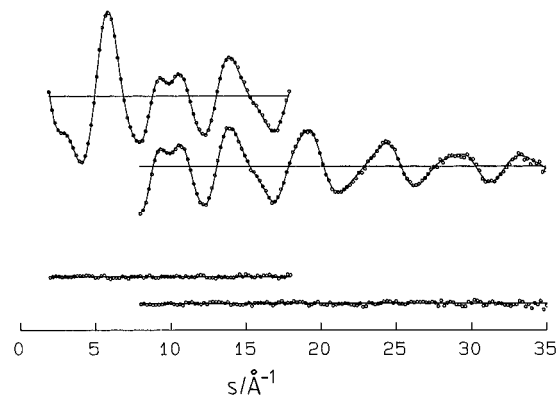
A commercial sample of *t*-BVE (Aldrich 98%) was used after condensation in vacuo. Z-MPE was synthesized according to the method described in ref 31. Its purity was checked by gas chromatography and was better than 99.5%.

The electron diffraction intensities were recorded with a Gasdiffraktograph<sup>32</sup> at 25 and 50 cm nozzle-to-plate distances and with an

(29) Tamagawa, K.; Takemura, M.; Konaka, S.; Kimura, M. *J. Mol. Struct.* **1984**, 125, 131.

(30) Liedle, S.; Mack, H.-G.; Oberhammer, H.; Imam, M. R.; Allinger, N. L. *J. Mol. Struct.* **1989**, 198, 1.

(31) Taskinen, E.; Liukas, P. *Acta Chem. Scand. Part B* **1974**, 28, 114.

**Figure 6.** Experimental (dots) and calculated (full line) molecular intensities and differences for (Z)-methyl 1-propenyl ether.

accelerating voltage of ca. 60 kV. The sample containers were kept at -15 (*t*-BVE) and -33 °C (Z-MPE), respectively, and the inlet system and gas nozzle were kept at room temperature. The electron wavelength was determined in each experiment from ZnO powder diffraction patterns. The photographic plates were analyzed by the usual methods<sup>33</sup> and averaged molecular intensities in the *s* ranges 2–18 Å<sup>-1</sup> and 8–35 Å<sup>-1</sup>, in steps of Δ*s* = 0.2 Å<sup>-1</sup>, are presented in Figures 5 and 6 (*s* = (4π/λ) sin θ/2, λ = electron wavelength, θ = scattering angle).

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(32) Oberhammer, H. *Molecular Structure by Diffraction Methods*; The Chemical Society: London, 1976; Vol. 4, p 24.

(33) Oberhammer H.; Gombler, W.; Willner, H. *J. Mol. Struct.* **1981**, 273.