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Molecular Structure and Conformation of Ethyl Methyl Ether as Studied by Gas Electron Diffraction

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The bond distances (r_g) and angles (r_α) in ethyl methyl ether have been determined by gas electron diffraction as follows: average of C(methyl)–O and C(methylene)–O$=1.418\pm0.002$ Å, C–C$=1.520\pm0.004$ Å, C–H$=1.118\pm0.004$ Å, ∠C–O–C$=111.9\pm0.5°$, ∠O–C–C$=109.4\pm0.3°$, ∠H–C–H$=109.0\pm0.4°$, where uncertainties represent estimated limits of experimental error. The two r_g(C–O) distances have been estimated independently with the aid of the rotational constants for the *trans* conformer reported by Hayashi *et al.*: C(methyl)–O$=1.413\pm0.009$ Å and C(methylene)–O$=1.422\pm0.007$ Å. The dihedral angle for the *gauche* conformer, $84\pm6°$, and the relative abundance of the *trans* and *gauche* conformers in the gas phase at 20 °C, $n_t/(n_t+n_g)=0.80\pm0.08$, have also been determined.

The conformation and the barrier to internal rotation about a C–O axis are of great importance in wide fields of chemistry, such as in polymer chemistry, and have been studied extensively by vibrational spectroscopy.[1–8] Ethyl methyl ether (Fig. 1) is one of the simplest molecules enabling such a study. This molecule is known to be a mixture of two conformers in the gas phase.[5–8] The infrared spectra observed by Kitagawa and Miyazawa[5] indicated that the more stable conformer was *trans*, and the enthalpy difference in the gas phase was measured to be 1.5 ± 0.2 kcal/mol. The rotational constants for the *trans* conformer have been determined by Hayashi *et al.* by microwave spectroscopy, from which the r_s atomic coordinates have been derived.[9] On the other hand, the conformation of the less stable conformer has only been inferred by vibrational spectroscopy to be *gauche*. Since electron diffraction provides direct information on interatomic distances, it is one of the most powerful methods for determining the mixing ratio of the conformers and the dihedral angle for the less stable conformer.[10]

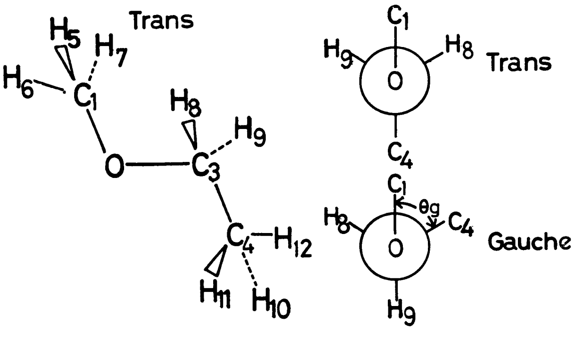

Fig. 1. Ethyl methyl ether. The dihedral angle for the *gauche* conformer measured from *cis* position is denoted by θ_g.

There are two non-equivalent C–O bonds in ethyl methyl ether. Though the average of these bond lengths can be obtained by electron diffraction, they cannot be determined individually. The moment of inertia I_a depends sensitively on these distances. Therefore, a joint analysis of electron diffraction intensity and the rotational constants can determine these nearly equal C–O distances separately, though the moments of inertia alone are not sufficient to determine a complete structure.

In the present study, the structure of ethyl methyl ether is determined first by use of the electron diffraction data alone. Then the difference of the two C–O distances is estimated by the use of the diffraction data and the rotational constants. Finally, the conformation is investigated and the structure of this molecule is compared with those of related molecules.

Experimental

The sample for spectroscopic use was supplied by Dr. Kitagawa.[7] Diffraction patterns were taken with an r^3-sector at camera lengths of 243.3 and 107.7 mm with 40 kV electrons. The electron wavelength was calibrated with reference to the r_a(C=O) distance of carbon dioxide (1.1646 Å) within 0.10%.[11] The sample reservoir was held in a Dry Ice-acetone bath in order to control the pressure of the sample at about 40 Torr during the experiment, and the sample gas was introduced into the diffraction chamber through a nozzle of 0.2 mm i.d. The exposure times were about 60 and 100 s for the long and short camera lengths, respectively. Other experimental conditions are described elsewhere.[11,12]

Four photographic plates taken at each camera length were selected for the intensity measurement by means of automated microdensitometry and data processing.[13] The optical densities (0.2—0.5) were assumed to be proportional to electron intensities. Molecular intensities in the ranges $s=3.1$—18.8 and 9.4—37.3 Å^{-1} were obtained from the long and short distance data, respectively, by use of hand-drawn backgrounds.

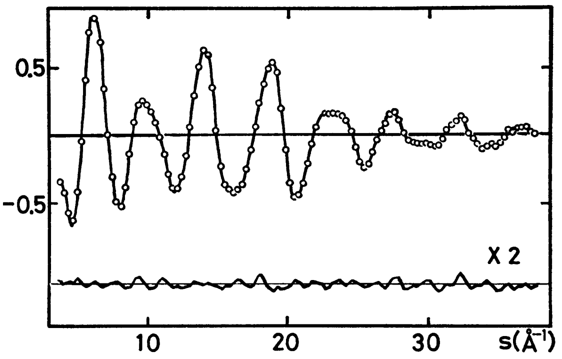

Fig. 2. Molecular intensities for ethyl methyl ether. Observed values are shown as open circles, and the solid curves represent the best-fit theoretical intensities. The lower solid curve represents the residuals.

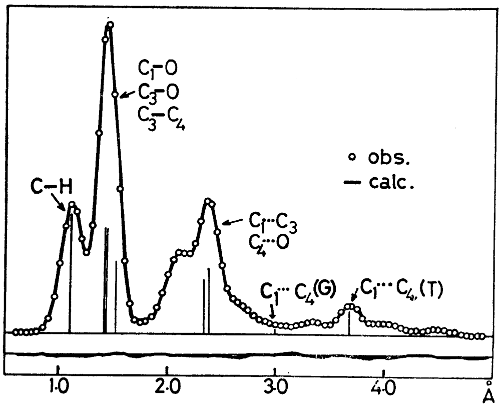

Fig. 3. Experimental and theoretical radial distribution curves. Damping factor, $\exp(-0.0016\, s^2)$, was used. The residuals are shown below in the same scale.

Since they agreed with each other in the overlapping region within experimental error, they were joined at $s = 12.6$ Å^{-1}. Four independent molecular intensity curves covering the whole s range were obtained by arbitrary combinations of four intensity curves for each camera length. The elastic and inelastic scattering factors and the phase shifts were taken from the tables prepared by Schäfer *et al.*[14] The molecular intensity and the corresponding radial distribution curve are shown in Figs. 2 and 3, respectively.[15] Most of the calculations were carried out on a HITAC 8800/8700 in the Computer Center of the University of Tokyo.

Analysis

The essential information on the conformation is contained in the distance of the C(methyl)···C(methyl) nonbonded pair. This distance for the *trans* conformer appears in the radial distribution curve (Fig. 3) as a peak at 3.7 Å, while the small shoulder at 3.0 Å consists of the corresponding distance for the *gauche* conformer. The relative abundance of the two conformers can be derived from the heights of the peak and the shoulder. By comparing the observed radial distribution curve with the curves calculated assuming various mixing ratios, the *trans* conformer was found to be dominant, being in agreement with the results from vibrational spectroscopy.[4,6] The shape of the shoulder at 3.0 Å carries information on the dihedral angle for the *gauche* form. The conformational analysis is discussed in detail in a later section.

In order to obtain a more precise skeletal structure, the molecular intensities were analyzed by a least-squares method with an empirical diagonal weight matrix[16] on the assumption that no stable conformer other than the above two existed in the gas phase at room temperature. The following additional assumptions were made so as to reduce the number of independent parameters without significant loss of accuracy:

1) The *trans* conformer has C_s symmetry in the r_α structure.

2) The *trans* and *gauche* conformers have identical bond distances and angles except for the dihedral angle about the C(methylene)–O bond. (This assumption was modified in the conformational analysis described in a later section).

3) All the C–H bond distances are equal.

4) The difference in the C(methyl)–O and C(methylene)–O bond distances is 0 ± 0.01 Å, on the basis of the structural data for dimethyl ether[17] and ethyl alcohol.[18] (The need for this assumption was removed in the joint analysis of the molecular intensities and the rotational constants).

5) The H–C(methylene)–H plane is perpendicular to the O–C–C plane, and each angle is bisected by the plane defined by the other angle at the methylene carbon atom.

6) Each of the methyl groups has local C_{3v} symmetry and no tilt. With these assumptions, the geometrical parameters were restricted to seven: the C–C, $(\text{C–O})_{\text{av}}$, $(\text{C–H})_{\text{av}}$ bond distances, the C–O–C, O–C–C, $(\text{H–C–H})_{\text{av}}$ bond angles and the dihedral angle for the *gauche* conformer. The dihedral angle for the *trans* conformer was set equal to 180° by assumption 1). In addition, the

Table 1. Mean amplitudes (l_{ij}) and shrinkage corrections ($r_a - r_\alpha$) for ethyl methyl ether[a] (in 10^{-4} Å)

	l_{ij}	$r_a - r_\alpha$		l_{ij}	$r_a - r_\alpha$
i) *trans* form					
C_1–H_5	787	59	$C_3 \cdots H_{11}$	1089	8
C_1–H_6	787	51	$C_1 \cdots C_3$	645	−6
C_3–H_8	789	74	$C_4 \cdots O$	664	−10
C_4–H_{10}	786	72	$C_1 \cdots H_8$	1407	10
C_4–H_{11}	786	65	$C_3 \cdots H_6$	1365	−3
C_1–O	480	5	$O \cdots H_{11}$	1426	−15
C_3–O	483	4	$C_3 \cdots H_5$	1275	78
C_3–C_4	527	3	$O \cdots H_{10}$	1015	−24
$O \cdots H_8$	1022	7	$C_1 \cdots C_4$	693	−51
$O \cdots H_5$	1012	13	$C_1 \cdots H_{11}$	1474	−105
$O \cdots H_6$	1014	9	$C_4 \cdots H_6$	1365	42
$C_4 \cdots H_8$	1078	5	$C_4 \cdots H_5$	1157	−68
$C_3 \cdots H_{10}$	1084	11	$C_1 \cdots H_{10}$	1147	−65
ii) *gauche* form					
C_1–H_5	787	58	C_1–H_7	787	50
C_1–H_6	787	55	C_3–H_8	789	89
C_3–H_9	789	86	$C_1 \cdots C_3$	649	−12
C_4–H_{10}	786	66	$C_4 \cdots O$	657	−14
C_4–H_{11}	786	60	$C_4 \cdots H_7$	1564	−46
C_4–H_{12}	786	66	$C_1 \cdots H_{11}$	1607	−137
C_1–O	481	0	$C_1 \cdots H_8$	1482	−41
C_3–O	483	7	$C_3 \cdots H_6$	1447	−49
C_3–C_4	529	−5	$C_3 \cdots H_7$	1351	−40
$O \cdots H_8$	1023	29	$O \cdots H_{11}$	1399	−42
$O \cdots H_9$	1022	29	$O \cdots H_{12}$	1513	−43
$O \cdots H_5$	1013	9	$C_1 \cdots C_4$	939	−25
$O \cdots H_6$	1015	6	$C_1 \cdots H_{12}$	1665	19
$O \cdots H_7$	1014	−1	$C_4 \cdots H_6$	1717	67
$C_4 \cdots H_8$	1079	7	$C_1 \cdots H_9$	1002	41
$C_4 \cdots H_9$	1044	10	$C_3 \cdots H_5$	1006	33
$C_3 \cdots H_{10}$	1086	0	$O \cdots H_{10}$	1018	27
$C_3 \cdots H_{11}$	1090	−5	$C_4 \cdots H_5$	1148	42
C_3–H_{12}	1090	0	$C_1 \cdots H_{10}$	1145	32

a) Calculated at 20°C. See Fig. 1 for the numbers of atoms. Nonlinear shrinkages due to the C(methylene)–O torsion and the methyl torsions are included. (See text.) The values for H···H pairs are not listed.

mixing ratio of the two conformers was taken as a variable parameter.

The mean amplitudes and the vibrational corrections for all interatomic distances,[19,20] listed in Table 1, were calculated with the force constants based on the valence force field.[4] Since the skeletal and methyl torsions were large-amplitude motions, contributions to the vibrational corrections from these motions were estimated by Karle's method[21,22] with the barrier heights (V_3) obtained from far infrared spectroscopy.[7] The contribution from the skeletal torsion to the vibrational correction for the C(methyl)···C(methyl) nonbonded pair, about 0.003 Å, had some influence on the dihedral angle, while those from the methyl torsions affected the corrections for the nonbonded C···H and O···H pairs by about 0.004 Å, and the H–C–H angle was influenced consequently. The asymmetry parameter κ for the bonded C–H distance was estimated to be 1.3×10^{-5} Å^3,[23,24] and the rest of the κ parameters were assumed to be zero, since they had little effect on molecular geometry. Since the C–C bond and two C–O bonds form a single peak in the radial distribution curve, the amplitudes for the C–O and C–C bonds could not be varied independently. Therefore, the amplitudes for the C–H and C–O bonds were taken as parameters and the rest of the mean amplitudes were fixed to the calculated values. The structure obtained in this analysis (average of the structures derived from the four molecular intensities mentioned above) is listed in Table 2. The error limits in the molecular parameters were estimated from random and systematic errors including the uncertainties originating from those in the amplitudes and the vibrational corrections.[25,26] The relative uncertainties in the amplitudes and the vibrational corrections for bonded pairs were tentatively estimated to be 5%. The mean amplitudes and the vibrational corrections for nonbonded pairs consist of the contributions from the small-amplitude and large-amplitude modes. The former contributions were estimated to have relative uncertainties of ±10%, while the latter contributions calculated by Karle's method were estimated to have uncertainties of 100% of the contributions. The uncertainties caused by the assumptions mentioned above were also estimated roughly and included in the errors given in Table 2. A typical error matrix is shown in Table 3.

TABLE 2. MOLECULAR STRUCTURE AND MEAN AMPLITUDES FOR ETHYL METHYL ETHER DETERMINED BY ELECTRON DIFFRACTION[a]

r(C–C)	1.520(4)	∠C–O–C	111.9(5)
$r(\text{C–O})_{\text{av}}$	1.418(2)	∠O–C–C	109.4(3)
r(C(methyl)–O)	1.413(9)[b]	∠H–C–H	109.0(4)
r(C(methylene)–O)	1.422(7)[b]	θ_g[d]	84(6)
$r(\text{C–H})_{\text{av}}$	1.118(4)	$n_t/(n_t+n_g)$[e]	80(8)
$l(\text{C–O})_{\text{av}}$[c]	0.050(3)		
$l(\text{C–H})_{\text{av}}$[c]	0.082(5)		

a) Bond distances (r_g) are in Å units. Angles (r_α) are in degrees. The numbers in parentheses represent estimated limits of error attached to the last significant digits. b) These distances were separately determined by the joint analysis. The other parameters obtained by the joint analysis were essentially equal to those given in this table. c) Observed mean amplitudes. d) The dihedral angle for the *gauche* conformer measured from the *cis* position. e) % *trans* form. $\Delta G=1.23\pm0.27$ kcal/mol.

Electron Diffraction and Microwave Data. The r_α structure derived from the electron diffraction data was used to calculate the rotational constants. For this purpose the r_α distances were extrapolated to zero kelvin by estimating the difference $r_\alpha{}^0-r_\alpha$.[19] The rotational constants, $A_\alpha{}^0$, $B_\alpha{}^0$, and $C_\alpha{}^0$, for the *trans* conformer were calculated from the average $r_\alpha{}^0$ structure, and are listed in Table 4. On the other hand, the zero-point average rotational constants, A_z, B_z, and C_z, for the *trans* conformer were derived by making vibrational corrections[27] from the A_0, B_0, and C_0 determined by microwave spectroscopy.[9] The uncertainties in A_z,

TABLE 3. ERROR MATRIX[a] AND CORRELATION MATRIX[b] FOR ETHYL METHYL ETHER[c]

	k_1	k_2	x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8	l_1	l_2
a)	73	186	343	16	4	10	51	39	45	420	12	5
k_1	100	23	−27	50	29	−39	−16	−30	44	12	0	−5
k_2		100	−35	71	−55	64	−73	62	28	13	87	85
x_1			100	−30	16	−24	23	−20	−19	−29	−31	−29
x_2				100	50	45	−56	−40	56	1	65	−22
x_3					100	−30	7	−64	45	−15	−43	−67
x_4						100	−46	39	49	−2	52	54
x_5							100	−80	−35	18	−65	−56
x_6								100	−53	−22	51	72
x_7									100	10	30	−7
x_8										100	10	14
l_1											100	65
l_2												100

a) Diagonal elements of error matrix. Units ($\times10^{-4}$) for the distances and mean amplitudes are Å, those for the indices and the relative abundance of the *trans* form are dimensionless. b) Correlation matrix. Units ($\times10^{-2}$) are all dimensionless. *c*) k_1,k_2=indices of resolution for the long and short distance data, (0.94±0.02 and 1.03±0.07) respectively, x_1=relative abundance of the *trans* form, $x_2=r$(C–C), $x_3=r(\text{C–O})_{\text{av}}$, $x_4=r(\text{C–H})_{\text{av}}$, x_5=∠C–O–C, x_6=∠O–C–C, x_7∠=H–C–H, x_8=dihedral angle for the *gauche* form, $l_1=l(\text{C–H})_{\text{av}}$ and $l_2=l\ (\text{C–O})_{\text{av}}$.

TABLE 4. OBSERVED AND CALCULATED ROTATIONAL CONSTANTS FOR *trans* ETHYL METHYL ETHER (in cm^{-1})

	$0^{b)}$	$z^{c)}$	$\alpha^{0\ d)}$	$\mathrm{av}^{e)}$
A	0.933712(1)	0.941(3)	0.940(4)	0.937(4)
B	0.138745(1)	0.1388(3)	0.1375(12)	0.1383(5)
C	0.129796(1)	0.1298(2)	0.1289(10)	0.1295(4)

a) Uncertainties attached to the last significant digits are given in parentheses. b) Observed rotational constants for the ground vibrational state, Ref. 9. c) Zero-point average rotational constants calculated from A_0, B_0, and C_0 with corrections for vibrational effects. d) Rotational constants calculated from the $r_\alpha{}^0$ parameters which are compatible with the structure given in Table 2 determined in the analysis of electron diffraction intensities. Uncertainties are estimated from those in the r_α parameters. e) Best fit rotational constants obtained by the combined analysis of diffraction and microwave data. The structural parameters (r_{av}) which reproduce these constants are essentially equal to those given in Table 2 if the distances are transformed into r_g. Uncertainties represent 2.5 times the estimated standard deviations.

B_z, and C_z were estimated from the following sources: a) Uncertainties in the corrections for the large-amplitude modes were estimated to be ±100% of the corrections. b) The uncertainties in the corrections for all the small-amplitude modes were estimated to be ±10% of the corrections. The rotational constants, $A_\alpha{}^0$, $B_\alpha{}^0$, and $C_\alpha{}^0$, calculated from the $r_\alpha{}^0$ structure agreed with the zero-point average rotational constants, A_z, B_z, and C_z, within their uncertainties. This suggests that the frame structures of the *trans* and the *gauche* conformers do not differ greatly.

The rotational constants, A_z, B_z, and C_z, were thus combined with diffraction intensities into a joint least-squares analysis.[23,28] The weights for A_z, B_z, and C_z used in the analysis were so chosen that 2.5 times their standard deviations were approximately equal to the estimated uncertainties in the rotational constants. They were 1×10^3, 1×10^5, and 1×10^5, respectively, where a unit weight was assigned to the molecular intensities from $s=6.3$ to 26.7 $\mathrm{Å}^{-1}$ taken at $\pi/10$ $\mathrm{Å}^{-1}$ intervals. The r_{av} structure agreed with the $r_\alpha{}^0$ structure, and the mean amplitudes also converged to essentially the same values as those obtained in the analysis of the electron diffraction data alone. The assumption 4) made in the analysis of the diffraction intensities was now excluded, and the two C–O bond distances were varied independently. The average of the two C–O bond lengths determined separately in the present analysis (listed in Table 2) is equal to that obtained from electron diffraction.

Rotational Isomerism. The differences in the geometrical parameters for the *trans* and *gauche* conformers have influence on the conformational analysis. For this molecule the dihedral angle for the *gauche* conformer is derived from the bonded distances, the skeletal angles and the nonbonded C(methyl)···C(methyl) distance. Among their uncertainties those in the skeletal angles have much influence on that of the dihedral angle. Since at present there are no experimental data on the differences of the geometrical parameters for the *trans* and *gauche* conformers, the O–C–C and C–O–C angles were assumed to be 0—3° larger in the *gauche* form than in the *trans* form on the basis of the structural data for analogous molecules.[29,30] The error limit in the dihedral angle listed in Table 2 includes the influence of these uncertainties.

The effective temperature of the sample system at the scattering point must be defined when the "thermal-equilibrium" fractions of rotational isomers are discussed. The following assumptions were made: When the sample gas leaves the jet, it has reached thermal equilibrium with the nozzle throat. With our nozzle design the cooling of the gas in the passage from the nozzle tip to the scattering point is negligible.[31] Therefore, the effective vibrational temperature was assumed to be equal to the room temperature. The population of the *trans* conformer given in Table 2, 80±8%, then implies that the *gauche-trans* free energy difference ΔG is 1.23±0.27 kcal/mol, the uncertainty including that in the effective temperature. This estimate is compatible with the enthalpy difference ΔH, 1.5±0.2 kcal/mol, obtained by the temperature dependence of spectral intensities.[5]

In order to further examine the rotational isomerism in ethyl methyl ether, the molecular intensities in the range from $s=3.5$ to 8.2 $\mathrm{Å}^{-1}$ were analyzed by the method of background function.[32,33] The background functions $I_b(s)$ were derived from the experimental total intensities $I_t(s)$ and from the theoretical molecular intensities $sM(s)$ based on models. The smoothness of the $I_b(s)$ function, *i.e.* the absence of systematic fluctuations with periods similar to that of the molecular terms, was taken as a criterion for the choice of a proper conformational model. The theoretical molecular intensities $sM(s)$ were calculated with the structural parameters determined in the preceding section, and the mixing ratio and the *gauche* dihedral angle were varied. Typical I_b curves for a number of models are illustrated in Fig. 4. The I_b curve corresponding to a *trans* population of 80% and a *gauche* dihedral angle of 85° is acceptable since it has no fluctuation exceeding 0.5% of I_b, whereas all the other models shown in the figure are unacceptable because they result in systematic oscillations in the I_b curves.

The limit of uncertainty in the background function was estimated from two principal sources of error:[32,33] the random and systematic errors in the intensity measurement and the uncertainties in the structural

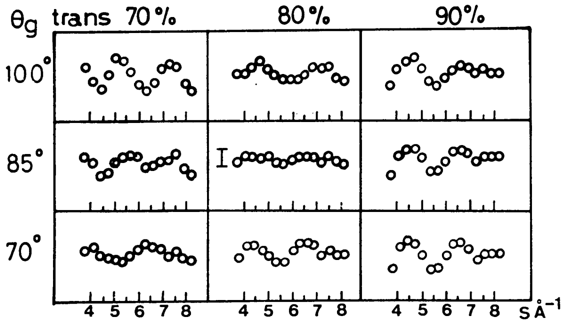

Fig. 4. Background functions I_b for different compositions of the *trans* and *gauche* conformers and dihedral angle (θ_g) for the *gauche* form. The vertical bar represents 0.5% of I_b. See text.

parameters assumed in this background analysis. The effect of the former was estimated by checking the reproducibility of the intensities obtained from different photographic plates and by examining various sources of systematic error.[26] The systematic error originating from the error in the frame structure was checked by calculating the background function with sets of the geometrical parameters varied within the limit of their estimated uncertainties. The limit of uncertainty in the background function was thus estimated to be $\pm 0.5\%$. This value corresponds to the limit of uncertainty of less than 10% in the mixing ratio and that of less than 10° in the dihedral angle. Consequently, the conformational parameters determined by the method of background function agree with those obtained from the least-squares method.

Comparison with Related Molecules

The skeletal structure of ethyl methyl ether is compared with those of analogous molecules (Table 5). The $(\text{C–O})_{\text{av}}$ bond length and the C–O–C bond angle agree with those in dimethyl ether [17] within their uncertainties. The C–C bond distance (1.520 ± 0.004 Å) is significantly shorter than that in butane (1.531 ± 0.004 Å).[29] The C–H bond length is very similar to that in butane. The r_g C–C bond length and the C–O–C and H–C–H bond angles in the r_α structure are nearly equal to those in the r_s structure,[9] while the C–H and $(\text{C–O})_{\text{av}}$ bond distances (r_g) are slightly larger than the corresponding r_s distances. In view of the known differences in the r_g and r_s structures for analogous molecules,[34] these r_g and r_s distances seem to correspond well. On the other hand, there seems to be a slight discrepancy between the r_g and r_s structures in regard to the difference of the C(methyl)–O and C(methylene)–O bond lengths: The r_g structure indicates a ***positive*** difference of the order of 0.01 Å, whereas the r_s structure indicates a ***negative*** difference of the same order of magnitude. However, neither trend can be regarded as conclusive, since these distance parameters have large uncertainties (particularly the r_s structure has systematic error because the oxygen coordinates were determined with the aid of the first-moment equation).

Table 5. Comparison of related molecules

	$CH_3OCH_2CH_3$[b]	CH_3OCH_3	CH_3CH_2-CH_2CH_3[d]
C–C	1.520(4)	—	1.531(2)
C–O	1.418(2)[e]	1.418(3)[f]	—
C–H	1.118(4)	1.100(6)[f]	1.117(5)
∠C–O–C	111.9(5)	111.5(15)	—
θ_g[g]	84(6)	—	65(6)
$n_t/(n_t+n_g)$[h]	80(8)	—	54(9)
ΔG[i]	1.23(27)	—	0.50(22)

a) Distances in r_g and angles r_α (r_a for c). Uncertainties represent estimated limits of error attached to the last significant digits. b) Present study. c) Ref. 17. d) Ref. 29. e) Average value of the two C–O bond lengths. f) Estimated from the r_a distance reported in the literature by addition of l^2/r_a. g) The dihedral angle for the *gauche* conformer measured from *cis* position. h) % *trans* form. i) Free energy difference (kcal/mol): $\Delta G = G_{gauche} - G_{trans}$.

The *gauche* dihedral angle in ethyl methyl ether ($84 \pm 6°$) obtained in the present study is significantly larger than that in butane ($65 \pm 6°$).[29]

Structures of a number of polyether crystals were recently determined by X-ray diffraction.[35–37] The C–C bond lengths adjacent to C–O bonds, determined to be about 1.48—1.52 Å, are shorter than the usual C–C bond distances. This trend is similar to that observed in the C_1–C_2 bond lengths in ethyl methyl ether. The conformation about the C–O bonds in polyethers is found to be most commonly *trans*. However, some intra- and intermolecular forces make the *gauche* conformation stable in some parts of a polymer, and in this case the dihedral angles about the C–O bonds for the *gauche* conformation are about 70—90°. This trend is analogous to that observed for small molecules in the gas phase by electron diffraction.

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