Can Simple Quantum-Chemical Continuum Models Explain the Gauche Effect in Poly(ethylene oxide)?

Florian Müller-Plathe* and Wilfred F. van Gunsteren

Laboratorium für Physikalische Chemie, Eidgenössische Technische Hochschule, ETH-Zentrum, CH-8092 Zürich, Switzerland

Received August 5, 1993; Revised Manuscript Received July 18, 1994[®]

ABSTRACT: We report ab initio quantum-chemical calculations at the level of second-order many-body perturbation theory aimed at the equilibrium between the all-trans (ttt) and the trans-gauche-trans (tgt) conformations of dimethoxyethane, which is the smallest analog of poly(ethylene oxide). Solvent effects are accounted for by two continuum models: one assumes statistically fluctuating electric fields around the dimethoxyethane molecule caused by the solvent, and the other is an Onsager reaction-field model. We find the ttt conformer to be more stable in the gas phase. Use of the stochastic field model has no effect on the relative stabilities, whereas the reaction-field method brings the energy of the tgt conformer down very close to the ttt energy. We conclude that the gauche effect in dimethoxyethane and, by analogy poly(ethylene oxide), is mainly due to the presence of a polarizable environment and not to some intrinsic conformational preference.

1. Motivation

The gauche effect in dimethoxyethane (DME, ethylene glycol dimethyl ether, glyme, $CH_3OCH_2CH_2OCH_3$) is the phenomenon that the central dihedral angle (OCCO) prefers the gauche conformation (~±60°) over the trans conformation (180°). This effect is also present in other compounds which contain the structural motif of oxygen-linked ethylene units. Our own interest is the molecular-dynamics simulation of poly(ethylene oxide) (PEO, $(-OCH_2CH_2-)_n$). For this purpose we need an analytical force field which reliably accounts for the gauche effect. Since DME is the simplest suitable analog of PEO (the even simpler ethylene glycol can form internal hydrogen bonds which are not present in PEO), we report in this article ab initio calculations on the trans-gauche equilibrium in DME. These we intend to use as reference points in the development of the torsional force field. The force field development is, however, not a part of the present contribution.

There appears to be a solid body of experimental and theoretical evidence that the all-trans conformation (ttt) is the most stable form of DME in the gas phase and at 0 K. Recent infrared measurements on DME trapped in an inert-gas matrix,[1] for instance, showed that a mixture of conformations representative of the gas phase can be frozen out at 18 K. Upon heating to 34 K, all DME assumed the most stable conformation ttt. On further heating (~40 K) the gauche conformation, tgt, is populated. The authors claim that intermolecular interactions between DME molecules become important at this temperature and lead to a stabilization of the tgt conformer. Virtually all quantum-chemical studies yield ttt as the most stable conformer. There are several recent ab initio studies in the literature.[1-4] The authors of ref 2 use a combination of SCF results in a 6-31G** basis and incomplete (no triple excitations) fourth-order many-body perturbation theory (MBPT) calculations in the smaller 6-31G basis to estimate the energy difference between ttt and tgt to be 0.613 kcal/mol (2.64 kJ/mol) in favor of ttt. By adding the zero-point energy obtained in yet another basis set (3-21G), the difference is marginally reduced to 0.518 kcal/mol (2.17 kJ/mol). It has been pointed out, though, that the procedure of combining SCF and correlation results obtained in different basis sets is not completely without danger.[5] More recently, calculations with larger bases, have given a similar gas-phase energy difference between the ttt and tgt states.[3] However, the authors of ref 4, who use an extensive basis set (Dunning double-ζ of the form (10s6p2d1f,4s1p)/[5s2p2d1f,2s1p]) and MBPT2, find the energy gap between ttt and tgt narrowed to 0.59 kJ/mol.

Once DME is surrounded by a polarizable medium (i.e., in the crystal, in the melt, or in solution), it seems to prefer the tgt conformation. This is evident from IR studies[1] measurement of NMR coupling constants,[6] and Raman spectroscopy.[7] Similarly, poly(ethylene oxide) favors a gauche conformation around its C-C bonds in the crystal, where this preference gives rise to the formation of helices (see, e.g., ref 8), as well as in the melt or in solution. The free-energy difference between trans and gauche in amorphous PEO has been estimated using rotational isomeric state theory to fall between -0.4 and -0.53 kcal/mol (-1.7 to -2.2 kJ/mol).[9] (A recent third-order RIS model, however, which allows for the apparent low energy of tg^+g^- conformations was able to explain PEO conformational statistics without the assumption of the energy of the gauche conformation being lower than that of the trans conformation.[20]) Throughout this article a negative energy difference indicates that the gauche conformer is more stable than the trans conformer. It is also interesting to note that the cyclic analog of PEO, the crown ether 18-crown-6, has one conformation with all C-C bonds being gauche (for a discussion, see, e.g., ref 11). This conformer has been found in crystals of 18-crown-6 complexed with K^+. Free 18-crown-6, however, crystallizes in another structure in which some of the C-C bonds are trans and some of the C-O bonds are gauche instead.

There have been several attempts to investigate theoretically the ttt-tgt equilibrium of DME in environments other than vacuum. Podo et al. reported an early molecular-mechanics[12] study, which already used a reaction-field approach to incorporate solvent effects. Andersson and Karlström[13] used a mixture of methods: SCF calculations in a polarized double-ζ basis set and adding a reaction-field correction afterward gave them an energy difference of 2-3 kJ/mol, indicating that this approach does not lead to a sufficient stabilization of the gauche

---

* Author to whom correspondence should be addressed.

[®] Abstract published in *Advance ACS Abstracts*, September 1, 1994.

0024-9297/94/2227-6040$04.50/0

conformer. They also did a Monte Carlo calculation on a model "molecule" of two joint dipoles in a solvent of single dipoles and found that this explicit solvent favored a gauche arrangement of the molecule provided the solvent dipoles were chosen large enough.

The most successful attack on the problem was probably the Monte Carlo study of Bressanini et al.[14] They used the ab initio gas-phase calculations of ref 2 as well as MM2[15] results to construct an empirical potential for DME, which in the gas phase favors ttt by 2.6 kJ/mol. With this they did a Monte Carlo simulation of liquid DME and found a preference for the tgt conformation. From the relative populations they give, the free-energy difference between ttt and tgt for liquid DME at 298 K can be estimated to be −0.82 kJ/mol. (Unfortunately, we cannot use their force field in our calculation, since united-atom force fields with rigid bond angles are not suitable for the purpose of our simulations.[16]) At present, however, the approach of explicitly including solvent molecules into the calculation is only possible for classical simulations.

In this contribution we examine the ttt–tgt equilibrium of DME with ab initio quantum-chemical methods. In particular, the so-called self-consistent reaction field (SCRF)[17] method has recently become available[18] as part of the Gaussian 92 program.[19] We study the equilibrium in the presence and in the absence of an Onsager reaction field. Since the SCRF methodology relies on molecular electric moments, we believe it is not sufficient to do these calculations at the SCF level, which notoriously gives inaccurate moments. Instead, we use second-order MBPT (MBPT2) throughout this work to account for electron correlation. For the same reason we use a polarized basis set (6-31G**) in our calculations. In addition to the SCRF method, we estimate the effect of randomly fluctuating electric fields caused by the motion of solvent molecules ("cavity fields"[20]), which have previously been suggested as the reason for the relative stability of the two conformers in polarizable media.[13]

2. Theory and Computational Methods

Assuming Debye relaxation of a solvent continuum with the dielectric constant ϵ, Hubbard and Wolynes[20] derived the time correlation function for the electric field $\mathbf{F}$ inside a spherical cavity of radius a,

$$\langle \mathbf{F}(t)\, \mathbf{F}(0) \rangle = \frac{6k_B T(\epsilon - 1)}{4\pi\epsilon_0 a^3(2\epsilon + 1)} \exp(-t/\tau) \tag{1}$$

where k_B is Boltzmann's constant, T is the temperature in K, ϵ_0 is the vacuum permittivity, t is time, and τ is a relaxation time. From this, the fluctuation in the field is readily calculated.

$$\langle F^2 \rangle = \frac{6k_B T(\epsilon - 1)}{4\pi\epsilon_0 a^3(2\epsilon + 1)} \tag{2}$$

Assuming $\epsilon = 80$ for the medium being water, $T = 300$ K, and $a = 0.4$ nm, the average absolute magnitude of the field inside the cavity is 1.32×10^9 V/m or 2.67×10^{-3} au (hartree/e bohr).

The total energy $E(\mathbf{F})$ of a molecule in the presence of a static electric dipole field $\mathbf{F}$ can be calculated by including the field in the one-electron Hamiltonian. For small enough fields it is also given approximately by

$$E(\mathbf{F}) = E(0) + \mu\cdot\mathbf{F} - \frac{1}{2}(\mathbf{F}\cdot\alpha\cdot\mathbf{F}) + O(\mathbf{F}^3) \tag{3}$$

where μ is the dipole moment vector and α is the polarizability tensor of the molecule.

The average total energy of a molecule in the presence of a fluctuating cavity field is given by

$$\langle E \rangle = \frac{\int w(\mathbf{F})\, E(\mathbf{F})\, d\mathbf{F}}{\int w(\mathbf{F})\, d\mathbf{F}} \tag{4}$$

$w(\mathbf{F})$ being the distribution function of the field.

It is worth looking at the approximations in the fluctuating cavity field model in more detail. There are no explicit solvent atoms but the solvent is a continuum. The cavity is spherical, which is the simplest possible geometry. The magnitude of the cavity field depends strongly on the cavity radius a (eq 2). How to pick this radius is not precisely defined (see below). The solute only feels the fluctuating field of a hypothetical unperturbed cavity and the field is limited to a dipole field uniform throughout the cavity. Furthermore, the presence of the solute does not change the cavity field. Moreover, the interaction between solute and solvent is only treated in an average mean-field way and there is no time dependence. Since relaxation times for the rearrangement of solvent molecules and for motions of the solute are of the same order, one would expect some coupling between solute and solvent motion.

The self-consistent reaction-field method[17] is a different approach. (For its implementation in Gaussian 92, see ref 18.) Here, the dipole moment μ of the solute induces a dipole in the surrounding medium which gives rise to a uniform dipolar field, the so-called reaction field $\mathbf{F}_{RF}$. The reaction field is proportional to the solute's dipole moment

$$\mathbf{F}_{RF} = \frac{2(\epsilon - 1)}{4\pi\epsilon_0(2\epsilon + 1)a^3}\mu \tag{5}$$

The reaction field in turn interacts with the solute dipole. This, first, leads to a stabilization of dipolar molecules by $\mu\cdot\mathbf{F}_{RF}$. Second, the reaction field induces a larger dipole moment in the solute, which stabilizes the solute even more.

Except for SCF calculations where the reaction field can be solved for simultaneously with the HF equations, the quantum-chemical version of this method is implemented as an iterative procedure: One calculates the dipole moment of the solute in the gas phase, determines the reaction field from eq 5, recalculates the solute dipole moment in the presence of the reaction field, and iterates this process until self-consistency is reached, i.e., until the dipole moment and the reaction field do not change any more. The convergence criterion in the Gaussian 92 implementation is that the reaction field changes less than 10^{-5} au between iterations. We reached convergence typically within 4–6 steps.

Let us briefly examine the approximations and possible limitations of the SCRF method. As before, the solvent is treated as a continuum, the reaction field is dipolar and uniform throughout the cavity, there is no time dependence, and the cavity is spherical. The medium responds only to the overall dipole moment of the solute, but not to finer details in the solute's charge distribution, as some of the more advanced continuum models do (for a review, see ref 21). In contrast to the cavity field treatment, the field inside the cavity now is completely determined by the solute. The medium generates no fields by itself.

One is also still faced with the problem of choosing a cavity radius a. We follow the suggestion in ref 18 and determine it from the molar volume V_m

$$a^3 = (3V_m)/(4\pi N_A) \qquad (6)$$

(N_A is Avogadro's number.) The molar volume, in turn, is calculated from the electron density. The boundary of the molecule is set at an electron density of 10^{-3} e/bohr^3. This gives a radius of 0.401 nm. For simplicity, we chose 0.4 nm.

From eq 5 it can be seen that the molecular dipole moment directly enters into the stabilization of the solute by the polarizable solvent. Its polarizability enters in a more indirect way. We therefore think it is mandatory to use a method and a basis set that are able of providing reliable dipole moments and polarizabilities. This requirement rules out SCF calculations and small basis sets. Ideally, one would like to use something of the quality of fourth-order MBPT and a double-ζ or triple-ζ basis set with polarization and possibly diffuse functions.[22] For this rather large molecule, however, we had to settle for MBPT2 calculations in a split-valence basis set with polarization functions on every atom (6-31G**), which leads to 140 basis functions. In the MBPT2 part we froze the 1s orbitals of the heavy atoms. Calculations were carried out on a Silicon Graphics 380 computer with the parallelized version of Gaussian 92[19] for UNIX workstations. We used default settings unless specified otherwise. These imply an integral accuracy of 10^{-10} and an SCF convergence criterion (density matrix) of 10^{-8}.

Aside from the electronic polarization of the rigid molecule, external electric fields can cause the molecule to distort and be polarized. This process is characterized by a conformational polarizability. The most rigorous way to estimate the total (electronic + conformational) polarizability would be to reoptimize the molecular geometry in the presence of an external field. This, however, appears to be impossible with the software as delivered today. To estimate the conformational part of the polarizability we have resorted to a much cruder model based on normal mode analysis. The harmonic force along a normal coordinate Q_l is given by $-k_lQ_l$, where k_l is the harmonic force constant for this normal mode. If the charge distribution of the molecule is approximated by point charges q_j on the atoms, the force on atom j by an external field $\mathbf{F}$ is given by $q_j\mathbf{F}$. The field exerts a force along the normal coordinate, which in equilibrium is balanced by the harmonic force

$$F\sum_i C_{li}q_i = k_lQ_l \qquad (7)$$

where i runs from 1 to the number of Cartesian coordinates, the q_i are assumed to be arranged in triplets, and C_{li} is the coefficient of Cartesian coordinate i in normal mode Q_l. Note that k_l and C_{li} are available from a standard normal mode analysis. The potential energy change caused by the field equals the change in harmonic potential energy due to deformation along Q_l.

$$\frac{1}{2}\alpha_lF^2 = \frac{1}{2}k_lQ_l^2 \qquad (8)$$

With this, F and Q_l in eq 7 can be eliminated to give

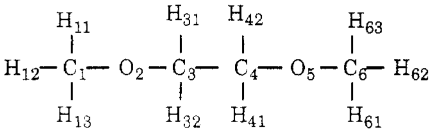
$$\alpha_l = \frac{1}{k_l}\left(\sum_i C_{li}q_i^{\,2}\right) \qquad (9)$$

Here, α_l denotes the conformational polarizability due to the normal mode Q_l. The total conformational polarizability is obtained by summing over all l. Naturally, those normal modes which have a low force constant and which cause a large change in the molecular dipole moment will contribute most to the polarizability. Thus, in practice, there are only few important normal modes.

Table 1. Optimized Geometries for the All-Trans (ttt) and Trans–Gauche–Trans (tgt) Structures of Dimethoxyethane (DME)[a]

parameter	ttt	tgt(ϵ=1)	tgt(ϵ=80)
total energy (au)	−307.9326781	−307.9317997	−307.932680
dipole moment (D)	0	1.4436	1.6360
distances			
C_1–H_{11}	0.1095	0.1095	
C_1–H_{12}	0.1087	0.1087	
C_1–H_{13}		0.1096	
C_3–H_{31}	0.1096	0.1099	
C_3–H_{32}		0.1097	
C_1–O_2	0.1416	0.1415	
O_2–C_3	0.1417	0.1415	
C_3–C_4	0.1512	0.1507	
angles			
H_{11}–C_1–O_2	111.4	111.5	
H_{12}–C_1–O_2	107.0	106.9	
H_{11}–C_1–O_2		111.5	
C_1–O_2–C_3	111.4	111.3	
O_2–C_3–C_4	107.1	108.5	
C_4–C_3–H_{31}	109.7	109.5	
C_4–C_3–H_{32}		109.2	
dihedral angles			
H_{11}–C_1–O_2–C_3	60.9	61.1	
H_{12}–C_1–O_2–C_3	180.0	180.4	
H_{13}–C_1–O_2–C_3	−60.9	−60.3	
C_1–O_2–C_3–C_4	180.0	183.7	
O_2–C_3–C_4–O_5	180.0	71.2	70.0
H_{31}–C_3–C_4–O_5	59.2	−49.8	51.0
H_{32}–C_3–C_4–O_5	−59.2	192.1	190.9

[a] Distances are in nanometers, and angles are in degrees. Symmetry-equivalent parameters are listed only once. For the tgt conformation with ϵ = 80, only the central dihedral angle was reoptimized; all other parameters are as for ϵ = 1.



$$H_{12}-\overset{H_{11}}{\underset{H_{13}}{C_1}}-O_2-\overset{H_{31}}{\underset{H_{32}}{C_3}}-\overset{H_{42}}{\underset{H_{41}}{C_4}}-O_5-\overset{H_{63}}{\underset{H_{61}}{C_6}}-H_{62}$$

Figure 1. Atom numbering of the dimethoxyethane molecule.

Since a normal mode calculation at the MBPT2 level for this molecule is prohibitively expensive, we had to restrict ourselves to the SCF level. SCF often overestimates vibrational frequencies which would lead to too small conformational polarizabilities. However, we only use them for the comparison of different structures and therefore do not attempt to correct them empirically. These SCF frequencies were also used to estimate the vibrational entropic contribution to the relative free energy of the two conformers. Atomic charges entering eq 9 were calculated at the MBPT2 level with various methods provided for in Gaussian 92.

3. Results and Discussion

We first optimized the geometries of both the ttt and the tgt conformers of DME. This was done at the full MBPT2/6-31G** level. The optimized parameters are given in Table 1. The ttt conformer has C_{2h} symmetry, and the tgt conformer C_2 symmetry. Only unique geometrical parameters are given in Table 1. The atom numbering is indicated in Figure 1. The orientation in the calculation is the Gaussian standard orientation. For the present case this means that the C_2 symmetry axis coincides with the z axis. The bond vector C_3–C_4 is almost parallel to the y axis. The ttt conformer has all heavy atoms lying in the *xy* plane. The tgt conformer is oriented such that C_3 and C_4 have a positive *z* coordinate and all other heavy atoms have a negative *z* coordinate.

The tgt structure was optimized first without a reaction field ($\epsilon = 1$). Gaussian 92 does not allow the evaluation of gradients at the MBPT2 level in the presence of a reaction field. Therefore, no automatic geometry optimization was possible for $\epsilon = 80$. However, it is possible to calculate SCF derivatives in the presence of a reaction field. We therefore optimized the tgt geometry at the SCF level with both $\epsilon = 1$ and $\epsilon = 80$. Most parameters are virtually unchanged: All distances change by less than 0.0002 nm, and all angles by less than 0.2°. The only exception is the central dihedral O_2–C_3–C_4–O_5 and the associated dihedrals involving H atoms on C_3 and C_4. This dihedral changed by 0.8°. We therefore optimized this dihedral by hand (bisection) at the MBPT2 level with a dielectric constant of 80, keeping all other parameters as they were. We find that the change induced by the polarizable medium is 1.2°, even larger than for the SCF calculation. The equilibrium value for the central dihedral in its gauche conformation is around ±71°.

The energy difference between the ttt and tgt conformers is 2.31 kJ/mol for $\epsilon = 1$ and -5×10^{-3} kJ/mol for $\epsilon = 80$; i.e., ttt and tgt are of essentially the same energy. (The partial relaxation of the central dihedral contributed 2×10^{-2} kJ/mol to the latter.) The gas-phase energy difference agrees well with previously reported values of around 2.6 kJ/mol.[1,2] The energy difference is brought down to zero by the reaction field of the solvent. It is interesting to note that in the SCF approximation (at SCF-optimized geometries) the energy difference is 5.84 kJ/mol in the gas phase and 3.06 kJ/mol in solution. The SCF approximation therefore introduces two errors: Firstly, the gas-phase energy difference is overestimated. Secondly, the stabilization due to the reaction field is also overestimated, probably because of the larger dipole moment of the tgt conformer in the SCF approximation (1.81 vs 1.44 D for MBPT2). However, the larger stabilization is not able to compensate the too large gas-phase energy difference.

We have also calculated the tgt conformer with $\epsilon = 80$, but shrinking the cavity radius *a* to 0.38 nm. For this value the energy difference becomes 2.44 kJ/mol at the SCF level and −0.45 kJ/mol at the MBPT2 level. This indicates that within the simple reaction-field model quantitative agreement with experiment can only be obtained at the expense of using an unphysically small cavity radius, i.e., by allowing the solvent to penetrate into the DME molecule.

Although a zero energy difference in solution means that there will be a larger fraction of tgt conformer than ttt conformer (there are two gauche states and only one trans state), the energy of the tgt conformer is still higher than found experimentally (−1 to −2 kJ/mol). One might wonder if extending the reaction field to the quadrupole moment could help solve the problem. Inspection of the quadrupole moments of the ttt and tgt conformers indicates that this is probably not the case: the traces of the quadrupole moment tensors are −109.9 au for the ttt conformer and −108.2 au for the tgt conformer. Thus, the differences in quadrupole moments are small and they would marginally favor the ttt conformer. However, it cannot be ruled out that a continuum model which is also sensitive to local features of the solute's electrostatic potential (rather than only the center-of-mass moments) would further stabilize the tgt conformer.

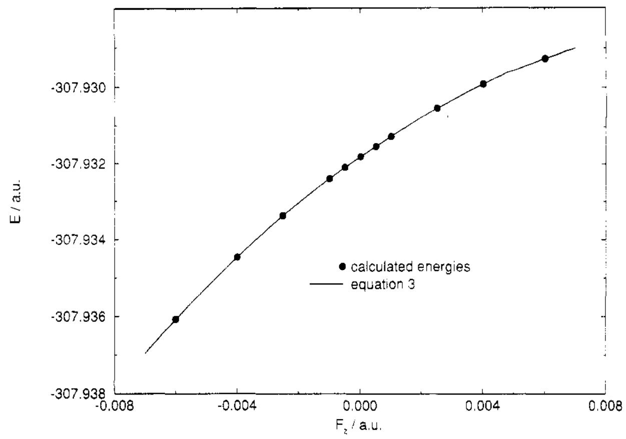


Figure 2. Total energy of a rigid dimethoxyethane molecule (tgt form) in the presence of a uniform electric field in the z direction (parallel to the C_2 axis). The filled circles indicate energies calculated quantum-chemically. The solid line is estimated from eq 3, with $\mu_z = 1.443$ D and $\alpha_{zz} = 48.256$ au.

Following the original submission of this article, we have become aware of a paper by Jaffe et al.[4], who point out that the energy of the gauche state is relatively sensitive to the choice of the basis set: The relative gauche state energy is lowered if one goes to a really huge basis sets (D95+(2df, p)). They did not, however, investigate the effect of solvent models on the relative energetics. To get a rough estimate of the basis set effect, we have performed SCF calculations with basis sets of up to 6-311++G(3df,2p): For this basis, the relative energy of the tgt state decreases to 3.88 kJ/mol in the gas phase and 2.69 kJ/mol in the reaction-field approximation, respectively. It is, therefore, very likely that the inclusion of electron correlation with such a basis would bring the tgt state below the ttt state if a reaction-field model of the solvent is used.

To investigate the contribution of fluctuating cavity fields to the total energy we have to calculate the integral in eq 4. We have calculated the total energy of the tgt conformer (in fixed geometry) at a number of values for a finite field in the *z* direction. These are indicated as filled circles in Figure 2. In some figure, we also show, as a solid line, the total energy calculated from eq 3, using the dipole moment and the electronic polarizability (*zz* component) at zero external field. From Figure 2 it is clear that both sets of energies are indistinguishable over the range shown here, which is larger than the estimated width of the distribution of the fluctuating field (2.67×10^{-3} au). Assuming that this is true also for the other Cartesian directions, we have used eq 3 to estimate the total energy for all components of the electric field and for all conformations of DME, thus avoiding some expensive calculations. The electronic polarizabilities were calculated by numerically differentiating the dipole moments with respect to the electric field. Values of the finite electric field of 0 and ±0.00189 au were used. The calculated electronic polarizabilities are listed in Table 2.

The energetic stabilization of a molecule by the z component of a randomly distributed field is

$$\Delta E(\langle F_z \rangle) = \mu_z \int F_z G(F_z)\, \mathrm{d}F_z - \frac{\alpha_{zz}}{2} \int F_z^{\,2} G(F_z)\, \mathrm{d}F_z \qquad (10)$$

(α_{xz} and α_{yz} are zero for our molecules) where $G(F_z)$ is a normalized Gaussian distribution in F_z of appropriate width. Since the Gaussian is symmetric around the origin, the first integral is zero. The stabilization by the randomly

Table 2. Electronic Static Dipole Polarizability (au) for the ttt and tgt Conformers of Dimethoxyethane[a]

	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$
ttt conformer	44.76	63.08	44.26	50.70
tgt conformer (ϵ = 1 geometry)	44.36	60.19	48.26	50.94
tgt conformer (ϵ = 80 geometry)	44.37	60.16	48.31	50.94

[a] These were obtained by the finite-difference method with an external electric field of 0.00189 au. Molecules are in their standard orientations as described in the text.

Table 3. Conformational Static Dipole Polarizability (au) for the ttt and tgt Conformers of Dimethoxyethane Calculated from Normal Modes by Eq 9[a]

	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$
ttt conformer				
Mulliken	13.0	5.6	119.9	46.2
Merz–Kollman	4.6	2.3	46.9	17.9
CHELP	3.9	2.7	49.0	18.5
CHELPG	4.3	2.3	47.7	18.1
tgt conformer				
Mulliken	72.8	16.0	53.9	47.6
Merz–Kollman	24.4	5.7	18.8	16.3
CHELP	28.3	6.3	21.4	18.7
CHELPG	24.7	5.5	18.8	16.3

[a] For references to the different ways of calculating atom charges, see ref 19. All charges are based on the MBPT2 density.

fluctuating field therefore involves only the dipole polarizability of the molecule. Using the electronic and conformational polarizabilities (Tables 2 and 3, respectively), the stabilization for the ttt and tgt conformers can be estimated by calculating stabilization energies for the diagonal components of the polarizability tensor and averaging. Since the traces of the polarizability tensors (both electronic and conformational) of the ttt and tgt conformers are almost the same, one expects that both conformers are stabilized by the same amount. This is indeed the case: The calculation shows that the stabilization due to fluctuating cavity fields is 1.4 kJ/mol for both conformers from the electronic polarizability. The absolute conformational polarizability, and hence the stabilization due to it, do not depend very strongly on the set of atomic charges used if one disregards the one calculated from Mulliken charges, which is only included for reference. The conformational polarizability calculated with any of the electrostatic-potential-fit charges contributes around 0.5 kJ/mol stabilization. The difference between the two conformers is small, no matter which charges are used (0.6–10%). This is partly due to the fact that within any one recipe for calculating atom charges the charges for both conformers are very similar indeed. The fact that the cavity-field approximation does not lead to a significant stabilization of one conformation is not too great a surprise. However, based on a statistical-mechanical simulation it had been hinted[13] that cavity fields could have a larger effect. Our results do not support this suggestion.

It is interesting to analyze the normal modes that contribute most to the conformational polarizabilities. For the ttt conformer, the most important four modes are l = 1 (73.5 cm^{-1}), l = 2 (122 cm^{-1}), l = 4 (159 cm^{-1}), and l = 6 (251 cm^{-1}). The l = 1 mode mainly involves the C–O–C–C dihedrals, l = 2 the O–C–C–O dihedral with some participation of the C–O–C–C dihedrals, l = 4 the C–O–C and C–C–O bond angles, and l = 6 the O–C–C–O dihedral along with some twisting of the methyl groups. The conformational polarizability of the tgt conformer is contributed by the lowest seven modes (79.6, 84.4, 133, 233, 246, 294, and 337 cm^{-1}). Here, l = 1 and l = 2 mainly involve the C–O–C–C dihedrals, l = 3 involves the O–C–C–O dihedral, l = 4 and l = 5 are methyl rotations with more or less involvement of the backbone dihedrals, and l = 6 and l = 7 involve backbone bond angles and, to a lesser extent, dihedrals.

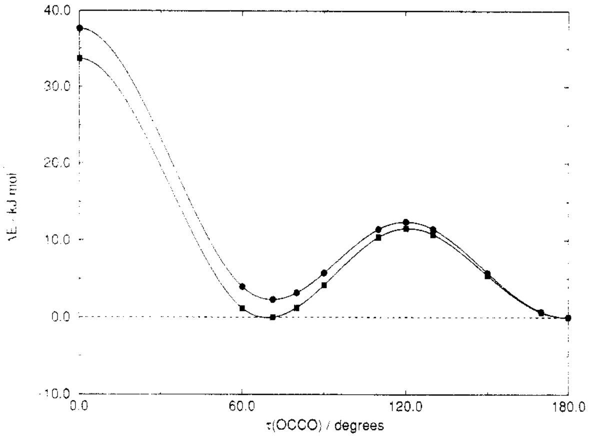


Figure 3. Energy of dimethoxyethane as a function of the central dihedral angle $\tau(O_2–C_3–C_4–O_5)$. The zero point is chosen at the trans conformation (τ = 180°). Filled circles indicate energies in vacuum (ϵ = 1), and filled squares indicate energies in solution (ϵ = 80, cavity radius a = 0.4 nm).

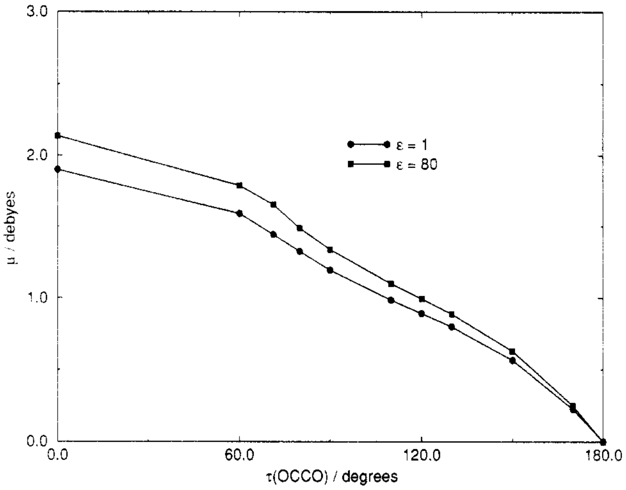


Figure 4. Dipole moment of dimethoxyethane as a function of the central dihedral angle $\tau(O_2–C_3–C_4–O_5)$. Filled circles indicate dipole moments in vacuum (ϵ = 1), and filled squares indicate dipole moments in solution (ϵ = 80, cavity radius a = 0.4 nm).

We have also estimated the effect of the reaction field on the torsional barriers of the central dihedral angle $\tau(O_2–C_3–C_4–O_5)$. We have fixed this dihedral at a selected value and optimzed all other degrees of freedom with ϵ = 1. At these geometries, the energies were calculated for both ϵ = 1 and ϵ = 80. We refrained from performing the rather cumbersome reoptimization by hand for this potential curve. The resulting energy profile is displayed in Figure 3. The gauche–trans barrier at ±120° and the cis barrier (0°) are decreased by the solvent but not shifted. The decrease was to be expected since both barrier conformers have a dipole moment. Since the cis barrier has a larger dipole moment (1.9 D) than the gauche–trans barrier (0.9 D), it is also decreased more by solvent effects: The cis barrier drops from 37.6 to 33.7 kJ/mol whereas the trans–gauche barrier changes only from 11.5 to 10.4 kJ/mol. The dipole moment as a function of the central dihedral (with and without reaction field) is shown in Figure 4.

The data of Figure 3 also allow a crude estimate of the contribution of the entropy associated with the central dihedral to the relative free energy of the two conformers.

The entropy difference ΔS is given as $S_{ttt} - S_{tgt} = -Nk_B \ln(Q_{ttt}/Q_{tgt})$. The configurational integrals Q_c for both conformations are calculated by integrating the Boltzmann factor over the respective potential wells

$$Q_c = \int_0^{\text{barrier}} \exp(-E/(k_B T))\, dE \qquad (11)$$

For $\epsilon = 1$, the contribution of the entropy term of this degree of freedom $-T\Delta S$ is 1.1 kJ/mol; for $\epsilon = 80$, this becomes 1.7 kJ/mol at $T = 300$ K. The reason for the solvent effect becomes clear from comparing the two curves in Figure 3. The solvent makes the trans minimum slightly wider and the gauche minimum slightly narrower. From the frequencies of the normal vibrations one can also estimate the entropy contribution of all vibrational degrees of freedom. This involves a number of severe approximations (gas phase, only harmonic motion around minima, SCF frequencies, etc.) so that this estimate is a very rough one. We find an entropic contribution to the free energy difference of −0.66 kJ/mol for $\epsilon = 1$ at 300 K. This would mean that inclusion of all degrees of freedom, as opposed to only considering the most conspicuous one, actually reverses the sign of the vibrational entropy difference between the two conformers. Since both approximations for estimating the entropy contribution yield different results, we cannot determine the entropy contribution conclusively. However, it is probably fair to say that the solvent effect on the entropy contribution is small and does not account for the remaining discrepancy with experiment.

4. Conclusions

In this contribution we are mainly concerned with the conformational equilibrium between the trans and gauche conformers of dimethoxyethane. The result for the gas phase is in agreement with other calculations at a similar level of theory and with recent experiments: the trans conformer is more stable. We have tried to account for solvation effects by two simple continuum models. Incorporation of fluctuating cavity fields in a mean-field way does not favor one conformation over the other, since both the electronic and the conformational polarizability of the two conformers turn out to be very similar. This finding desagrees with a previous suggestion.[13] The Onsager reaction-field model, in spite of being not very sophisticated, is capable of giving the qualitatively correct result that the gauche conformer is stabilized by solvation. It causes the gauche conformer to have about the same energy in solution as the trans conformer. This amount of stabilization is, however, not quite enough to match the experimental evidence that the gauche conformer of dimethoxyethane and related compounds in solution is actually favored by some −1 to −2 kJ/mol over the trans conformer. There is some indication that the remaining discrepancy can be reduced only by using very large basis sets. Nonetheless, the amount of stabilization calculated convinced us that the gauche effect in dimethoxyethane and, by inference, in poly(ethylene oxide) is very probably caused by the presence of a polarizable medium and is not due to some conformational preference of the molecule as such.

References and Notes

(1) Yoshida, H.; Kaneko, I.; Matsuura, H.; Ogawa, Y.; Tasumi, M. *Chem. Phys. Lett.* **1992**, *196*, 601.

(2) Barzaghi, M.; Gamba, A.; Morosi, G. *J. Mol. Struct.* (*Theochem*) **1988**, *170*, 69.

(3) Tsuzuki, S.; Uchimaru, T.; Tanabe, K.; Hirano, T. *J. Phys. Chem.* **1993**, *97*, 1346.

(4) Jaffe, R. L.; Smith, G. D.; Yoon, D. Y. *J. Phys. Chem.* **1993**, *97*, 12745.

(5) Sadlej, A. J.; Oddershede, J.; Sabin, J. R. Diercksen, G. H. F. *Chem. Phys.* **1988**, *122*, 297.

(6) Tasaki, K.; Abe, A. *Polym. J.* **1985**, *17*, 641.

(7) Matsuura, H.; Fukuhara, K.; Tamaoki, H. *J. Mol. Struct.* **1987**, *156*, 293.

(8) Wright, P. V. In *Polymer Electrolyte Reviews 2*; MacCallum, J. R., Vincent, C. A., Eds.; Elsevier: London, 1989.

(9) Mark, J. E.; Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1415; **1966**, *88*, 3702. Abe, A.; Mark, J. E. *Ibid.* **1976**, *98*, 6468. Abe, A.; Tasaki, K.; Mark, J. E. *Polym. J.* **1985**, *17*, 883.

(10) Smith, G. D.; Yoon, D. Y.; Jaffe, R. L. *Macromolecules* **1993**, *26*, 5213.

(11) Wipff, G.; Weiner, P.; Kollman, P. *J. Am. Chem. Soc.* **1982**, *104*, 3249.

(12) Podo, F.; Némethy, G.; Indovina, P. L.; Radics, L.; Viti, V. *Mol. Phys.* **1974**, *27*, 521.

(13) Andersson, M.; Karlström, G. *J. Phys. Chem.* **1985**, *89*, 4957.

(14) Bressanini, D.; Gamba, A.; Morosi, G. *J. Phys. Chem.* **1990**, *94*, 4299.

(15) Allinger, N. L.; Chang, S. H. M.; Hindman Glaser, D. *Isr. J. Chem.* **1980**, *20*, 51.

(16) Müller-Plathe, F.; Rogers, S. C.; van Gunsteren, W. F. *Macromolecules* **1992**, *25*, 6722.

(17) Tapia, O. In *Molecular Interactions*; Ratajczak, H., Orville-Thomas, W. J., Eds.; Wiley: Chichester, 1983; Vol. 3.

(18) Wong, M. W.; Frisch, M. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 4776.

(19) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92, Revision C*; Gaussian, Inc.: Pittsburgh, PA, 1992.

(20) Hubbard, J. B.; Wolynes, P. G. *J. Chem. Phys.* **1978**, *69*, 998.

(21) Tomasi, J.; Bonaccorsi, R.; Cammi, R.; Olivares del Valle, F. J. *J. Mol. Struct.* (*Theochem*) **1991**, *234*, 401.

(22) Diercksen, G. H. F.; Sadlej, A. J. *J. Chem. Phys.* **1981**, *75*, 1253. Diercksen, G. H. F.; Sadlej, A. J. *Chem. Phys.* **1981**, *61*, 293. Diercksen, G. H. F.; Kellö, V.; Sadlej, A. J. *J. Chem. Phys.* **1983**, *79*, 2918.