Conformational Analysis of Poly(propylene oxide) and Its Model Compound 1,2-Dimethoxypropane

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ABSTRACT: Conformational characteristics of poly(propylene oxide) (PPO) and its model compound, 1,2-dimethoxypropane (1,2-DMP), have been investigated. For 1,2-DMP, ab initio molecular orbital (MO) calculations at the MP2/6-31+G*, MP2/6-311+G*, and MP4/6-31+G* levels were carried out, and the free energies and dipole moments of all the possible conformers were evaluated. The bond conformations and the average dipole moments were calculated from the MO data and compared with the corresponding experimental values. The MO calculations, in general, reproduced the observations quite well. The unknown parameters in the Karplus equation expressing the dihedral-angle dependence of the vicinal coupling constant $^3J_{COCH}$ were determined by comparison of the $^3J_{COCH}$ values observed for 1,2-DMP with those calculated from the MO results. The free energies were broken down into conformational energy contributions corresponding to first-, second-, and third-order intramolecular interactions. All the first-order-interaction energies were found to be positive. On the other hand, the second-($E_{\omega 1}$ and $E_{\omega 2}$) and third-(E_χ) order-interaction energies, which reflect nonbonded C−H···O contacts, were found to be negative; for example, the $E_{\omega 1}$, $E_{\omega 2}$, and E_χ values determined for gaseous 1,2-DMP at the MP2/6-31+G* level are −1.236, −1.884, and −1.266 kcal mol^{-1}, respectively. As pointed out for 1,2-dimethoxyethane, the *gauche* stability of the C−C bond in the O−C−C−O sequence appears to arise from the nonbonded C−H···O interactions. Using the rotational isomeric state (RIS) scheme with up to third-order interactions, the characteristic ratio and dipole moment ratio of isotactic PPO were calculated and found to be in good agreement with the observations.

Introduction

It is well-known that the C−C bond in the O−C−C−O sequence of ethers often exhibits *gauche* preference.[1-4] The simplest polymeric chain including such a bond sequence may be poly(ethylene oxide), $[-CH_2CH_2O-]_x$ (PEO). Conformational characteristics of PEO and its monomeric model compound, 1,2-dimethoxyethane ($CH_3OCH_2CH_2OCH_3$, 1,2-DME), have been investigated by using a variety of theoretical and experimental techniques. Within the framework of the rotational isomeric state (RIS) approximation,[5] conformational energies of PEO were determined so as to attain the best agreement between calculated and observed unperturbed dimensions and dipole moments, and the *gauche* state of the C−C bond was revealed to be more stable by 0.4−0.5 kcal mol^{-1} than the *trans* one.[6-8] By the analysis of vicinal ^{1}H−^{1}H coupling constants of 1,2-DME,[9,10] it was indicated that the conformational energy, depending on the medium, varies from −0.4 kcal mol^{-1} (in the vapor phase) to −1.2 kcal mol^{-1} (in water). The *gauche* stability has been considered a characteristic feature of such bond sequences, thus being termed the *gauche* oxygen effect.[11] An electron diffraction study[12] has shown that gaseous 1,2-DME is composed of the tgt (23%), ttt (13%), ttg (3%), tgg (53%), gtg (5%), and ggg (3%) conformers. Vibrational spectroscopic studies[13,14] have estimated its conformational stability in the liquid phase to be in the order tgt > ttt > tgg > ttg, while the most populated conformation in an argon matrix at 34 K was found to be ttt. Accumulation of data has, in principle, supported the *gauche* stability, but not all of them are consistent in this respect.

Recent ab initio molecular orbital (MO) calculations for 1,2-DME[15,16] have suggested the presence of a specific attractive interaction between the 2-oxygen and the terminal 6-methyl hydrogen (hereafter designated as the C−H···O interaction), and the stabilizing energy was reported to amount to −1.2 to −1.4 kcal mol^{-1}. Then, the distance between the oxygen and hydrogen atoms ranges from 2.591 to 2.963 Å, thus being partly shorter than the sum of the van der Waals radii of the two atoms. This attractive interaction occurs in the $g^{\pm}g^{\mp}$ conformations for the C−O/C−C bond pair. It has been suggested that, owing to these attractions, the *gauche* state of the C−C bond is more stable than the *trans* one. However, the above-mentioned conformational analyses of PEO[8] and 1,2-DME[9,10] have been carried out on the assumption that the nonbonded C−H···O interaction should be repulsive. The conformer populations calculated from the MO results are comparable with those determined from the gas-phase electron diffraction.[12] Furthermore, the MO calculations have successfully reproduced the observations of not only ^{1}H- and ^{13}C-NMR vicinal coupling constants and dipole moments of 1,2-DME but also unperturbed dimensions and dipole moments of PEO.[16,17]

The *gauche* oxygen effect was also found for poly(propylene oxide), $[-CH_2CH(CH_3)O-]_x$ (PPO),[11] whose structural unit differs from that of PEO only by a methyl substituent. Because of the asymmetric methine carbon, PPO has two stereochemical arrangements (e.g., (*R*)- and (*S*)-optical forms),[18] and the two *gauche* states around the skeletal C−C bond are unequivalent. By fitting the RIS analysis to the observed unperturbed dimensions and dipole moments of PPO, conformational energies for the C−C bond were evaluated to be −0.3 kcal mol^{-1} (designated as E_α) for the g^+ state and 0.35−0.5 kcal mol^{-1} (E_β) for the g^- state.[11] Here the definition of the conformers is based on the (*R*)-configuration.[19] In order to clarify the *gauche* oxygen effect in PEO and PPO, it is useful to carry out a conformational analysis of PPO and its model compound 1,2-dimethoxypropane (1,2-DMP, $CH_3OCH_2CH(CH_3)OCH_3$) using ab initio MO

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Table 1. Free Energies (ΔG_k, kcal mol^{-1}) Relative to the *All-Trans* Conformation, Dipole Moments (μ_k, D), and Conformer Fractions (f_k) for All Possible Conformers of Gaseous 1,2-DMP at 298.15 K, Evaluated from ab Initio MO Calculations at MP2/6-31+G*, MP2/6-311+G*, and MP4/6-31+G* Levels[a]

					MP2/6-31+G*			MP2/6-311+G*			MP4/6-31+G*			
no. k	conformation[b]			statistical weight(s)	ΔG_k	μ_k^{MO}	f_k	ΔG_k	μ_k^{MO}	f_k	ΔG_k	μ_k^{MO}	f_k	μ_k^{BOND} [c]
1	t	t	t	1	0.000	0.354	0.236	0.000	0.348	0.272	0.000	0.378	0.249	0.413
2	t	t	g^+	γ	3.196	1.953	0.001	3.137	1.909	0.001	3.167	2.026	0.001	2.214
3	t	t	g^-	δ	0.429	1.538	0.114	0.563	1.501	0.105	0.412	1.624	0.124	1.774
4	t	g^+	t	α	0.617	1.191	0.083	0.631	1.179	0.094	0.643	1.283	0.084	1.527
5	t	g^+	g^+	$\alpha\gamma$	3.799	2.675	0.000	3.686	2.623	0.001	3.878	2.821	0.000	3.117
6	t	g^+	g^-	$\alpha\delta\omega_1$	−0.195	1.500	0.327	−0.064	1.482	0.303	−0.143	1.600	0.317	1.704
7	t	g^-	t	β	1.570	1.685	0.017	1.489	1.658	0.022	1.686	1.824	0.014	2.240
8	t	g^-	g^+	$\beta\gamma\omega_2$	2.183	1.799	0.006	2.271	1.775	0.006	2.302	1.881	0.005	1.796
9	t	g^-	g^-	$\beta\delta$	1.376	2.703	0.023	1.278	2.466	0.032	1.523	2.703	0.019	3.170
10	g^+	g^+	t	$\sigma\alpha$	2.300	2.625	0.005	2.420	2.580	0.005	2.339	2.759	0.005	3.016
11	g^+	g^+	g^+	$\sigma\alpha\gamma\chi$	4.021	1.407	0.000	3.766	1.398	0.001	4.167	1.511	0.000	1.701
12	g^+	g^+	g^-	$\sigma\alpha\delta\omega_1$	1.341	2.259	0.025	1.558	2.116	0.020	1.408	2.259	0.023	2.412
13	g^+	g^-	t	$\sigma\beta\omega_2$	0.986	1.833	0.045	1.174	1.804	0.038	1.113	1.938	0.038	2.024
14	g^+	g^-	g^-	$\sigma\beta\delta\omega_2$	1.511	2.159	0.018	1.680	1.987	0.016	1.642	2.159	0.016	2.412
15	g^-	t	t	σ	1.246	2.049	0.029	1.316	2.002	0.030	1.240	2.123	0.031	2.240
16	g^-	t	g^+	$\sigma\gamma$	4.463	0.230	0.000	4.546	0.205	0.000	4.413	0.230	0.000	0.404
17	g^-	t	g^-	$\sigma\delta$	1.867	2.491	0.010	2.063	2.450	0.008	1.845	2.491	0.011	2.632
18	g^-	g^+	t	$\sigma\alpha\omega_1$	0.797	1.257	0.061	1.030	1.240	0.048	0.815	1.312	0.063	1.230
19	g^-	g^+	g^+	$\sigma\alpha\gamma\omega_1$	4.281	2.224	0.000	4.408	2.180	0.000	4.320	2.317	0.000	2.456

[a] The MO calculations for the C_6H_{12}, C_6H_6, and DMSO solutions are given in the supporting information. [b] In the rotational isomeric state (RIS) approximation, 27 (=3^3) conformers may be enumerated. Of them, however, g^+tt, g^+tg^-, g^+tg^-, $g^+g^-g^+$, $g^-g^+g^-$, g^-g^-t, $g^-g^-g^+$, and $g^-g^-g^-$ conformations are essentially absent because of severe steric hindrance. [c] The dipole moment calculated using the geometries optimized at the HF/6-31G* level and bond dipole moments: m_{C-O} = 1.07 D and m_{C-C} = 0.00 D. For the optimized geometries, see the supporting information.

calculations and also investigate the various conformation-dependent properties experimentally observed. This is the object of the present study.

In this paper, the results of ab initio MO calculations for 1,2-DMP are reported first. Secondly, conformer fractions, bond conformations, and dipole moments calculated from the MO data are compared with experiment to examine the reliability of the MO calculations. Thirdly, the temperature dependence of vicinal $^{13}C-^1H$ coupling constants $^3J_{COCH}$'s of 1,2-DMP were analyzed to determine the unknown parameters of the Karplus equation for the C−O−C−H sequence of ether chains. The free energies evaluated for all possible conformers were broken down to obtain the conformational energies representing the first-, second-, and third-order interactions. Using the RIS scheme with up to third-order interactions, the unperturbed dimensions and dipole moment of isotactic PPO are calculated and compared with experimental values. Finally, the conformational characteristics of PPO are discussed in relation to the *gauche* oxygen effect.

Computational Procedure

Ab initio MO calculations were carried out by using the Gaussian92 program[20] installed on a Cray C916 supercomputer or a cluster of IBM RS/6000 computers in the Research Information Processing Station (RIPS), Tsukuba. For every possible conformer of 1,2-DMP in vacuo, its molecular structure was fully optimized at the Hartree-Fock (HF)/6-31G* level, and then the cavity radius required for the self-consistent reaction field (SCRF) calculation[21] was concomitantly estimated. Default convergence criteria were used for the SCF and geometry optimization. Next, all possible conformer geometries in other solvents (cyclohexane, benzene, and dimethyl sulfoxide (DMSO)) were optimized using HF/6-31G* including solvation.[22] With the geometries thus determined, single-point computations using the second-order Møller–Plesset (MP) perturbation and 6-31+G* (MP2/6-31+G*//HF/6-31G*) and 6-311+G* (MP2/6-311+G*//HF/6-31G*) basis sets were carried out. In addition, fourth-order MP calculations using the 6-31+G* basis set (MP4(SDQ)/6-31+G*//HF/6-31G*) were carried out for the gas phase only. Vibrational frequencies for the equilibrium geometries were evaluated at the HF/6-31G* level and scaled by 0.89 to correct overestimation of the frequencies.[24] Zero-point and thermal vibrational energy corrections were performed using the scaled frequencies. Furthermore, the corrected entropy change from 0 to 298.15 K was computed. Accordingly, the energy thus evaluated corresponds to the free energy at 298.15 K. In this paper, as an example, a calculation at the MP2/6-31+G* level in cyclohexane solution is abbreviated as MP2/6-31+G* (C_6H_{12}).

Experimental Section

^{13}C-NMR Measurements. For the ^{13}C-NMR experiments, 1,2-di(methoxy-$^{13}C_2$)propane (1,2-DMP-$^{13}C_2$) was prepared by the Williamson method; propylene glycol and iodomethane-^{13}C were heated with an excess of sodium hydride. The concentration of the solutions was 5% (v/v), and standard NMR glass tubes of 5-mm o.d. were used. Samples for gas-phase measurements were prepared as reported previously.[23] Carbon-13 NMR spectra of 1,2-DMP-$^{13}C_2$ were measured at 125.65 MHz on a JEOL JNM-GSX-500 spectrometer by using the gated decoupling technique. The FID signal was accumulated 16 (in solutions) or 512 (in vapor phase) times. During a measurement, the probe temperature was held constant within ±0.1 °C.

Results and Discussion

Ab Initio MO Calculations for 1,2-DMP. In Table 1 the results of the ab initio MO calculations for the gas phase are summarized. The MO results for the solutions and optimized geometrical parameters are given in the supporting information. For each conformer, the free energy ΔG_k relative to the *all-trans* conformation and the dipole moment μ_k^{MO} are listed. In this paper, for example, the notation tg^+g^- for 1,2-DMP denotes that bonds 2−4 take the t, g^+, and g^- states, respectively. For the bond and atom numbers, see Figure 1b. For 1,2-DMP, one may enumerate 27 (=3^3) conformers. Of them, however, eight states, g^+tt, g^+tg^+, g^+tg^-, $g^+g^-g^+$, $g^-g^+g^-$, g^-g^-t,$g^-g^-g^+$, and $g^-g^-g^-$, are absent because of steric hindrance. Indeed, for example, the g^+tt conformation, which has a severe

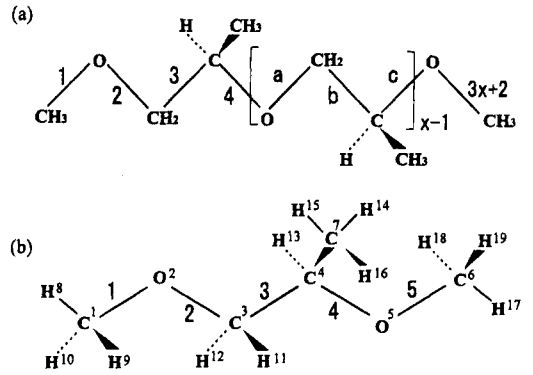


Figure 1. Schematic representation of (a) isotactic poly((*R*)-propylene oxide) dimethyl ether and (b) its monomeric model compound (*R*)-1,2-dimethoxypropane (1,2-DMP) in their *all-trans* conformations. As indicated, the atoms are numbered, and the bonds are termed. The degree of polymerization is represented by *x*.

steric conflict between the C^1H_3 and C^7H_3 groups, was led to ttt by the geometrical optimization. Thus, the MO results for 19 other conformers are given in Table 1.

The conformer fraction f_k can be evaluated from

$$f_k = \frac{\exp(-\Delta G_k/RT)}{\sum_k^K \exp(-\Delta G_k/RT)} \quad (1)$$

where R is the gas constant, T is the absolute temperature, and K is the number of the conformers (=19). The f_k values at 298.15 K (25 °C) are listed in Table 1. From the table, the most stable conformation can be seen to be tg^+g^-. In the gas phase ca. 57% of the ensemble is suggested to take either the tg^+g^- or ttt conformation. The dipole moment of a conformer has often been calculated as the sum of bond dipole moments m's.[5] Given in the most right-hand column of Table 1 are the dipole moments, μ_k^{BOND}'s, estimated from the optimized geometries and m's. In the calculations the following bond dipole moments were assumed: $m_{C-O} = 1.07$ D and $m_{C-C} = 0$ D.[8,25] It can be understood that the μ_k^{BOND} value is always slightly larger than the corresponding μ_k^{MO}.

The bond conformation, namely the η (t, g^+, or g^-) state fraction of the ith bond, can be calculated from

$$p_{\eta;i} = \sum_{k_{\eta;i}} f_{k_{\eta;i}} \quad (2)$$

where $k_{\eta;i}$ stands for the conformer whose ith bond takes the η state. From the ΔG_k values, the fractions for bonds 2–4 of 1,2-DMP were calculated according to eqs 1 and 2. Then the temperatures were set equivalent to those employed in the NMR measurements.[23,26] The results are summarized in Table 2. For comparison, the experimental values for bond 3, being obtained from the vicinal $^1H-^1H$ coupling constants, are also given. The conformational stability was shown by the experiments to be in the order $g^+ > t > g^-$ for the gas phase and the cyclohexane and benzene solutions, whereas $g^+ > g^- > t$ for the DMSO solution. For nonpolar solvents, the agreement between theory and experiment is satisfactory; however, the polar solvent dependence observed is not well reproduced. A comparison between the MP2/6-31+G* and MP4/6-31+G* results reveals that inclusion of higher-order electron correlation has little effect. Adoption of a larger basis set (6-31+G* → 6-311+G*) leads to a slight improvement in the agreement. It is thus difficult to determine which combination of MO method and basis set is most suitable. For this reason, all the MO data obtained were used in the following analysis.

Dipole Moments of 1,2-DMP. The ensemble average $\langle A \rangle$ of a quantity A_k can be obtained from

$$\langle A \rangle = \sum_k^K A_k f_k \quad (3)$$

According to this formula, the average dipole moments at 36 °C were calculated from the μ_k^{MO} and μ_k^{BOND} data, being compared in Table 3 with the experimental values.[25] The $\langle \mu_k^{MO} \rangle$ values are smaller than the observations by 6–12%. On the other hand, the $\langle \mu_k^{BOND} \rangle$ values for the C_6H_{12} solution exactly agree with the corresponding experimental data.

^{13}C-NMR Data from 1,2-DMP. Figure 2 shows examples of ^{13}C-NMR spectra of the two methoxy carbons of 1,2-DMP-$^{13}C_2$. The ^{13}C-NMR signal of C^1 is split into four by the direct couplings with H^8, H^9, and H^{10} and further divided into three by vicinal couplings with H^{11} and H^{12}. Similarly, it can be easily understood that the signal from C^6 is composed of four doublets. Shown in Figure 2 are the triplet of C^1 (left) and the doublet of C^6 (right) observed (a) from the gas phase at 145 °C and (b) from the DMSO solution at 58 °C. The

Table 2. Bond Conformations[a] of 1,2-DMP, Evaluated from the ab Initio MO Data

		bond 2			bond 3			bond 4		
medium	method	t	g^+	g^-	t	g^+	g^-	t	g^+	g^-
gas[b]	MP2/6-31+G*	0.721	0.141	0.138	0.372	0.460	0.168	0.496	0.023	0.481
	MP2/6-311+G*	0.749	0.126	0.125	0.387	0.439	0.174	0.515	0.025	0.460
	MP4/6-31+G*	0.727	0.130	0.143	0.393	0.456	0.151	0.502	0.022	0.476
	experiment[c]				0.38 ± 0.01	0.41 ± 0.01	0.21 ± 0.01			
C_6H_{12}[d]	MP2/6-31+G*	0.768	0.115	0.117	0.365	0.502	0.133	0.451	0.011	0.538
	MP2/6-311+G*	0.800	0.098	0.102	0.387	0.473	0.140	0.479	0.012	0.509
	experiment[c]				0.41 ± 0.00	0.41 ± 0.00	0.19 ± 0.01			
C_6H_6[e]	MP2/6-31+G*	0.765	0.117	0.118	0.362	0.503	0.135	0.447	0.011	0.542
	MP2/6-311+G*	0.797	0.100	0.103	0.384	0.474	0.142	0.475	0.012	0.513
	experiment[c]				0.34 ± 0.01	0.43 ± 0.01	0.23 ± 0.01			
DMSO[f]	MP2/6-31+G*	0.717	0.147	0.136	0.331	0.492	0.177	0.413	0.014	0.573
	MP2/6-311+G*	0.752	0.127	0.121	0.347	0.465	0.188	0.434	0.016	0.550
	experiment[c]				0.27 ± 0.01	0.43 ± 0.01	0.31 ± 0.01			

[a] Calculated from eq 2. [b] At 145 °C. [c] Determined from NMR vicinal $^1H-^1H$ coupling constants. Reference 23. [d] At 43 °C. [e] At 43 °C. [f] At 58 °C.

Table 3. Average Dipole Moments[a]

medium	method	$\langle\mu_k^{MO}\rangle$	$\langle\mu_k^{BOND}\rangle$
gas	MP2/6-31+G*	1.315	1.495
	MP2/6-311+G*	1.248	1.464
	MP4/6-31+G*	1.361	1.471
C_6H_{12}	MP2/6-31+G*	1.480	1.598
	MP2/6-311+G*	1.420	1.568
	experiment[b]	1.57	
C_6H_6	MP2/6-31+G*	1.506	1.613
	MP2/6-311+G*	1.447	1.584
	experiment[b]	1.65	
DMSO	MP2/6-31+G*	1.803	1.783
	MP2/6-311+G*	1.745	1.765

[a] In Debyes. Calculated from eq 3. At 36 °C. [b] Reference 25. Measured at 36 °C.

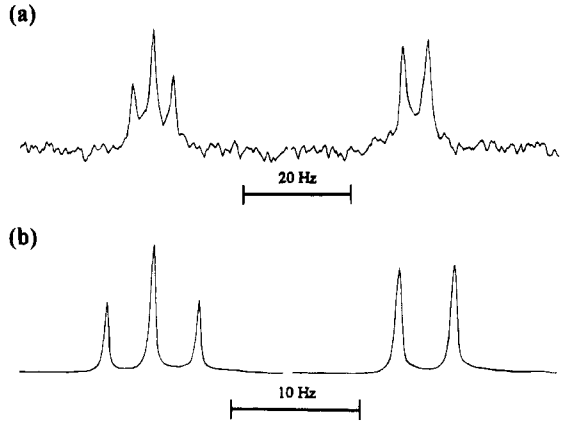


Figure 2. Examples of 125.65 MHz ^{13}C-NMR spectra of the C^1 (left) and C^6 (right) atoms of 1,2-DMP-$^{13}C_2$ ($^{13}CH_3OCH_2$-$CH(CH_3)O^{13}CH_3$) (a) in gas phase at 145 °C and (b) in DMSO-d_6 at 58 °C. The direct and vicinal coupling constants are as follows: (a) $^1J_{C^1H} = 139.45 \pm 0.10$, $^1J_{C^6H} = 139.52 \pm 0.06$, $^3J_{C^1H^{11,12}} = 3.76 \pm 0.02$, and $^3J_{C^6H^{13}} = 4.63 \pm 0.02$ Hz; (b) $^1J_{C^1H} = 140.48 \pm 0.02$, $^1J_{C^6H} = 140.36 \pm 0.00$, $^3J_{C^1H^{11,12}} = 3.60 \pm 0.00$, and $^3J_{C^6H^{13}} = 4.31 \pm 0.01$ Hz.

vicinal coupling constants, $^3J_{C^1H^{11,12}}$ and $^3J_{C^6H^{13}}$, that is, the splitting widths of the triplet and doublet, provide information regarding the conformational states of bonds 2 and 4, respectively. Figure 3 shows the temperature dependence of both coupling constants.

The observed $^3J_{C^1H^{11,12}}$ and $^3J_{C^6H^{13}}$ can be related to the conformer fraction f_k according to

$$^3J_{C^1H^{11,12}} = \frac{^3J_{C^1H^{11}} + {}^3J_{C^1H^{12}}}{2} \quad (4)$$

and

$$^3J_{C^sH^t} = \sum_k^K {}^3J_{COCH}(\phi_{k;i}^{st}) f_k \quad (5)$$

where $\phi_{k;i}^{st}$ is the dihedral angle between the carbon s and proton t around the C−O bond i of the kth conformer. The dihedral-angle dependence of $^3J_{COCH}$ is modeled by the Karplus equation[27,28]

$$^3J_{COCH}(\phi) = a\cos^2\phi - b\cos\phi + c \quad (6)$$

where a, b, and c are the coefficients. So far, derivations of the Karplus equation for $^3J_{COCH}$ have been attempted.[30] For example, on the basis of crystallographic and NMR data from monosaccharide derivatives, Tvaroška et al.[31] have offered an equation such as $^3J_{COCH}(\phi) = 5.7\cos^2\phi - 0.6\cos\phi + 0.5$. Despite the benefits of the elaborate work, these equations, being mostly determined for rigid carbohydrates, are known to give too small $^3J_{COCH}$ values for flexible ether chains. From the observed $^3J_{COCH}$ value of dimethyl ether, Dorman et al.[32] have estimated ^3J_T ($\sim{}^3J_{COCH}(180°)$) = 11.8 Hz and ^3J_G ($\sim{}^3J_{COCH}(60°)$) = 2.7 Hz. Doskočilová et al.[33] have found $10.4 < {}^3J_T < 11.1$ Hz and $2.2 < {}^3J_G < 2.6$ Hz from the observations for various ether chains.

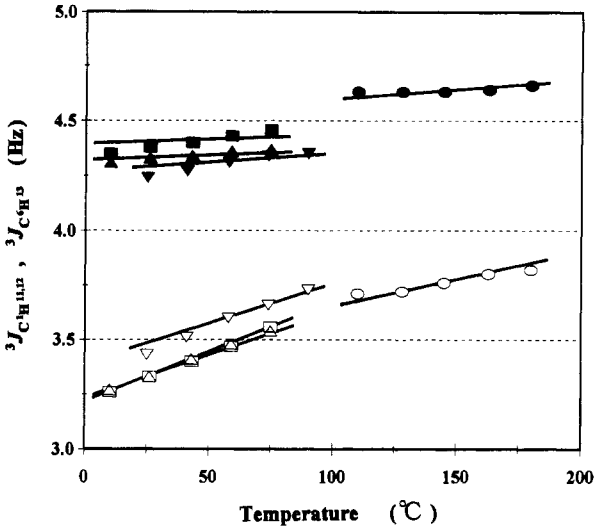


Figure 3. Temperature dependence of vicinal coupling constants $^3J_{C^1H^{11,12}}$ and $^3J_{C^6H^{13}}$ of 1,2-DMP-$^{13}C_2$; (○) $^3J_{C^1H^{11,12}}$ in the gas phase; (●) $^3J_{C^6H^{13}}$ in the gas phase; (□) $^3J_{C^1H^{11,12}}$ in C_6D_{12}; (■) $^3J_{C^6H^{13}}$ in C_6D_{12}; (△) $^3J_{C^1H^{11,12}}$ in C_6D_6; (▲) $^3J_{C^6H^{13}}$ in C_6D_6; (▽) $^3J_{C^1H^{11,12}}$ in DMSO-d_6; (▼) $^3J_{C^6H^{13}}$ in DMSO-d_6. The solid lines represent calculations using the free energies and dihedral angles obtained at the MP2/6-311+G*//HF/6-31G* level. Although the simulation was carried out for each medium and each set of MO data, the Karplus equations thus obtained can be expressed as $^3J_{COCH}(\phi) = (6.76 \pm 0.31)\cos^2\phi - (2.71 \pm 0.14)\cos\phi + (2.07 \pm 0.15)$ (Hz).

The MO calculations indicate that the dihedral angles treated here are scattered to a large extent; the observed $^3J_{COCH}$ values are the averages over various ϕ angles. Therefore, the Karplus equation for $^3J_{COCH}$ of ether chains may be derived from the MO data and the experimental $^3J_{C^1H^{11,12}}$ and $^3J_{C^6H^{13}}$ values. Since the substituent effect of a methyl group on the coupling constants is known to be virtually negligible,[34] it may be assumed that the Karplus equation is common to $^3J_{C^1H^{11}}$, $^3J_{C^1H^{12}}$, and $^3J_{C^6H^{13}}$.

The coefficients a, b, and c were adjusted by the simplex method[35] so as to minimize the sum of discrepancies between the calculated and observed coupling constants. This simulation was carried out for each set of MO data. All the three coefficients determined were, however, found to fall into a narrow range: $a = 6.76 \pm 0.31$, $b = 2.71 \pm 0.14$, and $c = 2.07 \pm 0.15$. In Figure 3, the solid lines represent the coupling constants calculated from the MP2/6-311+G* data, being found to be located on or around the observed data. For other sets of MO data, good agreement between theory and experiment was attained. The Karplus equation thus obtained gives $^3J_{COCH}(180°) = 11.54 \pm 0.37$ Hz and $^3J_{COCH}(60°) = 2.41 \pm 0.18$ Hz. These values agree well with the estimates of Dorman et al. and almost satisfy the criteria of Doskočilová et al. Raman spectroscopic studies[36] on isopropyl methyl ether $CH_3OCH(CH_3)_2$ have estimated the energy difference between the C_1 and C_s forms to be 2.2 kcal mol^{-1}. From its microwave spectrum,[37] the dihedral angles between the methoxy carbon and isopropyl hydrogen atoms of the C_1 and C_s

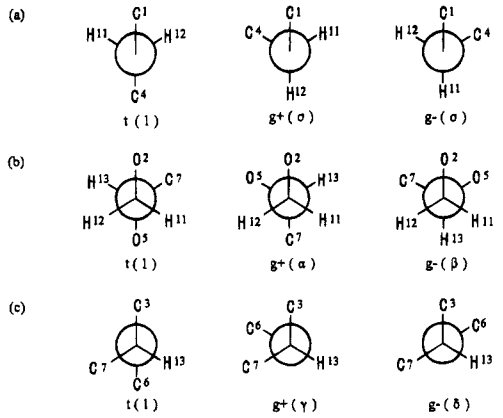


Figure 4. Preferred conformations and definition of the statistical weights for the first-order interactions of 1,2-DMP: (a) bond 2 (equivalent to bond a of PPO), (b) bond 3 (bond b), and (c) bond 4 (bond c). The Greek letter in parentheses represents the statistical weight of the first-order interaction. The superscript number of each atom corresponds to that in Figure 1b.

forms can be estimated to be 45.3 and 180°, respectively. Accordingly, the $^3J_{COCH}$ value at 298.15 K can be estimated as $[2\ ^3J_{COCH}(45.3°) + {}^3J_{COCH}(180°)\exp(-2.2/RT)]/[2 + \exp(-2.2/RT)] = 3.61 \pm 0.24$ Hz. The experimental value of 3.85 Hz has been reported.[32]

Conformational Energies. So far, it has been shown that the ab initio MO calculations can reproduce the observed conformation-dependent dipole moments and spin–spin coupling constants of 1,2-DMP fairly well. Next, the free energies of 19 conformers are broken down into conformational free energies corresponding to specific intramolecular interactions.

Inspection of the MO results and the molecular model of 1,2-DMP allows us to define the first-order interactions (between atoms and groups separated by three bonds), as shown in Figure 4, where the Greek letter stands for the statistical weight. These parameters are related to the conformational energies through the Boltzmann factor; that is, $\alpha = \exp(-E_\alpha/RT)$, etc. In the conventional RIS treatment,[5] interactions up to the second-order (between atoms and groups separated by four bonds) are taken into account. The statistical weight for the 1,5-C–H···O interaction mentioned in the Indroduction is denoted by ω.[38] Hereafter, it is simply referred to as the ω interaction. Therefore, the five first-order α, β, γ, δ, and σ and the second-order ω interactions are first considered. The E_ξ ($\xi = \alpha, \beta, \gamma, \delta, \sigma$, and ω) values may be obtained by minimizing the following function:[39]

$$S(\boldsymbol{E}) = \frac{1}{K}\sum_{k=1}^{K}\Delta_k^2(\boldsymbol{E}) \tag{7}$$

where

$$\Delta_k(\boldsymbol{E}) = \sum_{\xi}\mathbf{1}(\xi)E_\xi - \Delta G_k \tag{8}$$

The function $\mathbf{1}(\xi)$ gives a value of unity if the conformer k has the ξ interaction; otherwise it is set equal to zero.

For example, a least-squares fitting using the MP2/6-31+G* (gas) data yielded a standard deviation (the square root of $S(\boldsymbol{E})$) as large as 0.495 kcal mol^{-1}. Thus this result is unacceptable. Large discrepancies between ΔG_k and the sum of E_ξ's were found for the tg$^-$g$^+$ ($\Delta_k = +1.34$ kcal mol^{-1}), g$^+$g$^+$g$^+$ (+1.04), g$^+$g$^-$t (+0.59), and g$^+$g$^-$g$^-$ (+0.49) states. Of them, the g$^+$g$^+$g$^+$ conformation has the C–C bond in the g$^+$ state, and others in the g$^-$ state. Accordingly, it was assumed that the ω interaction consists of two contributions. One (ω_1) was assigned to a second-order C–H···O interaction with the C–C bond being in the g$^+$ state, and the other (ω_2) to that with the bond in the g$^-$ state. In addition, only the g$^+$g$^+$g$^+$ conformer was presumed to have an extra stabilization energy E_χ. The meanings of these interactions will be discussed later. The statistical weight(s) assigned to each conformer are listed in Table 1. Using this new assignment, a least-squares fitting was reattempted; the eight parameters E_α, E_β, E_γ, E_δ, E_σ, $E_{\omega 1}$, $E_{\omega 2}$, and E_χ were adjusted so as to minimze the $S(\boldsymbol{E})$ value. Consequently, the standard deviation for the MP2/6-31+G* (gas) results was reduced to 0.168 kcal mol^{-1}, indicating that the energy partition is satisfactory. The E_ξ values thus determined are summarized in Table 4. It should be noted that the E_α, E_β, E_γ, E_δ, and E_σ values are not exactly equal to the ΔG_k values of the tg$^+$t, tg$^-$t, ttg$^+$, ttg$^-$, and g$^-$tt states.

Absolute values of all the conformational energies are found to decrease with increasing solvent polarity. For example, the E_σ value varies from 1.6 (in the gas phase) to 1.3 (in DMSO) kcal mol^{-1}. The corresponding experimental values have been reported for compounds with similar bond sequences: diethyl ether, 1.1 kcal mol^{-1} by infrared and Raman spectroscopy;[40] ethyl methyl ether, 1.5 ± 0.2[41] and 1.11[42] kcal mol^{-1} by infrared spectroscopy and 1.23 ± 0.27 kcal mol^{-1} by electron diffraction.[43] When bond 4 takes the g$^+$ state, a steric conflict occurs among the C^3H_2, C^6H_3, and C^7H_3 groups; the E_γ value reaches as large as ca. 3 kcal mol^{-1}. At first sight of the Newman projection in Figure 4c, the t and g$^-$ states may not be distinguishable. Since the C^3 and C^7 atoms are the methylene and methyl carbons, respectively, however, a small energy difference (E_δ) arises. All the first-order-interaction energies, E_α, E_β, E_γ, E_δ, and E_σ, were found to be positive, whereas the second- ($E_{\omega 1}$ and $E_{\omega 2}$) and the third- (E_χ) order-interaction energies were negative. As found for 1,2-DME,[15,16] the nonbonded C–H···O interactions were characterized as attractive, and their *strengths* amount to −1.2 to −1.9 kcal mol^{-1} in the gas phase (cf. −1.2 to −1.4 kcal mol^{-1} for gaseous 1,2-DME). These facts indicate that the g$^+$ preference of the C–C bond is not due to the α interaction but to the ω_1 and χ ones.

Tayler and Kennard[44] have investigated 113 crystal structures determined by neutron diffraction and found many close C–H···O contacts. They have concluded that such interactions are more likely to be attractive than repulsive and proposed the criteria for the C–H···O contacts: (1) the O···H length shorter than the sum (~2.70 Å) of van der Waals radii of oxygen and hydrogen atoms; (2) the ∠C–H···O angle larger than 90°. From this point of view, the optimized geometries of all the conformers of 1,2-DMP were examined, and consequently, some short C–H···O contacts were found in the conformers having the ω_1, ω_2, and χ interactions. In Table 5 all the cases observed for gaseous 1,2-DMP are summarized. By way of example, the tg$^+$g$^-$, g$^+$g$^-$t, and g$^+$g$^+$g$^+$ states, which have the ω_1, ω_2, and χ interactions, respectively, are depicted in Figure 5. A 1,5-C–H···O contact between the oxygen and the terminal methyl hydrogen atoms is indicated to exist in the tg$^+$g$^-$, g$^+$g$^+$g$^-$, g$^-$g$^+$t, and g$^-$g$^+$g$^+$ conformers, which have the ω_1 interaction. A 1,4-C–H···O and a 1,5-C–H···O contact can be found in the tg$^-$g$^+$, g$^+$g$^-$t, and g$^+$g$^-$g$^-$

Table 4. Conformational Energies Evaluated by the ab Initio MO Calculations[a]

	MP2/6-31+G*				MP2/6-311+G*				MP4/6-31+G*
	gas	C_6H_{12}	C_6H_6	DMSO	gas	C_6H_{12}	C_6H_6	DMSO	gas
first-order interaction									
E_α	0.714	0.527	0.502	0.238	0.695	0.519	0.494	0.237	0.765
E_β	1.297	1.171	1.153	0.896	1.187	1.063	1.045	0.805	1.431
E_γ	3.057	2.979	2.967	2.813	3.031	2.938	2.925	2.781	3.065
E_δ	0.352	0.238	0.223	0.029	0.404	0.294	0.278	0.096	0.358
E_σ	1.516	1.419	1.406	1.256	1.625	1.529	1.516	1.376	1.502
second-order interaction									
$E_{\omega 1}$	−1.236	−1.064	−1.040	−0.787	−1.135	−0.971	−0.947	−0.704	−1.231
$E_{\omega 2}$	−1.884	−1.768	−1.753	−1.536	−1.689	−1.582	−1.567	−1.367	−1.870
third-order interaction									
E_χ	−1.266	−0.948	−0.908	−0.480	−1.545	−1.260	−1.222	−0.817	−1.125
$S(\boldsymbol{E})^{1/2}$	0.168	0.182	0.185	0.260	0.168	0.184	0.188	0.260	0.171

[a] In kcal mol^{-1}.

Table 5. Close C−H···O Contacts Found for Gaseous 1,2-DMP by the Geometrical Optimization at the HF/6-31G* Level

C−H···O interaction	conformation			O···H pair[a]	O···H distance (Å)	∠C−H···O (deg)
ω_1	t	g^+	g^-	2···18	2.506	114.4
	g^+	g^+	g^-	2···18	2.523	112.0
	g^-	g^+	t	5···10	2.558	114.1
	g^-	g^+	g^+	5···10	2.534	113.4
ω_2	t	g^-	g^+	2···16	2.590	94.1
				2···19	2.495	114.5
	g^+	g^-	t	2···16	2.649	93.0
				5···9	2.530	111.2
	g^+	g^-	g^-	2···16	2.643	93.0
				5···9	2.557	113.0
χ	g^+	g^+	g^+	2···19	2.631	111.4
				5···9	2.880	105.9

[a] For the oxygen and proton numbers, see Figure 1b.

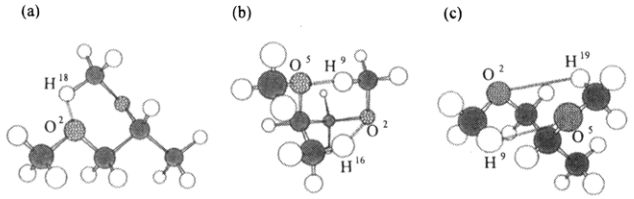


Figure 5. Illustration of the C−H···O interactions: (a) the tg^+g^- ($\alpha\delta\omega_1$) state with a 1,5-C−H···O contact, (b) the g^+g^-t ($\sigma\beta\omega_2$) state with a 1,4-C−H···O and a 1,5-C−H···O contact, and (c) the $g^+g^+g^+$ ($\sigma\alpha\gamma\chi$) state with two 1,5-C−H···O contacts. Here, the symbols in parentheses represent their statistical weights. For the oxygen and hydrogen numbers, see Figure 1b.

conformations. When bond 3 takes the g^- state, a hydrogen atom of the pendent CH_3 group may come into contact with its nearest oxygen atom. Therefore, the ω_2 interaction seems more attractive than ω_1 (e.g., at the MP2/6-31+G* (gas) level, $E_{\omega 1} = -1.236$ and $E_{\omega 2} = -1.884$ kcal mol^{-1}). The $g^+g^+g^+$ conformer would have two 1,5-C−H···O contacts; however, the O^5···H^9 distance does not satisfy one of the above criteria. The stabilization due to this third-order interaction is comparable with that of ω_1 ($E_\chi = -1.266$ kcal mol^{-1} at the MP2/6-31+G* (gas) level).

Statistical Weight Matrices for 1,2-DMP. The RIS scheme for chain molecules, developed by Nagai[45] and Flory[5] et al. is usually based on the first- and second-order interactions and three rotational isomeric states (i.e., t, g^+, and g^-). Then, all the statistical weight matrices assigned to the skeletal bonds are 3 × 3. According to the 3 × 3 matrix treatment, the statistical weights for the $g^+g^-g^+$ and $g^-g^+g^-$ states are given as $\sigma\beta\gamma\omega_2^2$ (2.10 kcal mol^{-1}) and $\sigma\alpha\delta\omega_1^2$ (0.11 kcal mol^{-1}), respectively, where the values in the parentheses are the free energies as calculated from the conformational energies of the MP2/6-31+G* (gas) data. In particular, the latter conformer appears as if to be stable and highly populated. In fact, steric repulsion between both terminal CH_3 groups does not allow these conformers to exist. As shown above, the χ interaction only appears in the $g^+g^+g^+$ conformation, thus being regarded as the third-order. Therefore, interactions up to the third-order should be taken into account for 1,2-DMP. According to the formulation by a Chinese group,[46,47] the statistical weight matrices for bonds 2−4 are respectively given by

$$\boldsymbol{U}_2 = \begin{array}{c} \\ t \\ g^+ \\ g^- \end{array} \begin{array}{c} \begin{array}{ccc} t & g^+ & g^- \end{array} \\ \begin{bmatrix} 1 & \sigma & \sigma \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \end{array} \tag{9}$$

$$\boldsymbol{U}_3 = \begin{array}{c} \\ t \\ g^+ \\ g^- \end{array} \begin{array}{c} \begin{array}{ccccccccc} t & g^+ & g^- & t & g^+ & g^- & t & g^+ & g^- \end{array} \\ \begin{bmatrix} 1 & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \alpha & \beta\omega_2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & \alpha\omega_1 & 0 \end{bmatrix} \end{array} \tag{10}$$

$$\boldsymbol{U}_4 = \begin{array}{c} \\ t\,t \\ t\,g^+ \\ t\,g^- \\ g^+t \\ g^+g^+ \\ g^+g^- \\ g^-t \\ g^-g^+ \\ g^-g^- \end{array} \begin{array}{c} \begin{array}{ccccccccc} t & g^+ & g^- & t & g^+ & g^- & t & g^+ & g^- \end{array} \\ \begin{bmatrix} 1 & \gamma & \delta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & \gamma & \delta\omega_1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & \gamma\omega_2 & \delta \\ 1 & \gamma & \delta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & \gamma\chi & \delta\omega_1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & \delta \\ 1 & \gamma & \delta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & \gamma & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & \gamma\omega_2 & \delta \end{bmatrix} \end{array} \tag{11}$$

Here the rows and columns of these matrices are indexed to rotational states for the preceding and current bonds. It should be noted that the (6,8) and (8,6) elements of U_4 corresponding to the $g^+g^-g^+$ and $g^-g^+g^-$ conformations are set equal to zero on the above-mentioned grounds.[48]

Characteristic Ratio and Dipole Moment Ratio of Isotactic PPO. In Figure 1a, isotactic poly((*R*)-propylene oxide) dimethyl ether is schematically represented.[49] For the reasons stated above, intramolec-

ular interactions up to the third-order should be considered for PPO as well. By comparison between Figure 1a,b, it can be easily understood that the U_2–U_4 matrices are the same as those of 1,2-DMP. For bond a, inspection of the molecular model leads to a 9 × 9 matrix such as

$$U_a = \begin{array}{c} \\ t\ t \\ t\ g^+ \\ t\ g^- \\ g^+\ t \\ g^+\ g^+ \\ g^+\ g^- \\ g^-\ t \\ g^-\ g^+ \\ g^-\ g^- \end{array} \begin{array}{c} \begin{array}{ccccccccc} t & g^+ & g^- & t & g^+ & g^- & t & g^+ & g^- \end{array} \\ \begin{bmatrix} 1 & \sigma & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & \sigma \\ 1 & \sigma & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & \sigma \\ 1 & \sigma & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & \sigma \end{bmatrix} \end{array} \tag{12}$$

For bond b, we have

$$U_b = \begin{array}{c} \\ t\ t \\ t\ g^+ \\ t\ g^- \\ g^+\ t \\ g^+\ g^+ \\ g^+\ g^- \\ g^-\ t \\ g^-\ g^+ \\ g^-\ g^- \end{array} \begin{array}{c} \begin{array}{ccccccccc} t & g^+ & g^- & t & g^+ & g^- & t & g^+ & g^- \end{array} \\ \begin{bmatrix} 1 & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \alpha & \beta\omega_2 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 1 & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \alpha & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 1 & \alpha & \beta & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \alpha & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & \alpha\omega_1 & 0 \end{bmatrix} \end{array} \tag{13}$$

Owing to steric conflicts, the elements corresponding to the tg^-g^+, $g^+g^+g^-$, $g^+g^-g^+$, and $g^-g^+g^-$ states in U_b are set equal to zero. The U_c matrix is the same as U_4 of 1,2-DMP.

In the RIS scheme, configuration-dependent properties such as the characteristic ratio $\langle r^2\rangle_0/nl^2$ and dipole moment ratio $\langle\mu^2\rangle/nm^2$ are treated as a function only of geometrical parameters and conformational energies. Here $\langle r^2\rangle_0$ is the unperturbed mean square of the end-to-end distance, n is the number of skeletal bonds, and l^2 is the averaged value of the square of the bond lengths. Of the geometrical parameters, positions of potential minima will largely change with the conformer. For simplicity, therefore, the geometrical parameters that Abe et al. designated as set I[11,50] have been employed in this study: bond lengths, C–C = 1.53 Å and C–O = 1.43 Å; bond angles, ∠COC = ∠CCO = 111.5°; dihedral angles, $\phi_{t;a} = 180°$, $\phi_{g^+;a} = -80°$, $\phi_{g^-;a} = 80°$, $\phi_{t;b} = 180°$, $\phi_{g^+;b} = -60°$, $\phi_{g^-;b} = 60°$, $\phi_{t;c} = 160°$, $\phi_{g^+;c} = -60°$, and $\phi_{g^-;c} = 80°$. For the bond dipole moments, the same values as for 1,2-DMP were used. From viscosity measurements under the Θ condition (in isooctane at 50 °C) of isotactic PPO,[53] the experimental values of the characteristic ratio were obtained, and the dipole moments were observed from the C_6H_{12} and C_6H_6 solutions. In the calculations, therefore, the conformational energies evaluated for these solutions were used, and temperatures were set equivalent to those employed in the correponding experiments. According to the conventional RIS scheme,[5] conbined with the modification by Xu et al.,[46,47] values of $\langle r^2\rangle_0/nl^2$ and $\langle\mu^2\rangle/nm^2$ for isotactic poly(propylene oxide) dimethyl ether were calculated. Then the degree of polymerization, x, was assumed to be 100. The results are listed in Table 6.

Table 6. Characteristic Ratio $\langle r^2\rangle_0/nl^2$ and Dipole Moment Ratio $\langle\mu^2\rangle/nm^2$ of Isotactic PPO,[a] Calculated from the Conformational Energies Listed in Table 4

method	medium	$\langle r^2\rangle_0/nl^2$ [b]	$\langle\mu^2\rangle/nm^2$ [c]
MP2/6-31+G*	C_6H_{12}	5.91	0.455
	C_6H_6	5.88	0.461
MP2/6-311+G*	C_6H_{12}	6.16	0.423
	C_6H_6	6.12	0.430
experiment	isooctane	6.01[d]	
	C_6H_{12}		0.47[e]
	C_6H_6		0.52[e]

[a] The degree of polymerization was assumed to be 100. [b] At 50 °C. [c] At 35 °C. [d] Allen et al. have determined the $(\langle r^2\rangle_0/M)^{1/2}$ values for seven fractions of isotactic PPO in the Θ state (in isooctane at 50 °C).[53] Here M is the molecular weight. From the data, the $\langle r^2\rangle_0/nl^2$ ratios can be estimated as follows: 5.81 (B1), 5.75 (B6), 5.91 (B8), 6.59 (C2), 6.03 (C3), 5.84 (C4), and 6.11 (C5), where the fraction numbers they used are given in the parentheses. The average value is 6.01. [e] Reference 25.

Configuration-dependent properties of PPO are known to exhibit explicit solvent dependence.[18] Indeed, a comparatively large difference in the $\langle\mu^2\rangle/nm^2$ value was observed between the C_6H_{12} and C_6H_6 solutions.[25] In the viscosity measurement, a nonpolar solvent, isooctane, was used. Thus, it may be assumed that the $\langle r^2\rangle_0/nl^2$ value reflects the configuration similar to that in nonpolar cyclohexane. If we examine the calculated values from this point of view, we can find that the conformational energies from the MP2/6-31+G* (C_6H_{12}) data have given the best agreement between theory and experiment. The MP2/6-311+G data have yielded rather mediocre agreement.

The bond conformations were evaluated from the E_ξ values of the MP2/6-31+G* (C_6H_{12}) data, and the results are given in Table 7. On the basis of the RIS analysis for the experimental $\langle r^2\rangle_0/nl^2$ and $\langle\mu^2\rangle/nm^2$ values, Abe et al.[11] have offered two combinations of conformational energies: (set I) $E_\sigma = 1.3$, $E_\alpha = -0.3$, $E_\beta = 0.35$, and $E_\omega = 0.4$ kcal mol^{-1}; (set II) $E_\sigma = 0.9$, $E_\alpha = -0.3$, $E_\beta = 0.5$, and $E_\omega = 0.4$ kcal mol^{-1}. From the two sets the $p_{\eta;i}$ values were calculated according to the 3 × 3 matrix treatment, being listed in Table 7. The fractions obtained from the MO data are comparable with the previous results.[11] Both studies have estimated the conformational stability of bond b to be in the order $g^+ > t > g^-$. This tendency can be confirmed from NMR data reported by Hirano et al.[54] and Oguni et al.[55] It can be concluded that, in terms of the bond conformation, the previous and present studies have reached almost the same solution. For the conformational energies, however, these two studies have given different conclusions; Abe et al. have suggested that the g^+ preference of the C–C bond is due to the attractive first-order α interaction, while the present MO calculations indicate that the *gauche* oxygen effect arises from the attractive C–H···O interactions (ω_1, ω_2, and χ). In their analysis, only E_α and E_β were adjusted so as to reproduce the experimental values of $\langle r^2\rangle_0/nl^2$ and $\langle\mu^2\rangle/nm^2$; then the E_ω value of 0.4 kcal mol^{-1}, which was obtained from the semiempirical potential energy functions, was fixed. By analogy with the "pentane effect" of *n*-alkanes,[56] it has been believed that the ω interaction should be replusive. Their semiempirical potential energy calculations gave positive E_α and E_β and hence failed to match the results of the analysis. The discrepancy was defined as the extra stabilization due to the *gauche* oxygen effect. In contrast to their results, the

Table 7. Bond Conformations of Isotactic PPO: Comparison of the Present with Previous Studies

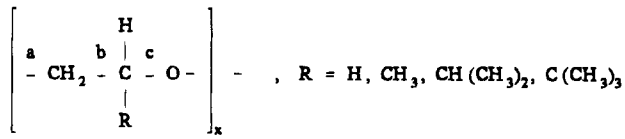
	method	medium	bond a			bond b			bond c		
			t	g^+	g^-	t	g^+	g^-	t	g^+	g^-
this study[a]	ab inito MO	C_6H_{12}	0.879	0.065	0.056	0.398	0.493	0.109	0.439	0.008	0.553
Abe et al.[b]	RIS scheme (set I)		0.93	0.04	0.03	0.35	0.45	0.20	0.57	0.00	0.43
	(set II)		0.87	0.07	0.06	0.36	0.48	0.16	0.57	0.00	0.43
Hirano et al.[c]	^{1}H-NMR	C_6H_{12}				0.38	0.52	0.10			
		C_6H_6				0.36	0.44	0.20			
		$CHCl_3$				0.32	0.47	0.21			
Oguni et al.[d]	^{1}H-NMR	C_6H_6				0.40	0.44	0.16			
		$CHCl_3$				0.34	0.47	0.19			

[a] At 25 °C. The conformational energies evaluated at the MP2/6-31+G* (C_6H_{12}) level, giving the best agreement between the calculated and observed values of $\langle r^2\rangle_0/nl^2$ and $\langle\mu^2\rangle/nm^2$, were employed. [b] At 25 °C. Calculated according to the 3 × 3 matrix scheme, by using two sets of energy parameters: (set I), $E_\sigma = 1.3$, $E_\alpha = -0.3$, $E_\beta = 0.35$, and $E_\omega = 0.4$ kcal mol^{-1}; (set II), $E_\sigma = 0.9$, $E_\alpha = -0.3$, $E_\beta = 0.5$, and $E_\omega = 0.4$ kcal mol^{-1}. Reference 11. [c] Reference 54. Reestimated by using the ^3J_T and ^3J_G values determined for *cis*-2,6-dimethyl-1,4-dioxane (ref 23): for the C_6H_{12} solution, $^3J_T = 9.80$ Hz and $^3J_G = 2.54$ Hz; for the C_6H_6 and $CHCl_3$ solutions, $^3J_T = 9.87$ Hz and $^3J_G = 2.54$ Hz. [d] Reference 55. Reestimated as noted in footnote *c*.

present MO calculations are self-consistent. The conformation- and configuration-dependent properties of 1,2-DME and PEO[15-17] as well as 1,2-DMP and PPO have been consistently interpreted in terms of the attractive C−H···O interaction. Thus, it seems reasonable to accept the presence of the C−H···O attractions.

Solvent Effects. From the ^{1}H-NMR experiments,[23,54,55] the solvent dependence has been found for the conformation of bond 3 (bond b) of 1,2-DMP (PPO); both *gauche* states were shown to be more stabilized with increasing solvent polarity. Such phenomena, being termed the attractive *gauche* effect,[4] have often been observed for dihetero-substituted hydrocarbons. However, the MO calculations using the SCRF method[21] have not well reproduced this experimental tendency. As seen from Table 4, the conformational energies decrease with increasing polarity of the medium. However, the bond conformations thereby calculated exhibit no specific change with the medium. In terms of solvent effects, Eliel et al.[1-3] have extensively studied the conformations of the O−C−C−O sequence mainly by using 2-isopropyl-5-methoxy-1,3-dioxane. They have also found apparent solvent dependence; solvents of higher dielectric constant shift the equilibrium toward the axial isomer, in which the C−C bond in the O−C−C−O array takes the *gauche* state. Of 17 solvents used, however, benzene, toluene, chloroform, methylene chloride, and methanol were indicated to behave as if they were more polar than expected from their dielectric constants. This nonmonotonic solvent behavior was suggested to be due to their polarizability. In the Onsager theory[57] adopted in the SCRF method, the solute is assumed to be placed in a spherical cavity surrounded by a continuous medium of a dielectric constant ϵ; the solvent is identified only by the ϵ value. Thus the SCRF calculation distinguishes little between cyclohexane ($\epsilon = 2.02$) and benzene ($\epsilon = 2.28$); between these two solvents, no particular difference can be found in the calculated $\langle r^2\rangle_0/nl^2$ and $\langle\mu^2\rangle/nm^2$ values. It is expected that the specific dipole−dipole interactions between solute and solvent are incorporated in the MO theory.

Crystal Structures of PPO and the Related Polymers.[58] Crystal structures of polyethers represented by



have been determined already. For example, PEO (R = H) is known to have two crystal modifications characterized by the (7/2) helix (bonds a, b, and c take the t, g, and t states, respectively) and the planar zigzag (ttt) molecular conformations.[59-61] Isotactic PPO (R = CH_3) forms a distorted planar zigzag structure (ttt).[62] On the other hand, poly(isopropylethylene oxide) (R = $CH(CH_3)_2$) (PIPEO)[63] and poly(*tert*-butylethylene oxide) (R = $C(CH_3)_3$) (PTBEO)[64] were found to take the tg^+g^- conformation. For PIPEO, this conformational state is known to be most populated even in solutions.[65] It has been believed that the bulky side group forces the main chain into this peculiar conformation. In the paper on the crystal structure of PIPEO,[63] however, we can find the following description:

> The conformation of the main chain is essentially the tg^+g^- conformation. The g^+g^- sequence is associated with the "pentane effect" and is accepted as attainable only with difficulty. When the generally accepted bond lengths and bond angles and exact *gauche* and *gauche* minus conformations (−60 and +60°) are adopted for poly(isopropylethylene oxide), the intermolecular distance between the oxygen atom and the hydrogen atom attached to the methylene group in the neighboring chemical units is calculated as 1.64 Å, which is too short to permit the g^+g^- sequence. However, in the structure analyzed, this distance is lengthened to 2.25 Å by the large value of the bond angle ∠CCO and the distortion of internal rotation angles from the exact *gauche* and *gauche* minus. This value is still shorter than the sum of the van der Waals radii of the oxygen and hydrogen atoms.

This can be interpreted as crystallographic evidence for the attractive C−H···O interaction.

In order to estimate the stability of the tg^+g^- conformation of PIPEO and PTBEO, ab initio MO calculations have been attempted at the MP2/6-31+G* (gas)//HF/6-31G* (gas) level for 1,2-dimethoxy-3-methylbutane ($CH_3OCH_2CH(CH(CH_3)_2)OCH_3$, DMMB) and 1,2-dimethoxy-3,3-dimethylbutane ($CH_3OCH_2CH(C(CH_3)_3)OCH_3$, DMDMB), which are the monomeric model compounds of PIPEO and PTBEO, respectively, the free energy difference between the tg^+g^- and ttt states was evaluated in the same manner as 1,2-DMP. Besides the three skeletal bonds, DMMB has the freedom of the internal rotation around the C−CHR bond. The geometrical optimization for the ttt conformation was begun with the CC−CH bond set at the t state, and that for tg^+g^-

with the bond at the g^- state. The former makes the ttt conformation the most stable, and the latter was found in an actual PIPEO crystal.[63] The ΔG_k value of the tg^+g^- state at 298.15 K was evaluated as −1.123 kcal mol^{-1} (cf. −0.195 kcal mol^{-1} of 1,2-DMP). For DMDMB, the ttt state should be absent because of steric repulsion. Thus, instead, the ΔG_k value of the tg^+g^- state relative to ttg^- was estimated to be −3.890 kcal mol^{-1}. It should be noted that the ttg^- state of 1,2-DMP has a ΔG_k value of 0.429 kcal mol^{-1}. From these data, the stability of the tg^+g^- conformation, being regarded as intrinsic to the O−C−CHR−O sequence, is proved to be enhanced with the increasing size of the pendent group R. The distances between the oxygen and the methoxy hydrogen atoms of the tg^+g^- conformers of DMMB and DMDMB were estimated to be 2.525 and 2.533 Å, respectively, thus being shorter than the sum of the van der Waals radii.

Summary

Conformational analysis of poly(propylene oxide) (PPO) and its model compound, 1,2-DMP, have been carried out. The following results and conclusions were obtained.

(1) The free energies and dipole moments of all possible conformers of 1,2-DMP were evaluated by ab initio MO calculations including the solvation effect at the MP2/6-31+G*, MP2/6-311+G*, and MP4/6-31+G* levels, and the conformer fractions, the bond conformations, and the average dipole moments were estimated according to the Bolzmann distribution. The bond conformations thus obtained are comparable with those determined from the vicinal $^1H-^1H$ coupling constants. The average dipole moments are, in general, in agreement with the observations.

(2) By comparison of vicinal $^{13}C-^1H$ coupling constants observed from 1,2-DMP with those calculated from the MO data, the Karplus equation for the $^{13}C-O-C-^1H$ sequence of ether chains was determined as $^3J_{COCH}(\phi) = (6.76 \pm 0.31)\cos^2\phi - (2.71 \pm 0.14)\cos\phi + (2.07 \pm 0.15)$ (Hz). This equation was shown to be valid for ethers having the bond sequence such as dimethyl ether and isopropyl methyl ether.

(3) The free energies obtained as above were broken down into conformational energies representing the first-, second-, and third-order interactions. All the first-order-interaction energies were evaluated to be positive, while the second- ($E_{\omega 1}$ and $E_{\omega 2}$) and third- (E_χ) order-interaction energies, which reflect the nonbonded C−H···O contacts, were estimated to be negative. Inspection of the optimized geometries revealed the following facts. The ω_1 interaction comes from a 1,5-C−H···O contact between the oxygen and the terminal methyl hydrogen atoms, ω_2 from a 1,5-C−H···O and a 1,4-C−H···O contact between the oxygen and the pendent methyl hydrogen atoms, and χ from two 1,5-C−H···O contacts. Then the O···H distances are, in principle, shorter than the sum of the van der Waals radii of oxygen and hydrogen atoms.

(4) The characteristic ratio and dipole moment ratio of isotactic PPO were calculated using the RIS method with the conformational energies determined from 1,2-DMP. Then interactions up to the third-order were taken into account. Both ratios calculated for a cyclohexane solution agree well with the experimental data.

As stated above, it was found that the ab initio MO calculations satisfactorily reproduced almost all the conformation-dependent properties available for 1,2-DMP and PPO. It has been believed that the nonbonded C−H···O interactions should be repulsive ($E_\omega \sim 0.4$ kcal mol^{-1}) and that the *gauche* stability of the C−C bond of these compounds is ascribed to the first-order α interaction. However, this study has clearly shown that the *gauche* preference is due to the C−H···O attractions. The stabilizing energies were evaluated to be −1.0 to −1.9 kcal mol^{-1} in nonpolar solvents.

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Supporting Information Available: Tables of the MO calculations (the ΔG_k, μ_k^{MO}, f_k, and μ_k^{BOND} values) for the cyclohexane, benzene, and DMSO solutions and the optimized geometries of 19 conformers of 1,2-DMP (24 pages). Ordering information is given on any current masthead page.

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$$^3J_{C^1H^{11,12}} = \frac{^3J_T(1 - p_{t;2}) + {}^3J_G(1 + p_{t;2})}{2}$$

and

$$^3J_{c^6H^{13}} = {}^3J_T\, p_{g^+;4} + {}^3J_G(1 - p_{g^+;4})$$

where ^3J_T and ^3J_G and the ^3J values between carbon and proton in the *antiperiplanar* and *synclinal* positions, respectively. However, the above relationships are only valid when the dihedral angles of the *i*th (i = 2 or 4) bond are in the standard *trans* (180°) and *gauche* (±60°) positions. In the case of 1,2-DMP there exist certain conformers which, because of the very large deviations from the standard positions, invalidate the use of the above expressions. For the geometrical parameters of 1,2-DMP, see the supporting information.
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$$\frac{p_{g^+;3}}{p_{t;3}} = \frac{1 + \sigma + \sigma\omega_1 + \gamma(1 + \sigma\chi + \sigma\omega_1) + \delta\omega_1(1 + \sigma)}{(1 + \sigma)(1 + \gamma + \delta)}\alpha$$

$$\frac{p_{g^-;3}}{p_{t;3}} = \frac{1 + \sigma\omega_2 + \gamma\omega_2 + \delta(1 + \sigma\omega_2)}{(1 + \sigma)(1 + \gamma + \delta)}\beta$$

and

$$p_{t;3} + p_{g^+;3} + p_{g^-;3} = 1$$

The fractional part of the first two formulas represents the effects of conformations of the neighboring bonds, being termed the preexponential factor ($\mathrm{pef}_{\eta;i}$). The energy parameter can be related to the conformational energy E_ξ by $\langle E_\xi \rangle = E_\xi - RT \ln \mathrm{pef}_{\eta;i}$.
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