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Conformational Properties of Model Compounds of Imide–Ether Molecular Chains

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ABSTRACT: Experimental values at different temperatures of the mean-square dipole moment, $\langle\mu^2\rangle$, of 2,2′-bisphthalimido diethyl ether (PTDE) and 1,8-bisphthalimido-3,6-dioxaoctane (PTDO), model compounds of imide–ether molecular chains, are reported. The values obtained for this quantity in dioxane are 8.28–8.31 D^2 and 11.04–11.22 D^2 for PTDE and PTDO, respectively, in the temperature range 20–50 °C. These results indicate that imide–ether chains exhibit much lower polarity than their benzamide–ether counterparts. The interpretation of the ^{1}H NMR spectrum of PTDE suggests that an increase in the polarity of the solvent raises the gauche population about NCH_2–CH_2O bonds. Both the NMR results and the conformational energy calculations by semiempirical methods suggest that these bonds are nearly freely rotating. However, the evaluation of the mean-square dipole moments as a function of the energy of gauche states about NCH_2–CH_2O bonds indicates that good agreement between theory and experiments is obtained for values of this energy 0.4 ± 0.2 K cal mol^{-1} above that of the alternative trans states.

Introduction

Aromatic polyimides are a class of polymers with great technological importance mainly due to their mechanical and electrical properties and their outstanding thermal resistance. The intractability of these polymers, which in many cases precludes melt molding and processing from solutions, has been circumvented by developing a number of copolymers, i.e., poly(amide–imide)s, poly(ester–imide)s, and poly(ether–imide)s, with averaged properties which make them suitable to be marketed as competitive engineering thermoplastics.[1]

Very few studies have been carried out to elucidate the relationship between structure and conformational properties for polyimides and copolyimides, in spite of the growing interest of these materials. Owing to the insolubility of aromatic polyimides in most organic solvents, experimental data relative to conformational characteristics of these chains are not available; only theoretical calculations have been performed dealing with the flexibility of isolated polyimides.[2] For these theoretical studies, geometry parameters have been determined from the analysis of the X-ray spectra of low molecular weight imides.

The technological importance of polyimides led many workers to try to improve their processability by separating the rigid imide cores with flexible spacers.[3] Thus, aliphatic polymethylene, poly(oxyethylene), and poly(dimethylsiloxane) segments of different lengths have been used as spacers. The solubility of the resulting polymers makes them amenable to the study of the dependence of the physical properties of polyimide chains on the nature and length of the spacers. An obviously interesting conformational property candidate for these studies is the mean-square dipole moment.[4–6] This property, unlike other more traditional conformational properties, can be measured for chains of any length, and whenever the chains have symmetry planes, axes, or points, excluded volume effects are not important.[5,6] However, the insolubility of most polyimides in nonpolar organic solvents is a limitation for the experimental measurement of the dipole moments of the chains, and therefore, this preliminary work addresses the study of the conformational dielectric properties of low molecular weight imide compounds whose structure resembles that of copolyimides. Thus, the dipole moments of 2,2′-bisphthalimido diethyl ether (Figure 1a) and 1,8-bisphthalimido-3,6-dioxaoctane (Figure 1b), model compounds of imide–ether polymers, are reported. The results are critically interpreted by using the rotational isomeric state (RIS) model, and the conformational population about certain bonds are compared with that obtained from the critical interpretation of the ^{1}H NMR spectra of these model compounds.

Experimental Part

Synthesis of the Model Compounds. Chemicals and solvents were reagent grade products, purchased from conventional sources. They were used as received unless otherwise indicated. 2,2′-Dichlorodiethyl ether was distilled through a 40 cm Vigreux column. 1,4-Dioxane was boiled over potassium hydroxide for 24 h and distilled at atmospheric pressure; it was then further distilled over sodium.

2,2′-Bisphthalimido diethyl ether (PTDE) was prepared with 88% yield from 2,2′-dichlorodiethyl ether and potassium phthalimide by the method previously described:[7] mp 156–157 °C (hexane/dioxane 50/50). Anal. Calcd for $C_{20}H_{16}N_2O_5$ (364.36): C, 65.93; H, 4.43; N, 7.69. Found: C, 65.97; H, 4.43; N, 7.58.

1,8-Bisphthalimido-3,6-dioxaoctane (PTDO) was synthesized by refluxing a mixture of 7.40 g (0.05 mol) of 1,8-diamino-3,6-dioxaoctane, 15.54 g (0.105 mol) of phthalic anhydride, and 250 mL of acetic acid for 4 h. A 10.20 g (0.10 mol) portion of acetic anhydride was then added and the reaction still proceeded 1 h further. The crystalline precipitate formed upon cooling was filtered off, washed several times with cold water, and finally dried over P_2O_5 in a vacuum oven for 20 h at 60 °C. After recrystallization from dioxane/heptane (2/1), 20.4 g (yield 79%) of pure product was obtained: mp 186–187 °C. Anal. Calcd for $C_{22}H_{20}N_2O_6$ (408.41): C, 64.70; H, 4.94; N, 6.86. Found: C, 64.71; H, 4.70; N, 6.84.

Dielectric Measurements. The static dielectric permittivity, ϵ, of solutions of PTDE and PTDO in dioxane was measured with a capacitance bridge (General Radio, Type 1620 A) coupled with a three terminal cell, at 10 kHz; at this

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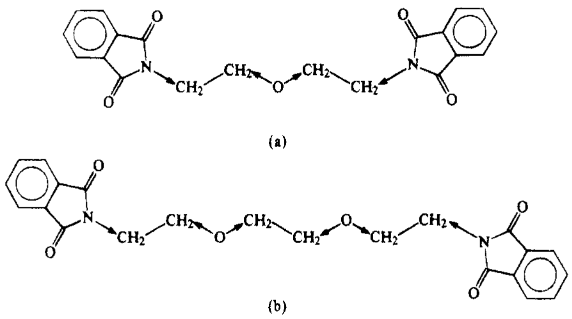


Figure 1. Scheme of 2,2′-bisphthalimido diethyl ether (PTDE) (a) and 1,8-bisphthalamido-3,6-dioxaoctane (PTDO) (b) in all trans conformation. The arrows indicate the direction of the dipoles in the backbone.

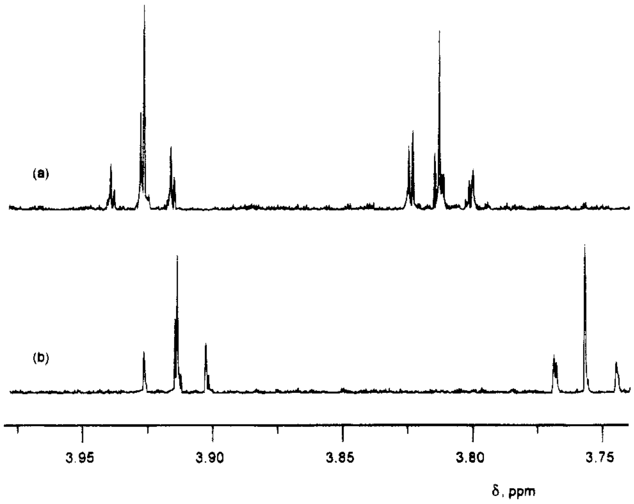


Figure 2. ^{1}H NMR spectra of the ethylene residues (NCH_2-CH_2O) corresponding to 2,2′-bisphthalimido diethyl ether (PTDE) (a) and 1,8-bisphthalimido-3,6-dioxaoctane (PTDO) (b).

frequency, the real part of the complex permittivity of the dilute solutions coincides with the static permittivity. Increments in the index of refraction of the solution with respect to that of the solvent were measured with an Abe refractometer.

NMR Spectra. The ^{1}H NMR spectra of PTDE and PTDO were recorded at 20 °C with a Varian UNITY 500 spectrometer operating at 500 MHz under the following conditions: pulse angle, 65°; acquisition time, 10 s; sweep width, 900 Hz; data size, 32 K. Dioxane-d_8 and dimethyl sulfoxide-d_6 were used as solvents.

2D Inverse proton detected heteronuclear shift correlation spectra were obtained using the HMQC pulse sequence. Data were collected in a 512 × 256 matrix with a spectral width of 809.7 Hz in the proton domain and 7811 Hz in the carbon domain and processed in a 512 × 512 matrix. The experiment was optimized for one-bond heteronuclear coupling constant of 140 Hz. The null time was empirically optimized at 300 ms.

Results

NMR Spectra and Dipole Moments. Figure 2 shows the region corresponding to the methylene protons in the ^{1}H NMR spectra of PTDE and PTDO in dioxane-d_8. The spectrum of PTDE presents a multiplet at 3.813 ppm corresponding to the methylenes linked to oxygen in the NCH_2-CH_2O sequence and a multiplet centered at 3.927 ppm associated with the methylenes linked to the nitrogen. The spectrum of PTDO exhibits a singlet at 3.672 ppm due to the methylenes of the OCH_2-CH_2O sequence, a multiplet at 3.758 ppm corresponding to the methylenes linked to oxygen in the NCH_2-CH_2O segment, and a multiplet centered at 3.915 ppm due to the methylenes linked to nitrogen. The proton assignments were established by 2D inverse proton detected shift correlation experiments. From these, a correlation between the higher field carbon, corresponding to the NCH_2 moiety, and the lower field protons was found, and vice versa.

Table 1. Summary of Dielectric Results for 2,2′-Bisphthalimido Diethyl Ether (PTDE) and 1,8-Bisphthalimido-3,6-dioxaoctane (PTDO) in Dioxane

T, °C	$2n_1\mathrm{d}n/\mathrm{d}w$	$\mathrm{d}\epsilon/\mathrm{d}w$	$\langle\mu^2\rangle$, D^2
		PTDE	
20	0.40_3	3.28_5	8.28
30	0.42_8	3.16_7	8.27
40	0.47_2	3.09_3	8.28
50	0.48_7	2.99_0	8.31
		PTDO	
20	0.34_6	3.77_1	11.04
30	0.35_4	3.64_4	11.10
40	0.36_3	3.51_1	11.16
50	0.37_7	3.39_3	11.22

Values of the mean-square dipole moment, $\langle\mu^2\rangle$, of the model compounds were obtained from the dielectric measurements by means of the standard expression[8]

$$\langle\mu^2\rangle = \frac{27k_BTM}{4\pi\varrho N_A(\epsilon_1+2)^2}\left[\frac{\mathrm{d}\epsilon}{\mathrm{d}w} - 2n_1\frac{\mathrm{d}n}{\mathrm{d}w}\right] \tag{1}$$

where k_B and N_A are, respectively, the Boltzmann constant and Avogadro's number, T is the absolute temperature, M and w represent, respectively, the molecular weight of the model compounds and the weight fraction of solute in the solutions, n and ϵ are, respectively, the index of refraction and the dielectric permittivity of the solution (these symbols with subindex 1 refer to the solvent), and ϱ is the density of the solvent. The terms $\mathrm{d}\epsilon/\mathrm{d}w$ and $\mathrm{d}n/\mathrm{d}w$ were obtained, respectively, from the plots of the increments $\Delta\epsilon = \epsilon - \epsilon_1$ and $\Delta n = n - n_1$ *vs* w, in the limit $w \to 0$. Values of these quantities at different temperatures are given in the second and third columns of Table 1, whereas in the fourth column the results for $\langle\mu^2\rangle$ are shown; the uncertainty in these values was estimated to be ±5%. The dipole moments show a slight positive temperature dependence; the temperature coefficient, expressed in terms of $\mathrm{d}\ln\langle\mu^2\rangle/\mathrm{d}T$, amounts to 0.1×10^{-3} and 0.5×10^{-3} K^{-1} for PTDE and PTDO, respectively.

Theoretical Dipole Moments. A schematic representation of the model compounds in all trans conformations is shown in Figure 1a,b, where the torsion angles associated with this conformation were taken as zero in further calculations. The value of the dipole moment associated with the imide group was considered to be 2.24 D, the dipole moment reported for methylphthalimide;[9] the symmetry of the imide group suggests that the dipole will lie along the $N-CH_2$ bond with the positive end pointing toward the CH_2 group. The dipole moments corresponding to the $O-CH_2$ and CH_2-CH_2 bonds were assumed to be[10] 1.07 and 0.00 D, respectively.

Theoretical values of the mean-square dipole moment of the model compounds were calculated by using matrix methods described in detail elsewhere.[4,11] In short, the values of $\langle\mu^2\rangle$ were obtained by means of the expression

$$\langle\mu^2\rangle = \frac{1}{Z}\mathbf{G}_1 \prod_{i=2}^{i=N-1} [(\mathbf{U}_i \otimes \mathbf{E}_5)\mathbf{G}_i]\mathbf{G}_N \tag{2}$$

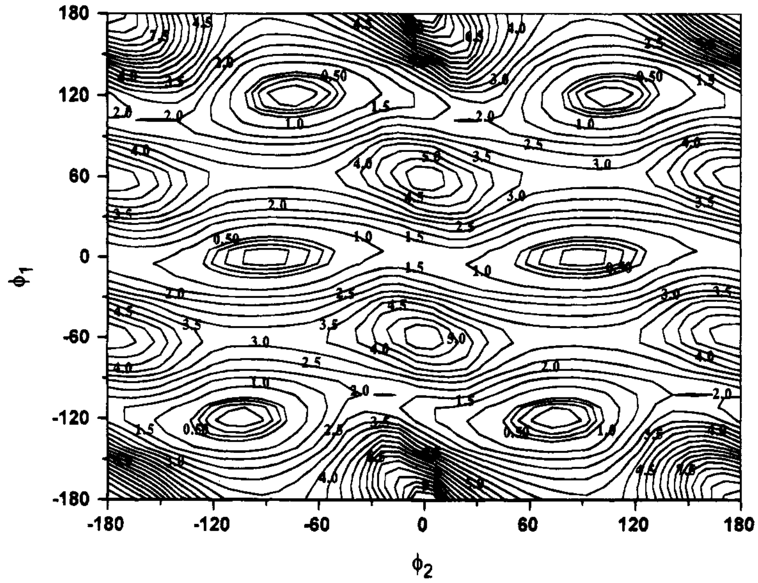


Figure 3. Contour map showing the conformational energy about the N–CH$_2$–CH$_2$O bonds.

where $\mathbf{E}_5$ is the unity matrix of order 5, $\mathbf{U}_i$ is the statistical weight matrix which accounts for the statistical weights of the rotational states (t, g^+, g^-) associated with bond i, and Z is the rotational partition function. The statistical weight matrices associated with the first and last bonds are, respectively, $\mathbf{U}_1 = 1$ and $\mathbf{U}_n =$ column (1 1 1). $\mathbf{G}_i$ is the pseudodiagonal matrix[11]

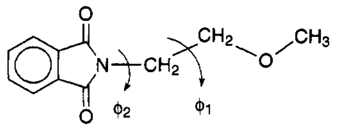
$$\mathbf{G}_i = diag[\mathbf{M}(\varphi_t), \mathbf{M}(\varphi_{g^+}), \mathbf{M}(\varphi_{g^-})] \qquad (3)$$

in which the matrices of the diagonal are given by[11]

$$\mathbf{M}_i = \begin{pmatrix} 1 & 2\mathbf{m}^T\mathbf{T} & \mathbf{m}^2 \\ \mathbf{0} & \mathbf{T} & \mathbf{m} \\ 0 & \mathbf{0} & 1 \end{pmatrix}$$

where $\mathbf{m}$ is the vector dipole moment associated with the skeletal bond, $\mathbf{m}^T$ is its transpose, and $\mathbf{T}(\theta,\varphi)$ (θ and φ are respectively, the skeletal bond angle and the rotational angles) is a transformation matrix which projects the dipole from the reference frame $i + 1$ to the reference frame i. The symbol ⊗ denotes the direct product; $\mathbf{G}_1 =$ row($\mathbf{M}_{11}$, 0, 0) and $\mathbf{G}_N =$ column($\mathbf{M}_{Nf}$(t), $\mathbf{M}_{Nf}(g^+)$, $\mathbf{M}_{Nf}(g^-)$), where $\mathbf{M}_{11}$ and $\mathbf{M}_{Nf}$ represent, respectively, the first row and the last column of the generator matrix $\mathbf{M}$.

The rotational angles about bonds of type CH$_2$CH$_2$–OCH$_2$ are located at 0° (t), ±100° ($g^\pm$), the energy associated with the gauche states having an energy, $\mathbf{E}_{\sigma''}$, 0.9 K cal mol^{-1} above that of the alternative trans states.[4,10] Gauche states about OCH$_2$–CH$_2$O bonds in PTDO, which produce first-order interactions between two oxygen atoms, have an energy, $E_{\sigma'}$, 0.4 kcal mol^{-1} below that of the corresponding trans states; the rotational angles about these bonds are located at[10] 0, ±120°. Gauche states about NCH$_2$–CH$_2$O bonds give rise to first-order interactions between an oxygen and a nitrogen atom. The rotational population about CH$_2$–CH$_2$ (ϕ_1) and N–CH$_2$ (ϕ_2) bonds was evaluated by molecular mechanics methods (MM+, derived from the MM2 force field of Allinger)[12,13] on the model



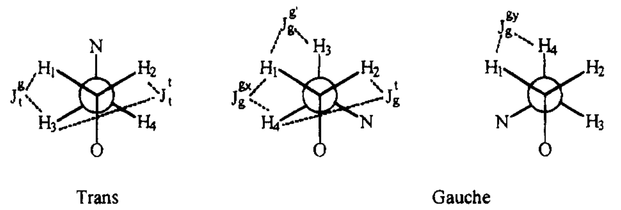


Figure 4. Abraham representation of the conformations of 1,2-disubstituted ethanes.

The contour map for rotations about ϕ_1, ϕ_2 bonds, represented in Figure 3 shows that relatively strong repulsive interactions occurring between the hydrogen atoms of the methylene group and the carbonyl groups in the planar trans conformation are relieved by rotation ca. ±110° about the N–CH$_2$ (ϕ_2) bond. Minima of nearly the same energy are obtained for rotations of the same and different sign about the consecutive bonds of the N–CH$_2$–CH$_2$–O moiety. In other words, the NCH$_2$–CH$_2$O (ϕ_1) bond may be considered nearly freely rotating, the energy minima being located at 0, ±110°.

Attempts were also made to determine the conformational population about NCH$_2$–CH$_2$O bonds from the critical interpretation of the ^{1}H NMR spectra of the model compounds, as will be discussed below. The residue NCH$_2$–CH$_2$O can be considered like 1,2-disubstituted ethanes, which have been described extensively in the literature.[14–16] Following Abraham's nomenclature,[15] the residue indicated above has three rotational isomers as shown in Figure 4, where superscripts denote the orientation of the coupled protons and subscripts denote the rotamers. The values of the vicinal coupling constants in the experimental spectrum correspond to the averaged values

$$J(\mathrm{H1,H3}) = n_t J_t^{\,g} + n_{g^+} J_g^{\,g'} + n_{g^-} J_g^{\,t} \qquad (5)$$

$$J(\mathrm{H1,H4}) = n_t J_t^{\,t} + n_{g^+} J_g^{\,gx} + n_{g^-} J_g^{\,gy}$$

$$n_t + n_{g^+} + n_{g^-} = 1$$

The values of n_t, n_{g^+} and n_{g^-} can be obtained by resolving the equations system or, if we consider that $n_{g^+} = n_{g^-}$, by means of the expression

$$X_{\mathrm{g}} = \frac{2[(J_{\mathrm{t}}{}^{\mathrm{g}} + J_{\mathrm{t}}{}^{\mathrm{t}}) - (J(\mathrm{H1,H3}) + J(\mathrm{H1,H4}))]}{2J_{\mathrm{t}}{}^{\mathrm{g}} + 2J_{\mathrm{t}}{}^{\mathrm{t}} - J_{\mathrm{g}}{}^{\mathrm{g}'} - J_{\mathrm{g}}{}^{\mathrm{t}} - J_{\mathrm{g}}{}^{\mathrm{g}_x} - J_{\mathrm{g}}{}^{\mathrm{g}_y}}; \quad n_{\mathrm{t}} = (1 - X_{\mathrm{g}}) \quad (6)$$

In order to obtain accurate values for the experimental coupling constants, J(H1,H3) and J(H1,H4), the spectra were simulated by using the iterative program[17] PANIC 86, and the values of the chemical shifts and coupling constants obtained are listed in Table 2.

Owing to the impossibility of obtaining the experimental coupling constants ($J_t{}^g$, $J_t{}^t$, $J_g{}^{g'}$, etc.) for the individual conformers, some approximate equations, based on the original Karplus equation,[18] were used to estimate the values of these constants. As in previous papers, we have used the Phillips and Wray[16] equation because it is well parametrized for disubstituted ethanes. The results obtained, shown in Table 2, indicate that the fraction of gauche states about NCH_2-CH_2O bonds is ca. 0.77 for PTDE and 0.72 for PTDO in dioxane-d_8. However, these values are ca. 0.83 for PTDE and 0.73 for PTDO when DMSO-d_6 is used as solvent. Therefore, a certain influence of the type of solvent on the relative population of the conformers can be observed. But even the results obtained in the same solvent show some discrepancy; for example, the results in dioxane suggest that the conformational energy associated with gauche states decreases from ca. −0.31 for PTDE to −0.15 K cal mol^{-1} for PTDO suggesting that these conformational energies cannot be obtained with accuracy high enough from the NMR experiments. Therefore, attempts were made to determine the conformational energy of gauche states about NCH_2-CH_2O bonds from the critical analysis of the dipole moments of the model compounds as will be described below.

The statistical weights $\sigma_{\alpha\beta}$ corresponding to matrices $\mathbf{U}_i$ are Boltzmann factors which are straightforwardly related to the conformational energy $E_{\alpha\beta}$; i.e., $\sigma_{\alpha\beta} = \exp(-E_{\alpha\beta}/RT)$. Second-order conformational statistical weight parameters associated with rotations of different sign about two consecutive bonds were considered to be zero with the exception of those corresponding to the $CH_2O-CH_2-CH_2O$ and $NCH_2-CH_2-OCH_2$ conformations;[4,10] the values of these energies were assumed to be $E_\omega = E_{\omega'} = 600$ cal mol^{-1}.

As can be seen in Figure 1b, the dipoles associated with the skeletal bonds are nearly in antiparallel direction for PTDO and, consequently, the dipole moment of the all trans conformation is ca. zero. The low value of μ^2 for the all trans conformation of PTDE, ca. 1.47 D^2, arises from the nearly antiparallel direction of the resulting dipole of the imide groups and the dipole moment associated with the CH_2OCH_2 group. Therefore, departure from the trans conformation should increase the polarity of the model compounds under study. Theoretical values of the mean-square dipole moment of PTDE and PTDO were obtained at 20 °C by the methods described above using the set of statistical weights $\sigma'' = 0.22$, $\sigma' = 1.95$, $\omega = \omega' = 0.36$. By assuming that the statistical weight associated with gauche states about NCH_2-CH_2O bonds is $\sigma = 1.28$, which corresponds to the energy obtained from the ^{1}H NMR analysis of PTDO, one finds $\langle\mu^2\rangle = 16.0$ D^2, a value that is significantly larger than the experimental result (11.04 D^2); these calculations give $\langle\mu^2\rangle = 12.3$ D^2 for PTDE, a value that is nearly 48% higher than the experimental result. In view of the discrepancies between the experimental results and the dipole moments calculated by using for E_σ the value obtained from the analysis of the ^{1}H NMR spectroscopy, the values of $\langle\mu^2\rangle$ for both molecular compounds were evaluated as a function of E_σ. The results obtained, shown in Figure 5, indicate that the polarity of these molecules is actually very sensitive to the rotational population about bonds of type NCH_2-CH_2O, in the sense that the lower the gauche population about these bonds is the lower $\langle\mu^2\rangle$ is. Fairly good agreement between theoretical and experimental results is found for values of $E_\sigma = 0.4 \pm 0.2$ K cal mol^{-1}. The polarity of PTDO is also sensitive to the conformational energy $E_{\sigma'}$ of gauche states about OCH_2-CH_2O bonds arisen from first-order interactions between two oxygen atoms. Thus, the value of $\langle\mu^2\rangle$ for this compound changes from 8.93 to 18.46 D^2 when $E_{\sigma'}$ decreases from 1 to −1 K cal mol^{-1}. The changes on $\langle\mu^2\rangle$ with the second-order conformational energies are negligible.

In general, the dipole moments of the imide compounds show a relatively strong dependence of the imide residue (μ_i) as indicated in Figure 6 where the values of $\langle\mu^2\rangle$ against E_σ are represented for PTDE. Thus, for $E_\sigma = 0$ K cal mol^{-1}, the value of $\langle\mu^2\rangle$ for PTDE goes up

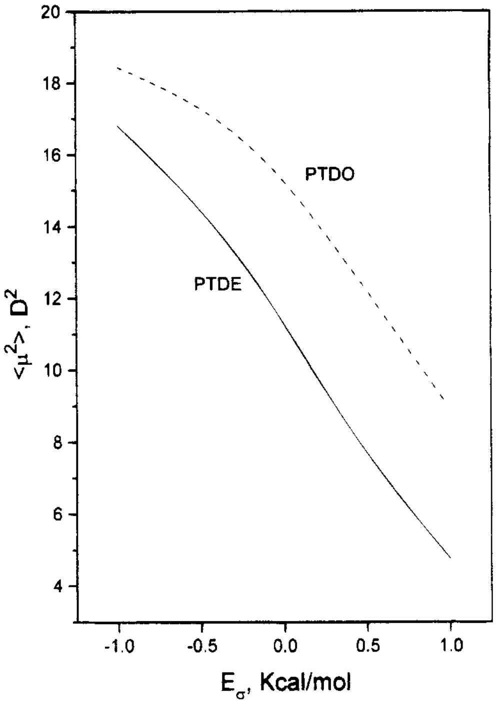


Figure 5. Dependence of the mean-square dipole moment on the conformational energy of gauche states about NCH_2-CH_2O bonds, relative to the trans states, for 2,2′-bisphthalimido diethyl ether (PTDE) and 1,8-bisphthalimido-3,6-dioxaoctane (PTDO).

Table 2. NMR Spectral Parameters, Chemical Shifts, δ(ppm), and Coupling Constants, J(Hz), Obtained from the Analysis of Spectra of 2,2′-Bisphthalimido Diethyl Ether (PTDE) and 1,8-Bisphthalimido-3,6-dioxaoctane (PTDO)

	PTDE		PTDO	
	dioxane-d_8	DMSO-d_6	dioxane-d_8	DMSO-d_6
δ H1, H2	3.813	3.613	3.758	3.544
δ H3, H4	3.927	3.672	3.915	3.665
J(H1,H2)	−14.7	−14.3		−14.9
J(H1,H3) = J(H2,H4)	6.2	6.5	6.5	6.5
J(H1,H4) = J(H2,H3)	5.4	4.6	5.5	5.4
J(H3,H4)	−9.8	−10.4		−11.2
X_g	0.77	0.83	0.72	0.73

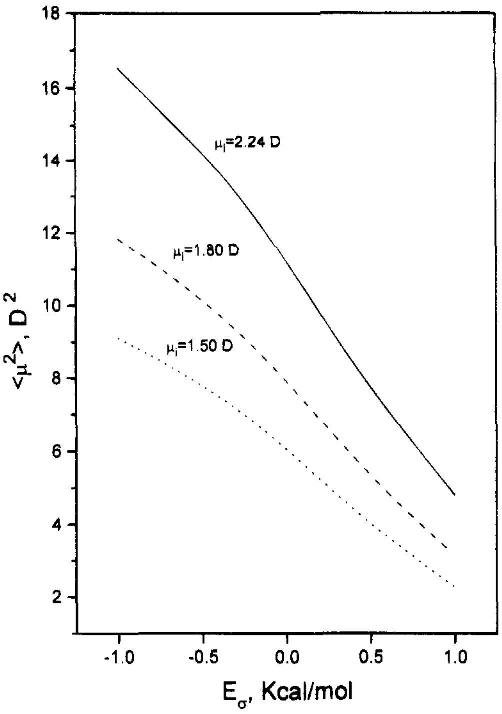


Figure 6. Variation of the mean-square dipole moment of PTDE with the conformational energy of gauche states about NCH_2-CH_2O bonds, relative to the trans states, E_σ, for different values of the dipole moment μ_i associated with the imide residue.

from 6.1 D^2 for $\mu_i = 1.5$ D to 11.2 D^2 for $\mu_i = 2.24$ D. In this case agreement between theoretical and experimental results would be obtained for $\mu_i = 1.84$ D, a value that is somewhat lower than the experimental dipole moment reported for *N*-methylphthalimide.

Smith et al.[19] reported a third-order rotational isomeric state model that gives a good account of the polarity of poly(oxyethylene) as expressed by the mean-square dipole moments, by assuming that the dipole moment of the ether group is 1.43 D instead of 1.07, the value most commonly admitted for this group. According to the model, conformational energies associated with gauche states about OCH_2-CH_2O bonds that give rise to first order O⋯O interactions have an energy 0.1 K cal mol^{-1} above that of the alternative trans states, a value that is much larger than that commonly admitted (−0.4 K cal mol^{-1}) for this conformation. Since the values of $\langle\mu^2\rangle$ for the imide compounds are very sensitive to the energy associated with NCH_2-CH_2O bonds, and very little to second- and even third-order energies, this scheme undoubtly would reproduce the experimental results if it is assumed that these states have higher energy than the alternative trans states.

As for the temperature dependence of the dipole moments of both compounds the calculations suggest that this quantity, expressed in terms of $10^3 \times (d \ln\langle\mu^2\rangle/dT)$, increases as the temperature increases (Figure 7). For example, the value of the temperature coefficient changes from 2.9 to −0.7 K^{-1} for PTDE when the conformational energy of gauche states about NCH_2-CH_2O bonds decreases from 1 to −1 K cal mol^{-1}; these changes are from 1.8 to −0.5 K^{-1} for PTDO. By using 0.4 K cal mol^{-1} for E_σ, one finds that the values of $10^3 \times (d \ln\langle\mu^2\rangle/dT)$ amount to 0.9 and 0.3 K^{-1} for PTDE and PTDO, respectively, in qualitative agreement with the experimental results, 0.1 and 0.5 K^{-1}, respectively.

By comparing the dipole moments of the imide compounds with those of their benzamide counterparts, 1,5-dibenzamido-3-oxapentane (DEBA) [$C_6H_5CONH(CH_2)_2O(CH_2)_2NHCO(C_6H_5)$] and 1,8-dibenzamido-3,6-dioxaoctane (TEBA) [$C_6H_5CONH(CH_2)_2O(CH_2)_2O(CH_2)_2NHCO(C_6H_5)$] one finds that the polarity of the imido compounds is significantly lower than that of the benzamide molecules. For example, the mean-square dipole moments at 30 °C of DEBA and TEBA amounts to[7] 24.6 and 25.4 D^2, whereas the values of these quantities for PTDE and PTDO are 8.3 and 11.0 D^2, respectively. This is due to the large dipole moment of the benzamide group (3.7 D),[9,20,21] on the one hand, and to the fact that the dipole moment associated with the benzamide group forms an angle of nearly 123 °C with the C*–CO bond[20–24] showing that the dependence of $\langle\mu^2\rangle$ on E_σ differs from that predicted for imide compounds, on the other hand. Thus, whereas the all trans conformation for the latter compounds is the conformation of lowest polarity, this conformation exhibits the highest and lowest polarity for DEBA and TEBA, respectively. For both benzamide compounds, however, their polarity increases as the conformational energy of gauche states about NCH_2-CH_2O bonds decreases in opposition with what occurs with the imide model molecules, where the opposite occurs.[7]

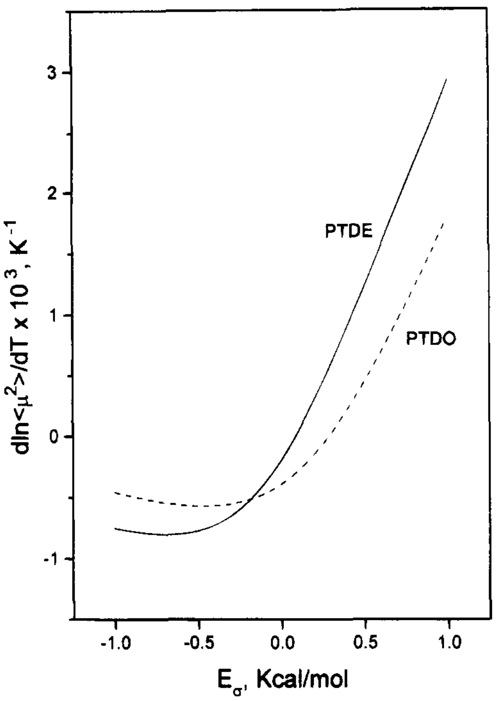


Figure 7. Variation of the temperature coefficient of the mean-square dipole moment with the conformational energy of gauche states about NCH_2-CH_2O bonds, relative to the trans states, for 2,2′-bisphthalimido diethyl ether (PTDE) and 1,8-bisphthalimido-3,6-dioxaoctane (PTDO).

Conclusions

The determination of the conformational energy associated with the rotational states about NCH_2-CH_2O bonds from the critical analysis of the ^1H NMR spectra suggests that the rotational population about these bonds depends on the solvent. Thus, in increasing the polarity of the medium the gauche population increases as a consequence of the fact that decrease the Coulombic repulsive interactions between the oxygen and nitrogen atoms. A decrease in the value of the conformational energy is observed as the molecular weight of the model compounds increases, this quantity coming close to zero for PTDO. Whereas both the analysis of the NMR spectra and the semiempiric quantic methods seem to suggest that NCH_2-CH_2O bonds are nearly freely rotating, the critical interpretation of the dipole moments firmly support preference for trans states over either g^+ or g^- states ($E_\sigma = 0.4 \pm 0.2$ K cal mol^{-1}). To come closer the theoretical and experimental results for freely rotating NCH_2-CH_2O bonds would only be achieved by assuming that the dipole moment associated with the imide group was close to 1.9 D.

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