Conformational Characteristics of Aliphatic Diesters Derived from Fluorinated Diacids

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A comparative study of the polarity and conformational characteristics of diethyl hexafluoroglutarate (DEFG) and its hydrogenated diester counterpart, diethyl glutarate (DEG), is reported. The value at 30 °C of the mean-square dipole moment $\langle \mu^2 \rangle$ of the latter compound, 5.26 D², is nearly 2 times larger the value of this quantity for the fluorinated diester, which amounts to 12.1 D² at the same temperature. Values of the conformational energies associated with the rotational states about the skeletal bonds of the acid residue were calculated by combining molecular mechanics with the critical interpretation of the mean-square dipole moment of these compounds, finding that the rotational populations about the different skeletal bonds are similar in both molecules. The evaluation of $\langle \mu^2 \rangle$ as a function of the conformational energies indicates that the experimental results are reproduced assuming that the conformation in which the C*=O* group eclipses the C^{α}-C^{β} bond in the C^{β}C^{α}C*(O*)O residue is less stable than the alternative conformation in which the carbonyl group eclipses the C^{α}-F (or C^{α}-H) bond. The analysis suggests that the high polarity exhibited by DEFG, in comparison with that of DEG, arises from differences in the orientation and the modulus of the dipoles in both compounds rather than from differences in their conformational characteristics.

Introduction

In spite of the efforts devoted to determine the conformational energies associated with the rotational states about the skeletal bonds of the acid residue of aliphatic diesters, a definite conclusion regarding the values of these quantities has not been reached. For example, from infrared and Raman spectroscopies, Dirlikov et al.¹ inferred that the conformation of the lowest energy about C^{α} —C* bonds in the $C^{\beta}C^{\alpha}C^{*}(O^{*})O$ residue arises when the C^{α} —H bond eclipses the C*=O* group, that is, when gauche states about these bonds are preferred over the alternative trans state, in sharp contrast with the conclusions reached later by Moravie and Corset² from an analysis of the same type of spectra, who reported the trans conformation is more stable than the alternative gauche forms by the enthalpy difference of $\Delta H(C^{\alpha}-C^{*}) = 1.1 \pm 0.3 \text{ kcal mol}^{-1}$. Similar results to those reported by Moravie et al. were obtained by Abe et al.^{3,4} from the critical interpretation of both the NMR spectra and dipole moments of aliphatic diesters. According to these studies, gauche states about C^{α} –C* bonds are more stable by ca. 1 kcal mol⁻¹ than the alternative trans form, whereas the trans form about C^{α} – C^{β} bonds was found to be more stable than the gauche conformation in the aliphatic diesters, with the exception of the dialkyl succinate,⁴ in which the gauche states seem to be preferred over the corresponding trans states. In contrast to these results, an intermediate value of $\Delta H(C^{\alpha}-C^*) = 0.08 \text{ kcal mol}^{-1}$ also has been reported for methyl propionate from the analysis of infrared and Raman spectra.5,6

If the spectroscopic studies regarding the stability of gauche states about $C^{\alpha}-C^*$ bonds are not consistent among them, the critical interpretation of the dipole moments of most aliphatic diesters are not conclusive either. Actually, the correlation between the dipoles associated with two ester groups in these compounds decreases very rapidly as the number of methylene groups, *n*, in the residue acid increases; for diesters with $n \ge 4$, the dipoler correlation is relatively small.⁷ In other words, only the dipole moments of dialkyl succinates and dialkyl propionates show a significant sensitivity to the population of rotational states about $C^{\alpha}-C^*$ bonds. However, the temperature coef-

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ficient of the unperturbed dimensions of polyesters in which $n \ge 4$ shows a strong dependence on the conformational energies associated with the rotational states about $C^{\alpha}-C^{*}$ bonds.^{8,9} In fact, the only way that the theoretical results reproduce the experimental ones is when gauche states about these bonds have similar or lower energies than the alternative trans states. Similar behavior was found in the theoretical evaluation of the temperature coefficients of the unperturbed dimensions of polyesters derived from succinic acid.¹⁰

The discrepancies we referred to above are investigated in a comparative study of the polarity of both diethyl glutarate (DEG) and diethyl hexafluoroglutarate (DEFG) carried out in this work. On the other hand, another goal of this paper is to study how the substitution of the hydrogen atoms in dialkyl esters for fluorine atoms may affect the polarity of the resulting molecule. It is expected that the presence of fluorine atoms may affect not only the dipole moment associated with the ester groups but also the conformational energies associated with the rotational states about the skeletal bonds of the acid residue. For that purpose, in parallel with the experimental determination of the mean-square dipole moment of DEG, the value of this quantity for DEFG is measured. The theoretical value of the mean-square dipole moment of the latter compound is obtained by calculating first the modulus and orientation of the dipole moment associated with the ester group from the charge distributions in the model compound CF₃CF₂COOCH₃. Then, the effect of the conformational energies on the mean-square dipole moment of DEFG is analyzed by using the conventional rotational isomeric state (RIS) model.¹¹ These studies are of interest to interpret and predict the physical properties of materials containing fluorine atoms in their structure. It should be pointed out in this regard that owing to the desirable properties that fluorine atoms confer to polymers, among them low-energy surface, good chemical resistance, and lower water absorption, there is growing interest in the development of new fluorinated materials.12-14

Experimental Section

Diethyl glutarate and diethyl hexafluoroglutarate were obtained, respectively, by esterification with ethanol of glutaric

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Figure 1. ¹H NMR spectrum of diethyl glutarate (DEG).

acid and hexafluoroglutaric acid. The reaction proceeded in nitrogen atmosphere, under reflux, for 16 h. The mixture alcohol—water and the remaining alcohol were removed from the reaction medium by distillation. Dry ethanol was added 2 more times and then removed until the esterification was complete as indicated by the absence of acid groups in the IR spectra. In the esterification of glutaric acid, about 1% (v/v) concentrated chlorohydric acid was added to the reaction medium. The diesters DEG and DEFG were distilled at 100 °C (10^{-2} mmHg) and 74 °C (10^{-2} mmHg), respectively, and finally characterized by NMR spectroscopy. The ¹H NMR spectra for DEG and DEFG, together with the assignment of the resonance peaks, are given in Figures 1 and 2, respectively. In Figure 2, the ¹³C NMR spectrum for DEFG is also shown.

Values of the dielectric permittivity (ϵ) of solutions of the compounds in benzene were obtained with a capacitance bridge (General Radio, Type 1640 A) coupled with a three-terminal cell, at 10 kHz. Increments in the values of the dielectric permittivity with respect to that of the solvent ($\Delta \epsilon = \epsilon - \epsilon_1$) were measured at each temperature of interest for several solutions in which the weight fraction of solute, *w*, was in the interval 0.015–0.003. Increments in the index of refraction (*n*) of the solvent ($\Delta n = n - n_1$) were measured with a Phoenix refractometer. Values of the mean-square dipole moment $\langle \mu^2 \rangle$ at different temperatures were determined by means of the method of Guggenheim and Smith:^{15,16}

$$\langle \mu^2 \rangle = \frac{27k_{\rm B}TM}{4\pi\rho N_{\rm A}(\epsilon_1 + 2)^2} \left[\left(\frac{\mathrm{d}\epsilon}{\mathrm{d}w}\right)^0 - 2n_1 \left(\frac{\mathrm{d}n}{\mathrm{d}w}\right)^0 \right] \tag{1}$$

where $k_{\rm B}$ and $N_{\rm A}$ are, respectively, the Boltzmann constant and Avogadro's number, ρ is the density of the solvent, and M is the molecular weight of the solute. The error involved in the determination of $\langle \mu^2 \rangle$ was estimated to be $\pm 2\%$.

Experimental Results

Values of $d\epsilon/dw$ and dn/dw at 30, 40, 50, and 60 °C for both DEG and DEFG are given respectively, in the second and third columns of Table 1. At each temperature of interest, one can

see that the value of $d\epsilon/dw$ for DEFG is nearly 30% larger than that of DEG, whereas dn/dw for the latter compound is ca. 2 times that of DEG. The results for $\langle \mu^2 \rangle$, shown in the fourth column of Table 1, reveal that the presence of fluorine atoms in the acid residue produces a considerable enhancement of the polarity of the resulting diester. The value of $\langle \mu^2 \rangle$ for DEG at 30 °C, 5.25 D², compares very favorably with the results (5.24, 5.57, 5.71, and 5.34 D²) reported for this quantity in the literature.^{4,17} As far as we know, the dipole moment of diethyl hexafluoroglutarate has not been measured.

The temperature dependence of the dipole moment of DEG, expressed in terms of $10^3 d \ln \langle \mu^2 \rangle / dT$, amounts to 1.9 K^{-1} , somewhat higher than the value reported earlier for this property.⁴ The low value of the temperature coefficient for DEFG, 0.6 K⁻¹, suggests that the dipole moment of this compound is, in comparison, rather insensitive to changes in temperature. It should be pointed out, however, that a few tenths of error in the determination of the mean-square dipole moment can produce significant changes in d $\ln \langle \mu^2 \rangle / dT$, and consequently, $\langle \mu^2 \rangle$ rather than its temperature coefficient should be used in the conformational analysis.

Theoretical Calculations

The bond angles required in the calculations were defined as $\angle C^*CC = \angle CCC = 112^\circ$ for both DEG and DEFG. The rotational states for the latter molecule, calculated by using semiempirical potential functions, were taken to occur at 0°, $\pm 120^{\circ}$. In the evaluation of the dipole moment of DEG, the rotational angles used were those suggested earlier by Abe et al.⁴: 0° , $\pm 123^{\circ}$ for $C^{\alpha}-C^{*}$ and 0° and 0° , $\pm 113^{\circ}$ for $C^{\alpha}-C^{\beta}$. The dipole moment associated with the ester group of the DEG compound amounts to⁴ 1.75 D; it is located in the plane of this group, forming an angle of 123° with the C^{α}-C^{*} bond.^{18,19} The dipoles associated with the DEFG molecule were obtained from the charge distributions calculated for a model compound of the diester. Molecular charges were computed with the Sybyl Molecular Modeling Package¹⁷ employing the MOPAC program and the AM1 procedure.^{21,22} The usefulness of this approach to determine the dipole moments of fluorinated compounds was tested by calculating the dipole moments of trifluoroacetaldehyde and methyl fluoroformate and comparing them with the experimental results. The calculated values amount to 1.90 and 2.54 D for the former and latter compound, respectively, which are in reasonable agreement with the experimental dipole moments reported for these compounds in the literature:²³ 1.65-1.92 D for trifluoroacetaldehyde and 2.61 D for methyl fluoroformate. In view of the good agreement obtained between the calculated and experimental results, we proceeded to determine the distribution of charges in the CF₃CF₂COOCH₃, model compound of the fluorinated diester. The distribution of residual charges for the CF_2 group is $F^{-0.118e}$ – $C^{+0.235e}$ – $F^{-0.118e}$. Hence, taking into account that the length of the C-F bond is 1.36 D, the dipole moment associated with the C-F bond has a value of 0.77 D, and consequently, each of the two C-C skeletal bonds adjacent to a CF2 group can be considered to have a dipole moment of 0.80 D. Moreover, from the distribution of charges of the COOCH₃ residue, one finds that this group has a dipole moment ($\mu_{\rm E}$) of 1.965 D located in the xy plane, its direction forming an angle of 15 $^{\circ}$ with the C*-(O*)-O bond of the ester group. It can be seen in Figure 3 that the dipole moments of the central C-C bonds of the DEFG cancel out so that the dipoles contributing to the polarity of this compound are restricted to a dipole of 0.80 D, $m_{\rm a}$ and $m_{\rm b}$ located along the C–C* bonds, and the dipole $\mu_{\rm E}$ indicated in the figure.



Figure 2. ¹H and ¹³C NMR spectra of diethyl hexafluoroglutarate (DEFG).

 TABLE 1: Dielectric Results for Diethyl Glutarate (DEG)

 and Diethyl Hexafluoroglutarate (DEFG)

compd	<i>T</i> , °C	$2n_1(\partial n/\partial w_2)^0$	$(\partial \epsilon / \partial w_2)^0$	$\langle \mu^2 \rangle$, D ²
DEG	30	0.17	3.11	5.25
	40	0.15	2.98	5.30
	50	0.13	2.89	5.48
	60	0.11	2.76	5.54
DEFG	30	0.32	4.64	12.10
	40	0.31	4.41	12.10
	50	0.31	4.23	12.20
	60	0.31	4.06	12.33

The critical interpretation of the ¹H NMR spectra and dipole moments of aliphatic diesters with general formula H₃CO(*O)-*C(CH₂)_nC*(O*)OCH₃ led Abe and co-workers^{3,4} to conclude that the energy of gauche states about C^{α}-C* bonds, E σ_{α} , is 1 kcal mol⁻¹ above that of the alternative trans states. According to these authors, however, gauche states about C^{α}-C^{β} bonds have an energy $E_{\sigma\beta}$ which seems to be dependent on the number of methylene groups in the residue acid. Thus, values of E σ_{β} = -0.6, 0.3, and 0.8 kcal mol⁻¹ have been reported, respectively, for the methyl esters of succinic, glutaric, and adipic acids.⁴ Rotations of different sign about two consecutive bonds were considered to have energies E_{ω} about 2 kcal mol⁻¹ higher than the alternative tt states.⁴

Molecular mechanics calculations carried out in this work suggest that gauche states about $C^{\alpha}-C^{*}$ bonds of DEFG have an energy $E\sigma_{\alpha}$ ca. 0.1 kcal mol⁻¹ below that of the alternative trans states, whereas the energy $E\sigma_{\beta}$ about $C^{\beta}-C^{\alpha}$ bonds is ca.





Figure 3. Schematic representation of diethyl glutarate and diethyl hexafluoroglutarate (DEFG) in the all-trans conformation showing the dipoles associated with the molecules.

0.8 kcal mol⁻¹ above that of the corresponding trans states. Rotations of different sign about two consecutive bonds were considered to be forbidden. It should be pointed out that preliminary calculations showed that the mean-square dipole moments of both DEG and DEFG are nearly insensitivity to the values of the second-order energies, E_{ω} and $E_{\omega'}$, for values of this quantities higher than 1.4 kcal mol⁻¹.



Figure 4. Dependence of the mean-square dipole moment of diethyl glutarate (DEG) and diethyl hexafluoroglutarate (DEFG) on the energy associated with gauche states about C^*-C^{α} bonds.

In view of the discrepancies concerning the energies of the rotational populations about C^{α} -C* bonds in aliphatic diesters, values of $\langle \mu^2 \rangle$ were obtained by using the conventional RIS scheme for $-2 < E\sigma_{\alpha} < 2$ kcal mol⁻¹, where $E\sigma_{\alpha}$ is the energy of gauche states about these bonds with respect to the corresponding trans states. In the evaluation of the mean-square dipole moment of DEG, it was assumed that the gauche population about $C^{\alpha}-C^{\beta}$ bonds has an energy, $E\sigma_{\beta}$, 0.7 kcal mol^{-1} above that of the alternative trans states. The curve depicting the variation of $\langle \mu^2 \rangle$ with $E\sigma_{\alpha}$ for DEG, shown in Figure 4, indicates that in changing this energy from 1.0 to -2kcal mol⁻¹, $\langle \mu^2 \rangle$ decreases from 7.11 to 4.66 D². This behavior is a consequence of the fact that an increase of the gauche population about $C^{\alpha}-C^*$ bonds will decrease the fraction of all-trans conformation in which the dipoles associated with the ester groups are in a parallel direction. On the contrary, owing to the fact that in the all-trans conformation the dipoles in DEFG are almost in an antiparallel direction, an increase of the gauche population about $C^{\alpha}-C^*$ bonds will increase the polarity of the compound, as is reflected in Figure 4, where the dependence of the mean-square dipole moment on $E\sigma_{\alpha}$ for this compound is shown. It can be seen in this curve that in decreasing $E\sigma_{\alpha}$ from 1.2 to -2 kcal mol⁻¹, the value of $\langle \mu^2 \rangle$ for DEFG will increase from 5.12 to 14.1 D². In other words, although the variation of $\langle \mu^2 \rangle$ with $E\sigma_{\alpha}$ follows opposite trends in DEG and in DEFG, in order to reproduce the experimental results, it is necessary to postulate that $E\sigma_{\alpha} < 0$ in both cases.

The curves showing the dependence of $\langle \mu^2 \rangle$ on $E\sigma_\beta$ for DEG and DEFG, represented in Figure 5, were calculated assuming $E\sigma_\alpha = -1$ kcal mol⁻¹ and $E_\omega = E_{\omega'} = 1.4$ kcal mol⁻¹. For the reasons outlined above, the variation of the polarity of the compounds with $E\sigma_\beta$ follows opposite trends in both compounds. Thus, $\langle \mu^2 \rangle$ for DEG diminishes from 8.52 to 4.53 D² when $E\sigma_\beta$ increases from -1.2 to 1 kcal mol⁻¹. On the contrary, the polarity of DEFG increases as $E\sigma_\beta$ goes up. As can be seen in Figure 5, in increasing $E\sigma_\beta$ from -1.2 to 1 kcal mol⁻¹, the value of $\langle \mu^2 \rangle$ changes from 6.21 to 11.31 D² for this latter compound. Very good agreement between theoretical and experimental values of DEG is achieved using the set of conformational energies $E\sigma_\alpha = -0.40$, $E\sigma_\beta = 0.7$, and $E\omega = E_{\omega'} = 1.4$ kcal mol⁻¹ for which the value of $\langle \mu^2 \rangle$ at 30 °C is 5.31 D², which compares very favorably with the experimental



Figure 5. Variation of the mean-square dipole moment of diethyl glutarate (DEG) and diethyl hexafluoroglutarate (DEFG) with the energy associated with gauche states about C^{β} – C^{α} bonds.



Figure 6. Variation of the temperature dependence of the mean-square dipole moment of diethyl glutarate (DEG) with the energy associated with gauche states about $C^{\alpha}-C^*$ bonds.

result, 5.25 D². In the same way, the experimental mean-square dipole moment of DEFG is reproduced for $E\sigma_{\alpha} = -0.5$ kcal mol⁻¹ and $E\sigma_{\beta} = 0.7$ kcal mol⁻¹; for this set of values, $\langle \mu^2 \rangle = 11.7$ D² at 30 °C, also in good agreement with the experimental result, 12.1 D², at the same temperature.

It is worth investigating how the conformational energies affect the temperature coefficient of the dipole moments of DEG and DEFG. The dependence of this parameter on the first-order energies for DEG, represented in Figure 6, shows that keeping $E\sigma_{\alpha} = -1.0$ kcal mol⁻¹, d $\ln\langle\mu^2\rangle/dT > 0$ for $E\sigma_{\beta} > 0$ kcal mol⁻¹. The temperature coefficient of the dipole moment of DEG is also positive for values of $E\sigma_{\alpha} \le 0$ kcal mol⁻¹ if $E\sigma_{\beta}$ = 0.7 kcal mol⁻¹. As for the temperature dependence of the dipole moment of DEFG, the calculations represented in Figure 7 reveal that d $\ln\langle\mu^2\rangle/dT > 0$ in the whole range of conformational energies, except in the interval in which $E\sigma_{\alpha} > 600$ cal mol⁻¹ ($E\sigma_{\beta} = 0.7$ kcal mol⁻¹) or $E\sigma_{\beta} < -500$ cal mol⁻¹ ($E\sigma_{\alpha}$ = -500 cal mol⁻¹) for which d $\ln\langle\mu^2\rangle/dT > 0$.



Figure 7. Influence of the conformational energies of gauche states about $C^{\alpha}-C^{\beta}$ bonds on the temperature dependence of the mean-square dipole moment of hexafluoroglutarate (DEFG).

Discussion

The calculations described above suggest that the gauche population about C–C* bonds in diethyl glutarate is preferred by ca. 500–1000 cal mol⁻¹ over the alternative trans population. To assume $E\sigma_{\alpha} = 1.0$ kcal mol⁻¹, as has been suggested by some authors,^{2–4} would give $\langle \mu^2 \rangle = 7.11$ D² for $E\sigma_{\beta} = 0.7$ kcal mol⁻¹; this quantity would reduce to 6.25 D² for $E\sigma_{\beta} = 0.3$ kcal mol⁻¹. Moreover, the calculations indicate that the dipole moment of DEG undergoes a significant decrease with increasing temperature, in contrast with the experimental results which suggest that the temperature coefficient is clearly positive. Therefore, in order to each agreement between the theoretical and experimental results of both $\langle \mu^2 \rangle$ and d $\ln \langle \mu^2 \rangle/dT$, it is necessary to postulate that $E\sigma_{\alpha} \leq 0$.

As first noted, DEFG exhibits a mean-square dipole moment whose value at 30 °C is almost 2 times larger than that of its hydrogenated homologous compound, DEG. In the study of the evolution of the mean-square dipole moment with the conformational energies, it was observed that DEG in the alltrans conformation exhibits the maximum polarity due to the fact that the dipoles of the ester groups are in nearly parallel direction, whereas the opposite occurs in DEFG as a consequence of the almost antiparallel direction of the dipole in this conformation. Therefore, the changes in polarity with the gauche population about the skeletal bonds of the acid residue follow opposite trends in both polymers. Thus, the dipole moment diminishes as the gauche population increases in DEG, whereas the polarity of DEFG increases as such a population increases. However, the fact that agreement between theoretical and experimental results of $\langle \mu^2 \rangle$ is found for the same values of the conformational energies seems to suggest that differences in the modulus and orientation of the dipoles in both compounds, rather than differences in conformational characteristics, are responsible for the much higher polarity of DEFG. The differences observed in the orientations of the dipole moments also explain the much lower temperature coefficient of the dipole moment of DEFG in comparison with that of DEG.

Neither this study nor others based on the critical interpretation of the dipole moments of dialkyl esters^{3,4} permits us to conclude that gauche states about $C-C^*$ bonds have higher energies than the alternative trans states. It should be pointed out that for the two compounds for which correlation between the ester dipoles is more important, dimethyl succinate and DEG, good agreement between theoretical and experimental results is also found for $E\sigma_{\alpha} \leq 0.4$ This conclusion is corroborated by the analysis of the temperature coefficient for the unperturbed dimensions of aliphatic polyesters, such as poly(neopentyl glycol succinate)¹⁰ and poly(neopentyl glycol adipate),⁸ whose dimensions are extremely sensitive to the gauche population about $C^{\alpha}-C^{*}$ bonds. From thermoelastic experiments carried out on poly(neopentyl glycol succinate), one finds that $10^3 \ln \langle r^2 \rangle_0 / dT$ $= 0.52 \pm 0.24$ K⁻¹. Studies performed on the evolution of this magnitude with $E\sigma_{\alpha}$, keeping $E\sigma_{\beta} = 0.7$ kcal mol⁻¹, show that d $\ln \langle r^2 \rangle / dT$ is negative and nearly independent of $E\sigma_{\alpha}$ for values of this energy lying in the range 1-0.5 kcal mol⁻¹; however, the temperature coefficient undergoes a sharp increase as $E\sigma_{\alpha}$ diminishes in the interval 0.5–0 kcal mol⁻¹, the theoretical results becoming close to the experimental ones for values of $E\sigma_{\alpha} \leq 0.10$ Theoretical calculations¹⁰ also performed on the polarity of this polymer show that its experimental dipolar correlation coefficient is reproduced better by assuming that $E\sigma_{\alpha}$ ≤ 0 . Similar results are found in the analysis of the temperature coefficients of the unperturbed dimensions of poly(neopentyl glycol adipate)⁸ and other polyesters prepared by condensation of both adipic and sebacic acids with 2,2-bis[4-(2-hydroxyethoxy)phenyl]propane.9

Summing up, the evidence at hand arising from the theoretical analysis of both the dipole moments of aliphatic diesters and the temperature coefficient of the unperturbed dimensions of aliphatic polyesters seems to suggest that $E\sigma_{\alpha} < 0$ and $E\sigma_{\beta} > 0$ for the DEG and DEFG compounds. The difference in polarity observed in both compounds arises from the differences in orientation of the dipoles associated with the diesters in the fluorinated compound caused by inductive effects of the fluorine atoms. These conclusions are important to predict the conformational properties of polyesters containing fluorine atoms in the acid residue of the repeating unit.

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