Dipole Moments and Conformational Properties of Low Molecular Weight Analogues of Acrylate Polymers with Mesogenic Side Groups

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ABSTRACT: The dipole moment of model compounds of the repeating unit of polyacrylates with rigid side groups (4-biphenyl isobutyrate (PPI), 4-phenoxyphenyl isobutyrate (PPOI), and 4-benzoylphenyl isobutyrate (PPCI)) were measured in benzene in the temperature range 30–60 °C. The values of the mean-square dipole moment $\langle\mu^2\rangle$ at 30 °C for PPI, PPOI, and PPCI amounted to 2.69, 4.40, and 12.68 D^2, respectively. The dipole moments of model compounds of diads of these polyacrylates (specifically of 4-biphenyl, 4-phenoxyphenyl, and 4-benzoylphenyl esters of 2,4-dimethylglutaric acid (PPG, PPOG, and PPCG)) were also measured in benzene. The values of $\langle\mu^2\rangle$ at 30 °C were 4.65, 7.17, and 23.79 D^2 for PPG, PPOG, and PPCG, respectively. The experimental results of the diesters were interpreted using a four-state rotational scheme. Good agreement between experimental and theoretical values was found by using the statistical weight parameters utilized in the theoretical calculations of the diads of phenyl and chlorophenyl esters of acrylic acid.

Introduction

The facility with which acrylate monomers can be prepared by esterification of acrylic acid with alcohols and the possibility that these monomers can polymerize to high molecular weight polymers by free-radical methods have opened the road to the synthesis of linear polyacrylates with a wide variety of side groups. The nature of these groups influences both the molecular flexibility and those conformation-dependent properties to which the lateral groups contribute in an important manner. Thus, recent studies[1,2] carried out on the conformation-dependent properties of poly(phenyl acrylate) (PPA), poly(*o*-chlorophenyl acrylate) (POCPA), poly(*m*-chlorophenyl acrylate) (PMCPA), and poly(*p*-chlorophenyl acrylate) (PPCPA) showed that the dipole moment ratio $\langle\mu^2\rangle/x\mu_0^2$ of these chains, where x is the polymerization degree and μ_0 is the dipole moment of the side groups, follows the trend PPCPA < PMCPA < PPA < POCPA, whereas the values of μ_0 for the side groups[3] increase in the order $(\mu_0)_{PP} < (\mu_0)_{POCPA} < (\mu_0)_{PMCPA} < (\mu_0)_{PPCPA}$. These studies also suggest that the dipole moment of the polymers with asymmetrical substitutions in the phenyl ring will be dependent upon the rotational angles Ψ about O–Ph bonds. Comparison between theory and experiment indicates that $\Psi = \pm 60°$ *and* $\pm 120°$ for PMCPA and $\Psi = \pm 75°$ for POCPA.

The versatility of polyacrylate-based chains permits the preparation of polymers with mesogenic side groups separated from the main chain by means of a flexible spacer.[4–11] The spacers partially decouple the motions of the mesogenic groups from those of the main chain, allowing the formation of mesophases. The fact, however, that some mesogenic groups directly attached to flexible backbones can give rise to mesophases[12] suggests that the backbone itself can act as a spacer. The results reported in the literature[12] indicate that most polymers lacking a spacer and capable of forming mesophases have a flexible polyacrylate backbone. Successful liquid-crystalline formation requires that the mesogenic groups are stiff and contain high-polarizability units such as biphenyl, azobiphenyl, etc. It is obvious that the capability of the flexible polyacrylate backbone to form liquid crystals is straightforwardly related to the molecular flexibility of the chains and the rigidity and polarity of the side groups. A first step in the critical interpretation of the properties of these chains will require us to study the polarity and conformational properties of the side chains, which contain the mesogenic groups, and the statistics of the polymer chains.

The aim of this work is to measure the dipole moments and their temperature coefficients of 4-biphenyl isobutyrate (PPI), 4-phenoxyphenyl isobutyrate (PPOI), and 4-benzoylphenyl isobutyrate (PPCI), which correspond to the dipole moments of the repeat units of poly(4-biphenyl acrylate) (PPA), poly(4-phenoxyphenyl acrylate) (PPOA), and poly(4-benzoylphenyl acrylate) (PPCA). Information on the conformational statistics of these polymers was obtained from the critical interpretation of the dipole moments of 4-biphenyl 2,4-dimethylglutarate (PPG), 4-phenoxyphenyl 2,4-dimethylglutarate (PPOG), and 4-benzoylphenyl 2,4-dimethylglutarate (PPCG), which can be considered model compounds of PPA, PPOA, and PPCA, respectively.

Experimental Part

Synthesis of Model Compounds. The 4-biphenyl, 4-phenoxyphenyl, and 4-benzoylphenyl esters of isobutyric and 2,4-dimethylglutaric acids were prepared by direct condensation of the acids with the corresponding phenol derivative in a solution of dry toluene by using an equimolecular mixture of *p*-toluenesulfonic acid and boric acid as catalyst. In a typical experiment, 0.1 mol of isobutyric acid or 0.05 mol of 2,4-dimethylglutaric acid was added to a solution of 0.1 mol of the corresponding phenol derivative and 0.1 g of *p*-toluenesulfonic acid plus 0.1 g of boric acid, in 100 mL of dry toluene. The reaction mixture was refluxed for 24 h in a Pyrex glass reactor equipped with a Dean–Stark separator under nitrogen atmosphere. The crude ester was concentrated at reduced pressure and purified by column chromatography (Kieselgel 60, Merck) by using a mixture

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Table I
Analytical and Spectroscopic Data for Aromatic Isobutyrates, $(CH_3)_2CHCOOR$[a]

		IR (ν), cm^{-1}			^{13}C NMR, δ			
R	mp or bp, °C	C=O	C=CAr	δ_{OOP}	CH_3	CH	Ar	C=O
4-biphenyl	74 ± 1 (mp)	1765	1610, 1590, 1510	750, 690	18.95	34.23	120–150 (8 peaks)	175.65
4-phenoxyphenyl	136 ± 1 (bp; 0.1 mmHg)	1770	1600, 1500	750, 685	18.30	35.20	115–160 (8 peaks)	174.50
4-benzoylphenyl	69 ± 1 (mp)	1750, 1710 (ketone)	1640, 1590, 1500	720, 690	17.80	36.80	120–160 (8 peaks)	173.80, 195.00 (ketone)

[a] The ^{1}H NMR spectra of isobutyrates present the following characteristic signals: CH_3 (δ = 1.32, d); CH (δ = 2.82, hept); aromatic ester residue (complex signals in the interval δ 7.00–7.80). All the chemical shifts are in ppm from TMS.

Table II
Analytical and Spectroscopic Data for Aromatic 2,4-Dimethylglutarates $CH_2(CHCH_3COOR)_2$

		^{13}C NMR, δ				
R	mp or bp, °C	CH_3[a]	CH_2	CH[a]	Ar	C=O[a]
4-biphenyl	105 ± 1 (mp)	17.40, 17.87	37.88	37.13, 37.60	120–150 (8 peaks)	174.49, 174.74
4-phenoxyphenyl	189 ± 1 (bp; 0.1 mmHg)	17.29, 17.71	37.62	37.02, 37.44	115–160 (8 peaks)	174.39, 174.64
4-benzoylphenyl	67 ± 1 (mp)	17.36, 17.67	37.74	36.90, 37.24	120–155 (8 peaks)	173.82, 174.04, 195.30 (ketone)

[a] These groups present resonance signals of similar intensity, which correspond to the contribution of equimolecular composition of meso and racemic stereochemical isomers. IR spectra: The main signals are similar to those of the corresponding isobutyrates except for the carbonyl ester group, which appear centered at ν = 1750 cm^{-1} in all cases.

of chloroform/heptane (80:20 v/v) as eluent. The yield was 70% in all cases, and the purity of the corresponding esters was tested by GLC and IR, exceeding 99.5%. The boiling points of the compounds were determined by microdistillation under vacuum (0.1 mmHg), and their values are indicated in Tables I and II. In these tables the values of the melting points of the compounds, determined with a Perkin-Elmer DSC-4 calorimeter at a heating rate of 4 °C/min, are also shown. The peak maximum at the second warming up cycle was taken as the melting point.

Characterization. The model compounds were characterized by IR (Perkin-Elmer 457), ^{1}H NMR (Varian XL-300, 300 MHz), and ^{13}C NMR (Varian XL-300, 75.5 MHz) spectroscopies. The ^{1}H and ^{13}C NMR spectra were recorded at 40 °C in 15% (w/v) deuterated chloroform solutions, by using TMS as an internal reference standard. The main characteristic signals of the spectra are recorded in Tables I and II for the esters of isobutyric and 2,4-dimethylglutaric acids, respectively.

The ^{1}H NMR spectra of the esters of 2,4-dimethylglutaric acid give information on the meso and racemic stereoisomers of the samples studied, the resonance signals of the aliphatic protons being similar to those reported for other phenyl and chlorophenyl derivatives.[2] In all the cases the methylene protons of the racemic isomer produce a well-defined triplet centered at 2.00 ppm from TMS, as a consequence of the magnetic equivalence of both protons. However, the nonequivalence of these protons for the meso isomer produces two multiplets centered at 1.75 and 2.50 ppm, respectively. The integrated intensities of these signals give the molar fraction of meso and racemic isomers in the samples prepared, all being equimolecular mixtures of both stereoisomers.

Table III
Summary of Experimental Dielectric Results for 4-Biphenyl Isobutyrate (PPI), 4-Phenoxyphenyl Isobutyrate (PPOI), and 4-Benzoylphenyl Isobutyrate (PPCI) in Benzene

compd	T, °C	$d\epsilon/dw$	$2n_1\ dn/dw$	$\langle\mu^2\rangle$, D^2
PPI	30	1.365	0.179	2.69
	40	1.302	0.185	2.67
	50	1.237	0.190	2.65
	60	1.200	0.195	2.68
PPOI	30	1.936	0.115	4.40
	40	1.857	0.121	4.43
	50	1.817	0.126	4.42
	60	1.700	0.132	4.45
PPCI	30	5.188	0.180	12.68
	40	4.931	0.185	12.69
	50	4.735	0.191	12.83
	60	4.462	0.196	12.40

Table IV
Dielectric Results for 4-Biphenyl 2,4-Dimethylglutarate (PPG), 4-Phenoxyphenyl 2,4-Dimethylglutarate (PPOG), and 4-Benzoylphenyl 2,4-Dimethylglutarate (PPCG) in Benzene

compd	T, °C	$d\epsilon/dw$	$2n_1\ dn/dw$	$\langle\mu^2\rangle$, D^2
PPG	30	1.194	0.193	4.65
	40	1.102	0.200	4.43
	50	1.079	0.207	4.52
	60	1.040	0.213	4.52
PPOG	30	1.608	0.159	7.17
	40	1.537	0.163	7.18
	50	1.455	0.167	7.11
	60	1.400	0.172	7.18
PPCG	30	4.811	0.216	23.79
	40	4.587	0.220	23.87
	50	4.373	0.226	23.94
	60	4.120	0.232	23.64

Dielectric Measurements. Values of the dielectric constant, ϵ, of solutions of the model compounds in benzene were determined with a capacitance bridge (General Radio, Type 1620 A) and a three-terminal cell, at 10 kHz. From the plots of the increments of the dielectric constant of the solutions with respect to that of the solvent ($\Delta\epsilon = \epsilon - \epsilon_1$) against the weight fraction, w, of polymer in the solutions, values of $d\epsilon/dw$ at each temperature of interest were obtained. These quantities at several temperatures, for different esters of the isobutyric and 2,4-dimethylglutaric acid, are shown in the third column of Tables III and IV, respectively. In the same way, values of the increments of the refractive index of the solutions with respect to that of the solvent ($\Delta n = n - n_1$) were measured at different temperatures with a He-Ne KMX-16 laser differential refractometer (Chromatix Inc.), operating at 632.8 nm. The results obtained for $2n_1\ dn/dw$ corresponding to isobutyrates and 2,4-dimethylglutarates are shown in the fourth column of Tables III and IV, respectively. The values of the mean-square dipole moments, $\langle\mu^2\rangle$, were determined by means of the equation of Guggenheim[13] and Smith[14]

$$\langle\mu^2\rangle = \frac{27\kappa TM}{4\pi\rho N_a(\epsilon_1 + 2)^2}\left(\frac{d\epsilon}{dw} - 2n_1\frac{dn}{dw}\right)$$

where κ is the Boltzmann constant, T is the absolute temperature, N_a is Avogadro's number, and ρ is the density of the solvent. The results obtained at different temperatures, shown in the last column of Tables III and IV, indicate that the polarity of the compounds depends on the nature of the phenolic residue in the sense that 4-biphenyl < 4-phenoxyphenyl < 4-benzoylphenyl. Moreover, the values of the mean-square dipole moment of these compounds seem to be independent of temperature.

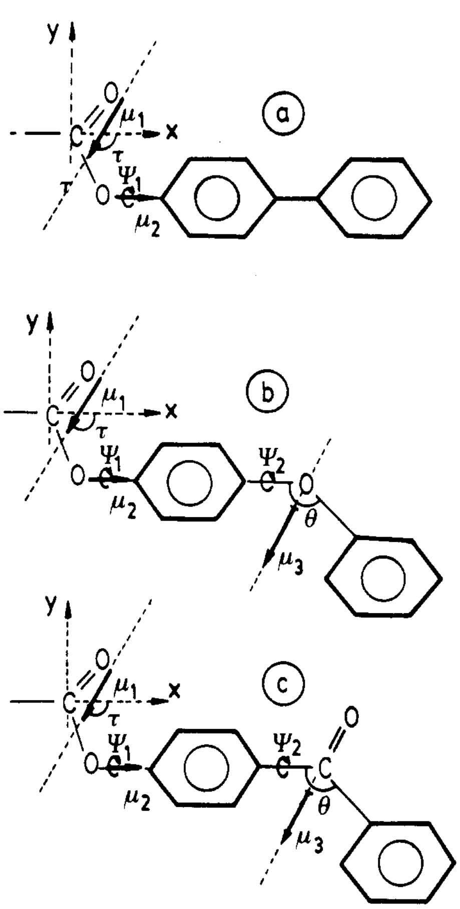

Figure 1. Ester groups of 4-biphenyl isobutyrate (a), 4-phenoxyphenyl isobutyrate (PPOI) (b), and 4-benzoylphenyl isobutyrate (PPCI) in the planar conformation, which is taken as the origin of the rotational angles $\Psi_1 = \Psi_2 = 0$.

Theoretical Analysis

Model Compounds for the Repeat Unit. 4-Biphenyl Isobutyrate (PPI). The ester group of this molecule is shown in Figure 1a. Its dipole moment can be obtained by addition of two contributions,[3] namely μ_1 representing the dipole moment of a methyl ester, for which the standard modulus[3,15,16] of 1.75 D and a direction[17] defined by an angle $\tau = 123°$ were used, and μ_2 representing the effect of replacing the methyl by another group having different polarity. If the group replacing the methyl is a phenyl, the value of μ_2 was found to be 0.3 D for benzene solutions.[3] The polarity of phenyl and *p*-diphenyl groups should be approximately the same, and therefore the value of μ_2 for the BPI molecule is expected to be close to 0.3 D. In fact, using this value for μ_2 and taking 7.5° for the difference between C*OPh and CC*O bond angles,[17] one obtains $\langle\mu^2\rangle = 2.72\ \mathrm{D}^2$, in excellent agreement with the experimental result shown in Table III. Thus this analysis confirms the equivalence of phenyl and *p*-biphenyl residues as far as the contribution to the dipole moment of the ester group is concerned.

4-Phenoxyphenyl Isobutyrate (PPOI) and 4-Benzoylphenyl Isobutyrate (PPCI). The ester groups of these two molecules are shown in parts b and c of Figure 1, respectively. The dipole moments of PPOI and PPCI have a third component, namely μ_3, representing the contribution of diphenyl ether for the former compound and diphenyl ketone for the latter. Consequently, the total dipole moment of these two molecules should depend on the magnitude and orientation of μ_3, this last characteristic being determined by the rotational angles Ψ_1 and Ψ_2 and by the valence angle θ at the ether or ketone group. There are four rotational isomers with the same energy for the Ψ_1 angle, corresponding to $\Psi_1 = \pm 60$ *and* $\pm 120°$, taking $\Psi_1 = 0$ for the conformation in which the phenyl ring is coplanar with the ester group. Under these circumstances, the averaged dipole moments of PPOI and PPCI do not depend on the rotational state of the Ψ_2 angle. This result may seem surprising, taking into account that Ψ_2 actually modifies the orientation of μ_3 relative to the other two contributions; however, it can easily be explained by the symmetry of the rotation over Ψ_1, which after averaging cancels any modification produced by Ψ_2. This is shown in Figure 2 where the values of $\langle\mu^2\rangle$ computed as function of Ψ_2 for the four rotational states of Ψ_1 are shown. It can be seen that if any pair of values of Ψ_2 is selected, the differences between the values calculated for the four orientations of Ψ_1 and each one of the positions of Ψ_2 cancel out and the average is the same regardless of Ψ_2. As a consequence, all the calculations presented below were performed using $\Psi_2 = 0$. The valence angle between the two phenyl rings (angle θ in Figure 1) has a minor incidence on the dipole moments of these molecules: thus a modification of 2° in θ changes the values of $\langle\mu^2\rangle$ in only 0.2%, and $\theta = 112°$ was used throughout this analysis. On the contrary, the dipole moments of both PPOI and PPCI are very sensitive to the value of the μ_3 contribution. The variation of $\langle\mu^2\rangle$ with μ_3 is indicated in Figure 3 where it can be seen that values of $\mu_3 \approx 1.1$ and 2.9 D are required, respectively, to reproduce the experimental dipole moments of PPOI and PPCI. These values are in excellent agreement with the results obtained in the experimental determinations[15] of the dipole moments of diphenyl ether (ca. 1.15 D) and diphenyl ketone (ca. 3.0 D), measured at 25 °C in benzene solutions. The dipole moments of these three esters should be almost independent of temperature since μ does not depend on any rotation for PPI and the only *effective* rotational parameter for PPOI and PPCI, Ψ_1, has the same energy for all its allowed states. Thus, the only way that the dipole moment could change with temperature would be a variation of the bond lenths or bond angles, which is practically negligible at low temperatures. This is in agreement with the experimental results, since the experimental values of μ do not show a significant variation with *T* within the limits of experimental error.

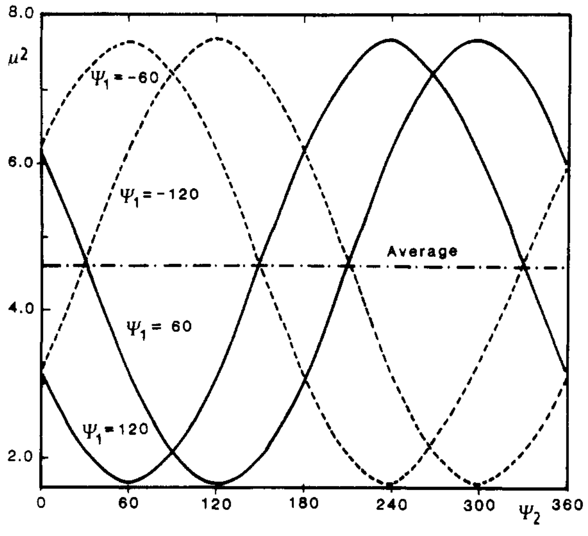

Figure 2. Dipole moment of 4-phenoxyphenyl isobutyrate (PPOI) as a function of Ψ_2 for the four rotational states of Ψ_1. Values of $\mu_1 = 1.757$, $\mu_2 = 0.3$, $\mu_3 = 1.15$ D, $\tau = 123°$, and $\theta = 112°$ were used.

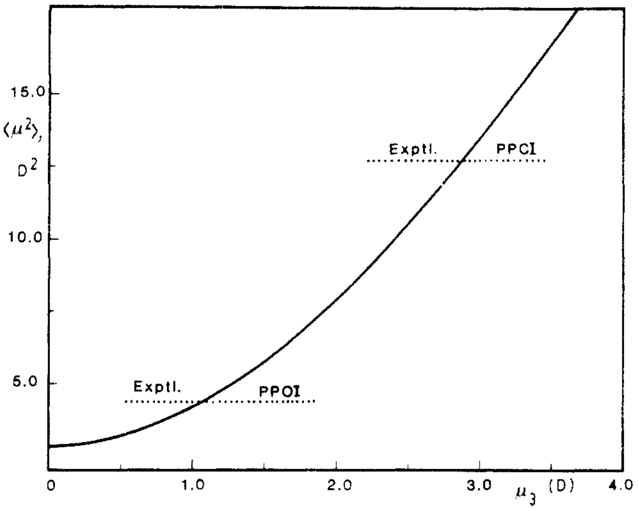

Figure 3. Mean-square dipole moment $\langle \mu^2 \rangle$ for 4-phenoxyphenyl isobutyrate (PPOI) and 4-benzoylphenyl isobutyrate (PPCI) as a function of the dipole moment μ_3. The average was performed over the four isoenergetic orientations $\Psi_1 = \pm 60$ and $\pm 120°$ with $\Psi_2 = 0$. All other parameters are as in Figure 2.

Model Compounds for the Dimers. The calculations of $\langle \mu^2 \rangle$ for the meso and racemic stereoisomers of PPG, PPOG, and PPCG were performed using the four-states rotational isomers scheme developed for poly(methyl acrylate)[18] (PMA) and applied to phenyl and chrorophenyl polyacrylates and their model compounds.[1,2,18] The required statistical weight matrices are

$$\mathbf{U}' = \begin{pmatrix} 1 & 0 & 1 & 0 \\ 0 & \rho & 0 & \rho \\ 1 & 0 & 0 & 0 \\ 0 & \rho & 0 & 0 \end{pmatrix}$$

for the CH_3–CH–CH_2 pair of skeletal bonds and

$$\mathbf{U}_r'' = \begin{pmatrix} 1 & \gamma_1 & 0 & 0 \\ \gamma_1 & \gamma_2 & 0 & 0 \\ 0 & 0 & \alpha & \alpha \\ 0 & 0 & \alpha & \alpha \end{pmatrix}$$

$$\mathbf{U}_m'' = \mathbf{A} \times \begin{pmatrix} 1 & \gamma & \beta & \beta \\ \gamma & 1 & \beta & \beta \\ \beta & \beta & 0 & 0 \\ \beta & \beta & 0 & 0 \end{pmatrix}$$

for racemic and meso moieties of the CH–CH_2–CH pair of bonds. The location of the rotational isomers and the values of the statistical weights were taken from the literature[1,2,18] with the only exception of α, which governs the stability of gg versus tt on the racemic diad. A value $\alpha = 0$ has been used in several cases,[1,2,18] thus allowing only tt conformations for racemic moieties. However, ^1H and ^{13}C NMR analysis of racemic o-chlorophenyl diesters[19] suggests that there is a fraction of diads having gg conformation, which amounts to ca. $f_{gg} = 0.18$. In the present work f_{gg} was used as an adjustable parameter by employing a value of α defined as

$$\alpha = \frac{(1 + 2\gamma_1\rho + \gamma_2\rho^2)f_{gg}}{(1 + 2\rho + \rho^2)(1 - f_{gg})}$$

4-Biphenyl 2,4-Dimethylglutarate. Using the statistical weights employed in the analysis of poly(phenyl acrylate) (PPA) and its model compounds[1,2] (i.e., $\rho = 1.1$; $\beta = 1.8$; $\gamma_1 = 1.4$; $\gamma_2 = 2.5$; $\gamma = 4.5$ at 30 °C), one obtains $\langle \mu^2 \rangle = 4.43$ D^2 for the meso isomer regardless of the value of f_{gg}. The results for the racemic moieties, shown as a function of f_{gg} by the broken line of Figure 4, indicate that $\langle \mu^2 \rangle$ increases by almost a factor of 2 when the fraction of gg conformations is raised from 0 to 50%. Since the experimental measurements were carried out on equimolecular mixtures of meso and racemic isomers, the experimental values should be compared with the average of the theoretical results for both. This average is shown by the solid line of Figure 4 in which one can see that the experimental result is reproduced with $f_{gg} \approx 0.10$–0.15, which is very close to the experimental fraction obtained in the o-chlorophenyl diester.[19] If the statistical weights of any other diester (for instance, those of methyl[2] or o-, m-, or p-chlorophenyl[1,2]) are used, the experimental value of $\langle \mu^2 \rangle$ is not reproduced with any value of f_{gg}.

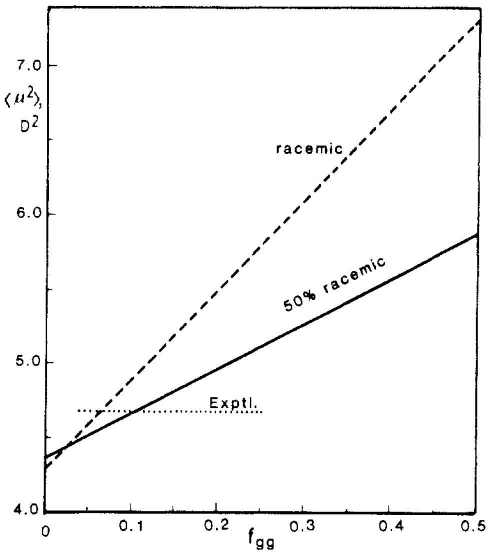

Figure 4. Values of $\langle \mu^2 \rangle$ for 4-biphenyl 2,4-dimethylglutarate (PPG) as a function of the gg conformation in the racemic diad, f_{gg}: broken line, results for racemic; solid line, results for an equimolecular mixture of meso and racemic isomers. Statistical weights at 30 °C are $\rho = 1.1$, $\beta = 1.8$, $\gamma_1 = 1.4$, $\gamma_2 = 2.5$, and $\gamma = 4.5$.

4-Phenoxyphenyl 2,4-Dimethylglutarate and 4-Benzoylphenyl 2,4-Dimethylglutarate. Computations were performed allowing four equally weighted[1,2] orientations of Ψ_1 (see above), keeping $\Psi_2 = 0$. Exploratory calculations showed that $\langle \mu^2 \rangle$ changes by only 0.6% when Ψ_2 moves between 0 and 180°. The best set of statistical weight parameters for these two molecules is that previously obtained for p-chlorophenyl esters[2] (i.e., $\rho = 1.1$; $\beta = 5.0$; $\gamma_1 = 1.4$; $\gamma_2 = 2.3$; $\gamma = 0.2$ at 30 °C). Some calculations were performed in order to check the variation of $\langle \mu^2 \rangle$ with f_{gg}, proving that the average between the results obtained for meso and racemic moieties increases by ca. 5% for PPOG and ca. 3% for PPCG, when f_{gg} changes from 0 to 50%. This difference in sensitivity to f_{gg} as compared with PPG is due to the contribution μ_3, which changes the direction of the dipole moment of the whole ester group and therefore modifies the way in which the dipoles of consecutive units add for different conformations of the skeleton. Thus $\langle \mu^2 \rangle$ for the gg conformation of the racemic isomer of PPG ($\mu_3 = 0$) exceeds that of racemic tt by roughly a factor of 2, whereas for PPOG ($\mu_3 \approx 1.15$ D) the racemic gg is only ca. 5% larger than racemic tt. All the results presented below for PPOG and PPCG were computed with $f_{gg} = 0.18$.

The mean-square dipole moment $\langle \mu^2 \rangle$ is very sensitive to the value of the μ_3 contribution, as is shown in Figure 5 where the results for equimolecular mixtures of meso and racemic isomers are plotted as function of μ_3.

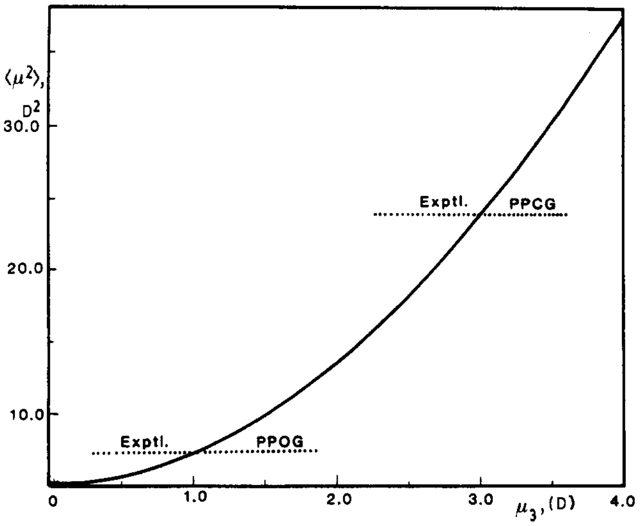

Figure 5. Values of $\langle \mu^2 \rangle$ for equimolecular mixtures of meso and racemic stereoisomers of 4-phenoxyphenyl 2,4-dimethylglutarate (PPOG) and 4-benzoylphenyl 2,4-dimethylglutarate (PPCG) as a function of μ_3. Fraction of gg conformation in racemic; $f_{gg} = 0.18$. Statistical weights at 30 °C are $\rho = 1.1$, $\beta = 5.0$, $\gamma_1 = 1.4$, $\gamma_2 = 2.3$, and $\gamma = 0.2$.

Individual values for meso and racemic lie too close (respectively, above and below) to the average and are not shown in this figure. Comparison of the experimental results shown in Table IV with the theoretical values of Figure 5 indicates that agreement between theory and experiment is obtained using $\mu_3 \approx 1.0 \pm 0.1$ D for PPOG and $\mu_3 \approx 3.0 \pm 0.1$ D for PPCG, which agree with the values used for the PPOI and PPCI molecules, respectively, and with the experimental dipole moments of diphenyl ether and diphenyl ketone.

The variation of $\langle \mu^2 \rangle$ with temperature is small for the three molecules. Thus, the values of the temperature coefficient $10^3 \, \mathrm{d} \ln \langle \mu^2 \rangle / \mathrm{d}T$ computed in the vicinity of 30 °C are 0.6, 0.4, and 0.3 for PPG, PPOG, and PPCG, respectively. These results suggest that the dipole moments of the diesters have a small temperature dependence, in concordance with the experiments that show that the changes of $\langle \mu^2 \rangle$ with temperature are very small.

It can be concluded that the dipole moments of PPI, PPOI, and PPCI can be obtained by addition of three contributions, μ_1 and μ_2 being the same for all the phenyl and phenyl-derived esters studied so far, while μ_3 coincides with the experimental dipole moment of the molecule appearing as alcoholic residue in the ester. The analysis of the dimers shows that the conformational characteristics of diphenyl esters are the same as those of phenyl esters whereas *p*-phenoxyphenyl and *p*-benzoylphenyl esters both have the same conformationl behavior as the *p*-chlorophenyl compound; the difference in polarity among these molecules is only due to the magnitude and orientation of the μ_3 contribution.

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