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Configurational and Conformational Characteristics of the Diastereoisomers of Bis(*o*-chlorophenyl) 2,4-Dimethylglutarate

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ABSTRACT: The meso and racemic isomers of bis(*o*-chlorophenyl) 2,4-dimethylglutarate were separated by fractional crystallization in hot heptane. The racemic isomer is crystalline with a melting point of 360 ± 1 K whereas the meso is liquid at room temperature. From the analysis of the ^1H and ^{13}C NMR spectra of both isomers it can be concluded that the former is predominantly in the tt conformation (f_{tt} = 0.82 and f_{gg} = 0.18), whereas the latter is in tg conformations. Dielectric measurements were performed at 30 °C in benzene solution, giving values of 5.70 D^2 and 6.07 D^2 for the mean-square dipole moment of the meso and racemic isomers, respectively. Critical analysis of the dipole moments was used to obtain information on the statistical weights, which account for the two possible rotational angles about the C_α–CO bonds, and the value of the rotational angle about the ortho phenyl bonds.

Introduction

High-resolution NMR spectroscopy has been a powerful tool in the determination of the stereochemical configuration of a great number of asymmetric polymers.[1] However, the fact that stereoregularity effects may be superimposed upon conformational effects, leading to an ambiguous resolution of the resonance peaks, makes advisable the analysis of the NMR spectra of model compounds in order to interpret the spectra of polymers in terms of their stereochemical configurations. In this regard, several derivatives of 2,4-dimethylpentane and 2,4,6-trisubstituted heptanes have been extensively studied from a microstructural point of view, as model compounds of vinyl and acrylic polymers.[2–5] However, the isolation of the meso and racemic components of the low molecular weight model compounds is a difficult task in many cases and, consequently, the NMR spectra of only a limited number of stereoisomers have been studied so far.[6–11]

Low molecular weight compounds have also been used to obtain information on the conformational energies and rotational angles of polymers with structural features similar to those of the model compounds.[12] Thus, the dipole moments of several phenyl and halophenyl derivatives of 2,4-dimethylglutaric acid have recently been measured,[13] and the results were interpreted by using statistical mechanics procedures as a first step to a further analysis of the conformation-dependent properties of poly(phenyl acrylate) and its halogenated derivatives. It was found that the dipole moments of chlorophenyl esters of 2,4-dimethylglutaric acid are strongly dependent on the location (ortho, metha, or para) of the chlorine atom in the phenyl ring. Thus, whereas the value of the mean-square dipole moment of bis(*o*-chlorophenyl) 2,4-dimethylglutarate (OCPDG) is 6.17 D^2 (close to the value of 4.40 D^2 found for diphenyl 2,4-dimethylglutarate), the value of this quantity for bis(*m*-chlorophenyl) and bis(*p*-chlorophenyl) 2,4-dimethylglutarates amounts to 9.73 and 10.30 D^2, respectively, at the same temperature.[13] It is obvious that knowledge of the dipole moments corresponding to the meso and racemic components would assist the critical interpretation of the polarity of the molecules and, in addition, would help in the analysis of the conformation-dependent properties of poly(phenyl acrylates) and their phenyl halogenated derivatives.

This paper reports the synthesis, isolation and characterization of the meso and racemic stereoisomers of OCPDG, which can be considered the dimer analogous of isotactic and syndiotactic poly(*o*-chlorophenyl acrylate)s, respectively. The dielectric results were then theoretically interpreted, using the rotational isomeric state model, with the aim of obtaining more information on the conformations of these diester compounds.

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Table I
Summary of Dielectric Results of Racemic and Meso Bis(*o*-chlorophenyl) 2,4-Dimethylglutarates in Benzene Solution

sample	temp, °C	$d\epsilon/dw$	$2n_1\ dn/dw$	$\langle\mu^2\rangle$, D^2
rac-OCPDG	30	1.782	0.096	6.07
	40	1.745	0.103	6.24
	50	1.657	0.111	6.21
	60	1.600	0.115	6.28
meso-OCPDG	30	1.676	0.094	5.70
	40	1.654	0.101	5.90
	50	1.565	0.109	5.84
	60	1.500	0.117	5.85

Experimental Part

Synthesis of the Diastereoisomers. An equimolecular mixture of the meso and racemic isomers of bis(*o*-chlorophenyl) 2,4-dimethylglutarate was prepared by condensation of 2,4-dimethylglutaric acid (Fluka A.G.) with *o*-chlorophenol (FEROSA) in solution of dried toluene, using *p*-toluenesulfonic acid as catalyst. Other experimental details are given elsewhere.[13] Both diastereoisomers were isolated by repeating fractional crystallization in hot heptane.

Characterization. The isolated *meso*- and *rac*-OCPDG diastereoisomers were characterized by IR (Perkin-Elmer 457), ^1H NMR (Bruker AM-200, 200 MHz), and ^{13}C NMR (Varian XL-300, 75 MHz) spectroscopies, using deuteriated chloroform solutions and TMS as internal reference standards. The temperature was 30 °C.

The melting temperature and melting enthalpy of *rac*-OCPDG were determined with a Perkin-Elmer DSC-4 calorimeter. Measurements and calibration were carried out at heating rates of 4, 8, and 16 °C/min. The values of the melting temperature and melting enthalpy amounted to 360 ± 1 K and 6.0 ± 1 Kcal·mol^{-1}, respectively. The *meso*-OCPDG is a liquid at room temperature and it does not crystallize at lower temperatures.

Dielectric Measurements. Values of the dielectric constant ϵ of solutions of *meso*- and *rac*-OCPDG were obtained at 30, 40, 50, and 60 °C, using a capacitance bridge (General Radio, type 1620 A) with a three-terminal cell, at 10 kHz. Values of the increment of the index of refraction n of the solutions with respect to that of the solvent n_1 were measured with a He–Ne KMX-16 laser differential refractometer (Chromatix Inc, USA), operating at 632.8 nm. Values of the mean-square dipole moment were calculated by the method of Guggenheim[14] and Smith,[15] which results in the equation

$$\langle\mu^2\rangle = [27kTM/4\pi\rho N_A(\epsilon_1 + 2)^2][(d\epsilon/dw) - 2n_1(dn/dw)]$$

where k is the Boltzmann constant, T is the absolute temperature, N_A is Avogadro's number, ρ is the density of the solvent, w is the weight fraction of polymer in the solution, and ϵ_1 is the dielectric constant of the solvent. Values of the required derivatives are given in the second and third columns of Table I. In the fourth column of the table, the values of $\langle\mu^2\rangle$ for *meso*-OCPDG and *rac*-OCPDG are also shown; the uncertainty of these values was estimated to be ±3%.

Results and Discussion

^1H NMR Spectroscopic Studies. Racemic Bis(*o*-chlorophenyl) 2,4-Dimethylglutarate. It has been suggested that the racemic diastereoisomers of model compounds of acrylic and vinyl polymers, i.e., glutarates and 2,4-disubstituted pentanes, are in tt and gg conformations.[16–18] Accordingly, the populations of these two conformational states should be dependent on temperature, the tt conformation being clearly favored at room temperature.[16,17] Thus, from the analysis of the ^1H NMR spectrum of *rac*-2,4-dimethylglutarate, Doskocilová and Schneider[3] have concluded that the central line of the β-CH_2 triplet splits into two components of similar intensity, probably caused by dynamic equilibrium between the tt and gg conformations. In the same way, from the critical interpretation of the ^1H NMR spectrum of 2,4-dibenzoylpentanes, on the basis of the most probable tt and gg conformations, Merle-Aubry and Merle[19] considered the β-CH_2 coupled with the α-methine protons as a four-spin system AA′XX′.

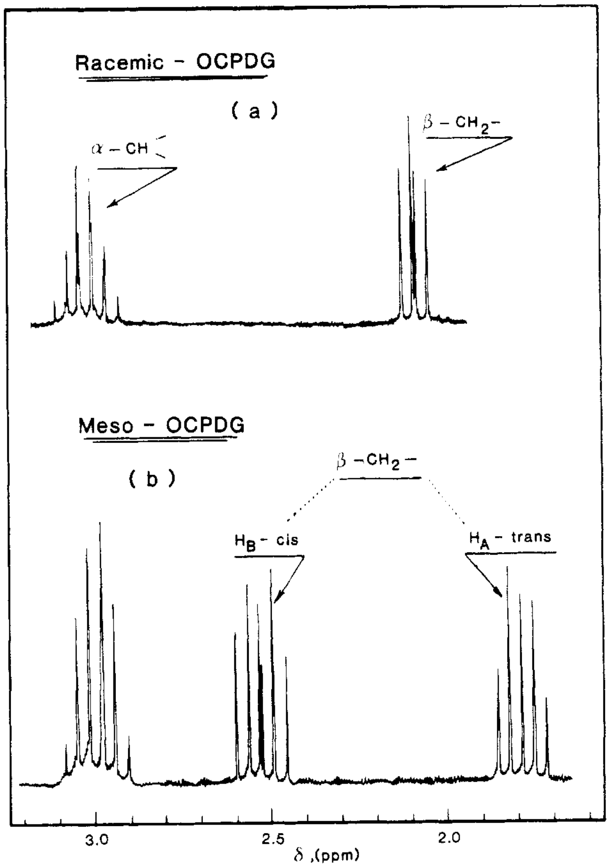

Figure 1. 200-MHz ^1H NMR spectra of bis(*o*-chlorophenyl) 2,4-dimethylglutarate. (a) racemic isomer; (b) meso isomer.

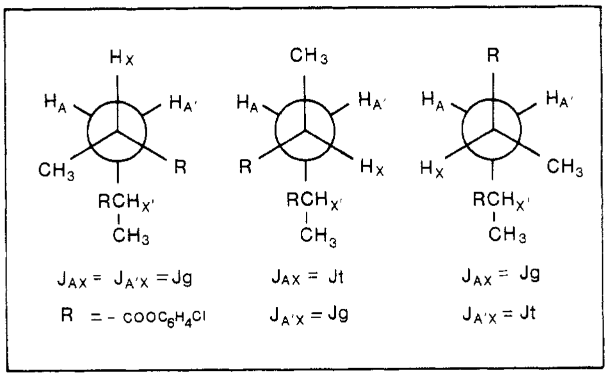

Figure 2. Schematic representation of racemic and meso isomers of bis(*o*-chlorophenyl) 2,4-dimethylglutarate in the most probable staggered conformations.

An inspection of the ^1H NMR spectrum of rac-OCPDG, represented in Figure 1 indicates that the α-methine protons give rise to a rather complex multiplet centered at ca. 3.05 ppm. The β-methylene protons give a well-resolved quadruplet, which has been analyzed on the basis of an AA′XX′ spin coupling system.

The observed vicinal coupling constants J_{AX} and $J_{A'X}$ are the result of the rotational averages of the coupling constants of trans J_t and gauche J_g conformations (see Figure 2), the sum $J_{AX} + J_{A'X} = J_g + J_t$ being little affected by the temperature and solvent.[19,20] Since the individual coupling constants J_t and J_g cannot be determined from the NMR spectra, it is necessary to consider values taken from measurements on model compounds with well-defined geometry.[19-23] According to NMR studies performed by Merle-Aubry and Merle[19] on 1,3,5-tribenzoylcyclohexane, $J_t = 12.0$ Hz and $J_g = 3.30$ Hz, whereas Booth and Thornburrow[21] have reported $J_{1a2a} = 12.23$ Hz and $J_{1a2e} = 3.75$ Hz, for phthalimidocyclohexanes; recently Abe et al.[20] have found $J_t = 11.84$ and $J_g = 3.64$ Hz for 2,4-di-*N*-carbazoylpentane. In view of these results we consider $J_t = 12.00$ Hz and $J_g = 3.60$ Hz as likely values for meso- and *rac*-OCPDG.

In order to determine the most reliable values of J_{AX} and $J_{A'X}$ that reproduce the resonance signals of β-CH$_2$ for the racemic isomer (Figure 1a), the NMR spectrum was analyzed by using the LAOCOON III program on the basis of the four-spin system AA′XX′. The optimized vicinal coupling constants were $J_{AX} = 10.02$ Hz and $J_{A'X} = 4.60$ Hz. These values are similar to those reported by Abe et al.[20] for a rather similar system, 2,4-di-*N*-carbazolylpentane, which is a model compound of the sequences of diads in poly(*N*-vinylcarbazole). The whole fraction at 30 °C of tt and gg conformers was evaluated from the values of J_{AX}, $J_{A'X}$, J_g, and J_t indicated above, using the method described by Bovey et al.,[7] obtaining for f_{tt} and f_{gg} values of 0.82 and 0.18, respectively.

***meso*-Bis(*o*-chlorophenyl) 2,4-Dimethylglutarate.** As is well documented in studies of glutaric esters and 2,4-disubstituted pentanes,[24] the β-protons of a meso methylene group are magnetically nonequivalent, giving rise to multiplets with different chemical shift. As is shown in Figure 1b, the β-methylene protons of *meso*-OCPDG give two multiplets centered at 1.79 and 2.53 ppm from TMS. According to assignments proposed by Yoshino et al.[5] and by Schuerch et al.[25] for other model compounds of polyacrylates, it seems that one of the methylene protons responsible for the higher field signals of the ^{1}H NMR spectrum of *meso*-OCPDG is the β-proton oriented trans (anti or threo) to the carboxyl group, in the planar zigzag skeletal conformation of the Me–C–C–C–Me chain, whereas the lower field multiplet may be assigned to the β-methylene proton oriented cis (syn or erythro) to the carboxyl group. This is in fact the preferred spatial arrangement for isotactic chains,[26-28] which has been demonstrated for polyacrylates by Yoshino et al.[5] and polymethacrylates by Bovey et al.[29]

Therefore, the difference in the chemical shift of both -CH$_2$- protons arises from the relative spatial orientation of the corresponding methylene protons with respect to the substituents in the α-position, the separation of the two multiplets being of 0.74 ppm, even higher than that found by Yoshino et al.[5] for the *meso*-methylene group of poly(methyl acrylate) where the multiplets due to the methylene protons are separated by about 0.5 ppm.

A detailed analysis of the expanded multiplet centered at 1.79 ppm from TMS (Figure 1b) reveals that it consists of five peaks, which are the result of two well-defined triplets, as a result of the contribution of the geminal coupling between the magnetically nonequivalent β-methylene protons and the vicinal coupling with both α-methine protons, which can be considered as a typical ABX$_2$ spin system. From the expanded spectrum, values of $J_{gem} = -13.95$ Hz and $J_{vic} = 6.92$ Hz were obtained. The magnitude of the coupling constant of the geminal methylene protons is very close to that reported by Fujishige[2] for dimethyl 2-(methoxymethyl)-2,4-dimethylglutarate ($J_{gem} = -14.0$ Hz) in benzene-d_6 at 35 °C and it is comparable to that of meso dimethyl 2,4-dimethylglutarate ($J_{gem} = -13.1$ Hz) in carbon tetrachloride at 20 °C.[3]

The analysis of the fine structure of the multiplet centered at 2.53 ppm (Figure 1b) suggests that it corresponds to the overlapping of two triplets, with a coupling constant $J_{gem} = -13.95$ Hz for the β-methylene protons. The values of the vicinal coupling constants between the β-methylene and α-methine protons, determined by using the LAOCOON III program on the basis of the spin system ABX$_2$, were $J_{AX} = 7.02$ Hz and $J_{BX} = 7.60$ Hz, which correspond to the contribution of the energetically equivalent g$^-$t and tg$^+$ conformational states.

From the critical interpretation of the IR spectra of *meso*-2,4-dichloropentane[30] and the NMR spectra of *meso*-2,4-pentanodiol diacetate,[3] *meso*-2,4-diphenylpentane, and dimethyl glutarate,[19] it can be considered that two rotational conformers are possible at room temperature, which correspond to the energetically equivalent g$^-$t and tg$^+$ rotamers. The conformational arrangment represented by the rotamers g$^-$t and tg$^+$ agrees adequately with the NMR pattern of the β-methylene proton resonances represented in Figure 1. The slight difference between the values of J_{AX} and J_{BX} presumably arises from a very small contribution of the tt conformation.

Dipole Moments

Values of the dipole moment of both the *rac*- and *meso*-OCPDG were theoretically calculated by assuming that each skeletal bond in Figure 2 is restricted to two states (t and g), each of these states being, in turn, split into another two states in order to account for the two possible orientations 0 and 180° in which the carbonyl oxygen is respectively synperiplanar and antiperiplanar with the methine hydrogen. Accordingly, the statistical weight matrix for the CH$_3$–CH–CH$_2$ bond pair is[31,32]

$$\mathbf{U}' = \begin{array}{c|cccc|} & (\mathrm{t},0) & (\mathrm{t},\pi) & (\mathrm{g},0) & (\mathrm{g},\pi) \\ (\mathrm{t},0) & 1 & 0 & 1 & 0 \\ (\mathrm{t},\pi) & 0 & \rho & 0 & \rho \\ (\mathrm{g},0) & 1 & 0 & 0 & 0 \\ (\mathrm{g},\pi) & 0 & \rho & 0 & 0 \end{array}$$

whereas the statistical weight matrices for racemic and meso configurations of the CH–CH$_2$–CH bond pair are

$$\mathbf{U}''_{\mathrm{r}} = \begin{array}{c|cccc|} & (\mathrm{t},0) & (\mathrm{t},\pi) & (\mathrm{g},0) & (\mathrm{g},\pi) \\ (\mathrm{t},0) & 1 & \gamma_1 & 0 & 0 \\ (\mathrm{t},\pi) & \gamma_1 & \gamma_2 & 0 & 0 \\ (\mathrm{g},0) & 0 & 0 & \alpha & \alpha \\ (\mathrm{g},\pi) & 0 & 0 & \alpha & \alpha \end{array}$$

$$\mathbf{U}''_{\mathrm{m}} = A\begin{vmatrix} 1 & \gamma & \beta & \beta \\ \gamma & 1 & \beta & \beta \\ \beta & \beta & 0 & 0 \\ \beta & \beta & 0 & 0 \end{vmatrix}$$

A and β are defined as $A = \omega''(\delta_m/\delta_r)$ and $\beta = (1/\eta)\delta_m\omega''$ representing the weight for the second-order interaction between two ester groups juxtaposed as in the meso tt state, η is the first-order statistical weight for trans versus gauche, and δ_m and δ_r represent Boltzmann factors of the Coulombic interactions in the (t,0), (t,0) side-chain orientations of meso and racemic diads. Average values of $(\Phi_1)_{tt} = (\Phi_2)_{tt} = 16°$, $(\Phi_1)_{tg} = (\Phi_2)_{gt} = 3°$, and $(\Phi_1)_{gt} = (\Phi_2)_{tg} = 114°$ were used for the meso diad, whereas $(\Phi_1)_{tt} = (\Phi_2)_{tt} = 3°$ and $(\Phi_1)_{gt} = (\Phi_2)_{gt} = 114°$ were used for the racemic diad. Values of the mean-square dipole moment of the meso and racemic OCPDG were obtained

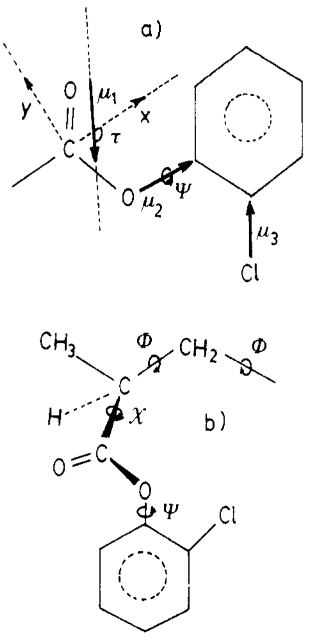

Figure 3. Orientation of the dipoles associated with the bond of the side groups (a) and rotational angle about different bonds of bis(*o*-chlorophenyl) 2,4-dimethylglutarate (b).

by assuming that the dipole moment associated with the side groups, drawn in Figure 3, is the result of three contributions chosen to reproduce the dipole moment of *o*-chlorophenyl propionate,[31] namely, $\mu_1 = 1.757$ D with $\tau = 123°$, $\mu_2 = 0.3$ D, and $\mu_3 = 1.6$ D. The value of the dipole moment associated with the ester group is a function of the rotational angle Ψ governing the rotation about the O–Ph bond; the allowed positions for this angle were found to be[13] $\Psi = \pm 75°$. Standard methods were used to transform the vectors associated with the side groups into the coordinates affixed to skeletal bond C_α–CH_2 for $\chi = 0$ and $\chi = 180°$ orientations of both ester groups.

Recent studies on the polarity of meso/racemic (50/50) diastereoisomers of bis(*o*-chlorophenyl) 2,4-dimethylglutarate suggest that the experimental dipole moments of these compounds can be reproduced by using for the statistical weight parameters ρ, β, γ_1, γ_2, and γ the values of 1.1, 0.3, 2, 0.2, and 2.3, respectively. The value of the statistical weight parameter α, associated with the gg conformation in the racemic OCPDG, was obtained from the fraction f_{gg} of gg conformations, evaluated from the analysis of the ^{1}H NMR spectrum of this isomer described above. Actually, since $f_{gg} = Z_{gg}/Z$, where Z and Z_{gg} represent the total conformational partition function and the conformational partition function of the gg conformations, respectively, α is given by

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

From this equation and by using the value of the parameters given above one obtains $\alpha = 0.41$ if f_{gg} is assumed to be 0.18.

An inspection of the curves of Figure 4 reveals that *meso*-OCPDG is more sensitive to ρ than *rac*-OCPDG. In the former case, the value of $\langle\mu^2\rangle$ diminishes as ρ increases, reaching a minimum at $\rho = 1$, and then it goes up with increasing values of ρ. An increase in ρ raises the stability of the (tπ,tπ) conformations in the racemic compound, which depends on ρ^2, but it also stabilizes (t0,tπ) and (tπ,t0), which depend on ρ, and the net result is a small increase in $\langle\mu^2\rangle$ with increasing ρ. Fair agreement between theory and experiment is found for values of ρ in the vicinity of unity, the value reported by Flory et al.[32] for this quantity in the analysis of the conformation-dependent properties of poly(methyl acrylate).

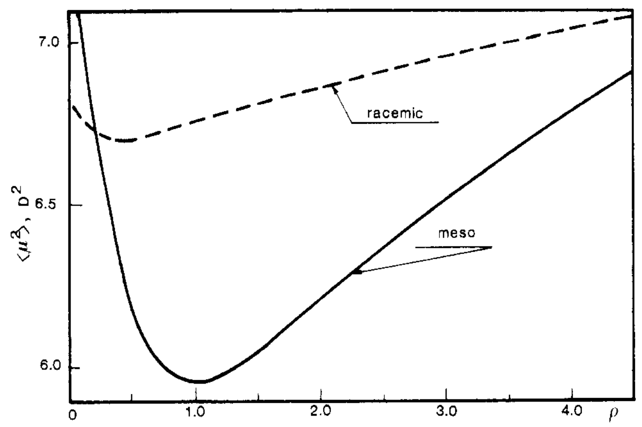

Figure 4. Influence of the statistical weight parameters on the mean-square dipole moments of meso and racemic bis(*o*-chlorophenyl) 2,4-dimethylglutarates.

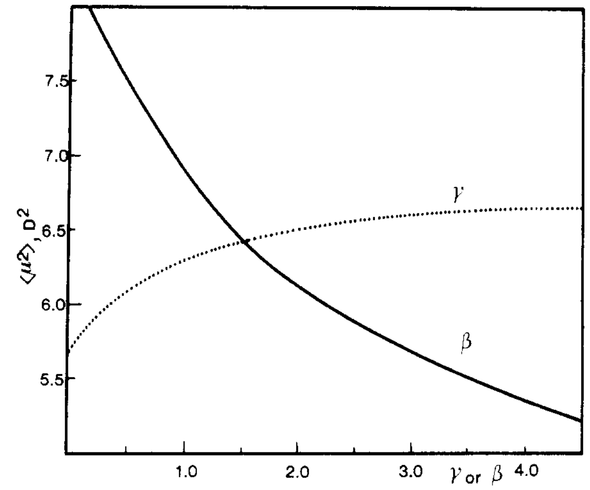

Figure 5. Dependence of the mean-square dipole moment on the skeletal weight parameters α and β for meso bis(*o*-chlorophenyl) 2,4-dimethylglutarate.

The dipole moment of *meso*-OCPDG is more sensitive to γ than to β and the changes that take place in $\langle\mu^2\rangle$ with variations of the same sign in these two statistical weight parameters are opposite (Figure 5). Thus increasing γ from 0.2 to 3 causes the mean-square dipole moment to decrease from ca. 7.8 to 5.8 D^2, whereas the same variation in β raises the value of $\langle\mu^2\rangle$ from 5.9 to only 6.5 D^2. Comparison of theoretical and experimental results reveals that in order to reach agreement between theoretical and experimental results it is necessary to postulate that t0,tπ (or tπ,t0) conformations are strongly favored over t0,t0 conformations; moreover, t0,g0 and t0,gπ should have about the same conformational energy as t0,t0 conformations.

As for the dependence of the mean-square dipole moment of *rac*-OCPDG on γ_1 and γ_2 (the statistical weight parameters that account for the incidence of t0,tπ or tπ,t0 and tπ,tπ with respect to t0,t0 conformations), the calculations indicate that $\langle\mu^2\rangle$ moderately increases and decreases with increasing values of the γ_1 and γ_2 parameters, respectively. The occurrence of gg conformations in this isomer increases the polarity of the compound, the value of $\langle\mu^2\rangle$ increasing from 6.17 D^2 for $\alpha = 0$ to 6.76 D^2 for $\alpha = 0.41$. In any case the theoretical value of the meso/racemic (50/50) mixture, which amounts to 6.37

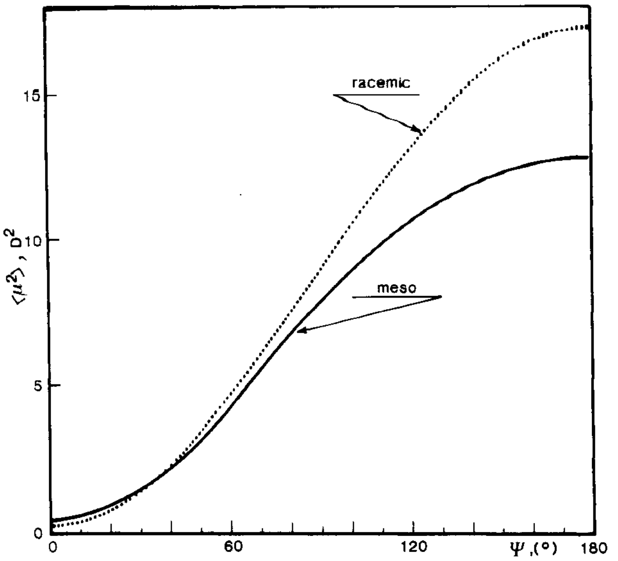

Figure 6. Variation of the mean-square dipole moment with the rotational angle Ψ governing the rotation about O–Ph bonds for meso and racemic bis(*o*-chlorophenyl) 2,4-dimethylglutarate.

D^2, is in good agreement with the experimental result, which was found to be 6.17 D^2.

The sensitivity of the dipole moments of both diastereoisomers to the statistical weight parameters is rather small in comparison with the sensitivity of this conformation-dependent property to the rotational angles about O–Ph bonds. As shown in Figure 6, the curves that represent the dependence of $\langle\mu^2\rangle$ on Ψ are similar for values of Ψ lying in the range 0–60°, but for $60° < \Psi < 180°$ the mean-square dipole moment of *rac*-OCPDG exceeds the value of this quantity for *meso*-OCPDG. In both cases, however, the variations of $\langle\mu^2\rangle$ with Ψ are of considerable magnitude, since the value of the mean-square dipole moment increases from 0.25 to ca. 12.8 D^2 for meso and *rac*-OCPDG, when Ψ increases from 0 to 180°.

Temperature coefficients obtained from experimental results are $10^3\ \mathrm{d}\ln\langle\mu^2\rangle/\mathrm{d}T = 0.7$ and 1.0 K^{-1} for meso and racemic stereoisomers, respectively. Theoretical values of these coefficients are 0.6 and 0.1. Thus in the case of the meso isomer the agreement between theory and experiment is very good, whereas in the racemic isomer the experimental value is much larger than the theoretical one. It should be stressed, however, that the experimental results are not accurate enough; for instance, neglecting the experimental result at 30 °C for the racemic isomer lowers the temperature coefficient to ca. 0.3 K^{-1}.

As was indicated in the Experimental Part, crystalline *rac*-OCPDG has a melting enthalpy of ca. 6.3 kcal/mol and its melting temperature is 360 K; accordingly, the melting entropy ΔS_m of the compound is ca. 18 cal/(mol K). One of the principal contributions to ΔS_m in high molecular weight compounds such as polymers is the conformational entropy S_c and there are some experimental results suggesting that $S_c \simeq (\Delta S_m)_v$, the melting entropy at constant volume.[33,34] The high conformational entropy that most polymers exhibit is therefore responsible for their relatively low melting temperatures. This, however, may not be the case for low molecular weight compounds. The conformational partition function for *rac*-OCPDG is

$$Z = 1 + 2\rho\gamma_1 + \rho^2\gamma_2 + \alpha(1 + 2\rho + \rho^2)$$

The conformational entropy could be expressed by

$$S_c = R\left(\ln Z + T\frac{\partial \ln Z}{\partial T}\right)$$

Evaluation of the conformational entropy using this equation with the main set of statistical weights given above leads to $S_c = 2.7$ cal/(mol K). This result suggests that the contribution of the conformational entropy to the melting entropy is negligible in comparison with the long-range disorder contributions[33] and the change in volume contribution.

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