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Comparative Study of the Modulus and Orientation of the Dipole Moments Associated to the Side Groups of Poly(chlorophenyl acrylates)

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ABSTRACT: The dipole moments of model compounds of the repeating unit of phenyl and substituted phenyl acrylate polymers (phenyl propionate and its halogenated derivatives *o*-chlorophenyl propionate, *m*-chlorophenyl propionate, and *p*-chlorophenyl propionate) were measured in solutions of the compounds in benzene and cyclohexane at several temperatures. The polarity of the halophenyl propionates is extremely dependent on the location of the chlorine atom in the phenyl group in the sense that the value of the dipole moment increases from 1.77 ± 0.03 D at 20 °C for *o*-chlorophenyl propionate to 2.59 ± 0.03 D at the same temperature for *p*-chlorophenyl propionate. Comparison of the dipole moment of phenyl and *p*-chlorophenyl propionates suggests that inductive effects do not account for the difference of their polarity. The critical analysis of the dipole moment of *m*-chlorophenyl propionate and *o*-chlorophenyl propionate indicates that the rotational angles about Ph–O bond are ±60° and ±120° for the former compound and only ±75° for the latter.

Introduction

Although the kinetic phenomena involved in the free radical addition of halogenated phenyl acrylate monomers have been the subject of several investigations,[1-4] no study has been carried out, to our knowledge, focused on the analysis of the configuration-dependent properties of the resulting polymers. It is evident that the substitution of a methoxy group for a phenoxy or a halophenoxy group will alter both the structural geometry and the potentials affecting the torsional rotations of the side groups and the main chain and will have a great incidence in the values of the spatioconfigurational properties such as dipole moments and unperturbed dimensions. Among these properties, the dipole moments should be the most sensitive not only to the halogenation of the phenyl group but also the location of the substitution.

A preliminary step in the investigation of the polarity of poly(halophenyl acrylate)s is to determine the dipole moment associated to the repeating units of the chains. The dipole moment modulus and orientation within esters

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Table I
Analytical Data for Phenyl and Chlorophenyl Propionates, CH_3–CH_2–COOR[a]

R	bp, °C (3 mmHg)	found (required) C	H	O	Cl	IR, ν, cm^{-1}
phenyl	69–70	71.8 (72.0)	6.5 (6.7)	21.7 (21.3)	0 (0)	C=O 1766 C=C_{Ar} 1590, 1490, 1460 δ_{oop} 755, 690
o-chlorophenyl	94–95	58.4 (58.6)	4.8 (4.9)	17.4 (17.3)	19.4 (19.2)	C=O 1760 C=C_{Ar} 1580, 1475, 1450 δ_{oop} 750, 685
m-chlorophenyl	89–90	58.7 (58.6)	4.7 (4.9)	17.5 (17.3)	19.1 (19.1)	C=O 1765 C=C_{Ar} 1590, 1475, 1430 δ_{oop} 775, 680
p-chlorophenyl	98–99	58.5 (58.6)	5.1 (4.9)	17.4 (17.3)	19.0 (19.1)	C=O 1755 C=C_{Ar} 1580, 1485, 1460 δ_{oop} 830, 810

[a] ^1H NMR: CH_3 (δ 1.22), CH_2 (δ 2.45), aromatic protons (δ 7.20); complex signals characteristics of the number and position of the substituent. Chemical shifts are in ppm from TMS.

of general formula RCOOR′ seems to be insensitive to the nature of R and R′ provided that these groups are nonpolar.[5] Thus, values ranging from 1.65 to 1.88 D have been reported for the dipole moment of phenyl acetate (PA). These values are close to those reported for the dipole moments of the alkyl benzoates which lie in the range 1.80 ± 0.05D.[6-9] Therefore, it is expected that the dipole moment and its direction, associated to the reppeating unit of poly(phenyl acrylate) (PPA), coincide with the respective values of these quantities for PA.

Owing to the planarity of the phenyl group, rotations about Ph–O bonds will greatly influence not only the properties of PPA and its halophenyl counterparts, but also they will affect the properties of aromatic polyesters and polyamides in which the Ph–O bonds are located in the main chain.[10] It is important to investigate these rotations as well as to obtain information about whether there are significant inductive effects between the ester and the phenyl groups. In the present work, we have measured the dipole moments of phenyl propionate (PP), *o*-chlorophenyl propionate (OCPP), *m*-chlorophenyl propionate (MCPP), and *p*-chlorophenyl propionate (PCPP), which correspond to the dipole moments associated to the repeating units of PPA, poly(*o*-chlorophenyl acrylate) (POCPA), poly(*m*-chlorophenyl acrylate) (PMCPA), and poly(*p*-chlorophenyl acrylate) (PPCPA), respectively. The configurational properties of these polymers are being investigated in our laboratories. The critical interpretation of the dipole moment of PCPP will indicate whether inductive effects are present which could perturb the modulus and orientation of the molecular dipole moment. On the other hand, the analysis of the dipole moments of both OCPP and MCPP will permit the establishment of the values of the rotational angles about Ph–O bonds.

Experimental Section

Synthesis of the Model Compounds. Phenyl propionate was prepared by the reaction of propionyl chloride with phenol in a 5% aqueous sodium hydroxide solution, at 0 °C. The halo derivatives *o*-chlorophenyl propionate, *m*-chlorophenyl propionate, and *p*-chlorophenyl propionate were obtained in the same way by the reaction of propionyl chloride with the corresponding chlorophenol, following the procedure described by Patai et al.[11] Yield of the reactions lies in the range 60–65% with respect to the corresponding phenol derivative. The purity of the corresponding esters was tested by GLC, exceeding 99.5%. Microanalysis results, boiling points, and spectroscopic characteristics of the phenyl propionate derivatives obtained are listed in Table I.

Dielectric Measurements. Dielectric measurements were made at different temperatures on dried solutions of the esters in both benzene and cyclohexane, with a capacitance bridge and a three-terminal cell operating at 10 kHz.[12] The apparatus was calibrated at each temperature of interest with substances of known dielectric constant.[13] Analytical grade benzene (Merck), cyclohexane (Merck), and carbon tetrachloride (Merck) were exhaustively dried over molecular sieves before their use. Increments in the indices of refraction of the solutions were determine with a Chromatix KHX laser differential refractometer at 632.8 nm. Values of the dipole moment μ were determined by means of the equation of Guggenheim and Smith:[14,15]

$$\mu = \{[27KTM/4\pi\rho N_A(\epsilon_1 + 2)^2][(d\epsilon/dw) - 2n_1(dn/dw)]\}^{1/2}$$

where k and N_A are the Boltzmann constant and Avogadro's number, respectively; M is the molecular weight of the solute, ϵ_1 and n_1 are the dielectric constant and index of refraction of the solvent, respectively; ρ is the density of the solvent; and w is the weight fraction of solute in the solution. Values of the derivatives $d\epsilon/dw$ and dn/dw (each ten degrees from 30 to 60 °C in the case of benzene solutions and from 20 to 50 °C for cyclohexane solutions) were obtained from plots of the increments in dielectric constant ($\Delta\epsilon = \epsilon - \epsilon_1$) and in index of refraction ($\Delta n = n - n_1$) against w. The results obtained for the derivatives at the temperatures indicated above, together with the values of the dipole moments in benzene and cyclohexane, are shown in Tables II and III, respectively. The uncertainty in the values of μ was estimated to be ca. ±3%, coming from the calibration procedure and from neglecting the atomic contribution to the total polarizability. Close agreement between the values of μ obtained for PP in this work (1.68 ± 0.04 D at 30 °C) with those reported in the literature for PA[5,6] (1.65–1.88 D) is apparent. The polarity of the halophenyl propionates seems to be extremely dependent on the location of the substitution. Thus, the dipole moment increases from 1.77

Table II
Summary of Dielectric Results of Phenyl and Chlorophenyl Propionates, CH_3–CH_2–COOR, in Benzene Solutions

R	T, °C	$d\epsilon/dw$	$2n_1\,dn/dw$	μ, D
phenyl	20	1.94_4	-0.08_0	1.64_7
	30	1.90_9	-0.05_6	1.66_9
	40	1.88_0	-0.02_9	1.67_9
	50	1.82_8	0.00_2	1.69_9
	60	1.78_2	0.02_9	1.70_0
p-chlorophenyl	20	3.98_0	0.02_3	2.56_2
	30	3.88_3	0.03_0	2.59_0
	40	3.80_0	0.03_8	2.63_8
	50	3.63_5	0.04_5	2.64_8
	60	3.50_0	0.05_3	2.69_4
m-chlorophenyl	20	3.62_4	0.00_6	2.44_7
	30	3.45_1	0.01_0	2.45_6
	40	3.29_4	0.01_8	2.46_3
	50	3.14_7	0.02_2	2.47_1
	60	3.01_0	0.02_9	2.47_7
o-chlorophenyl	20	1.94_9	0.01_6	1.79_1
	30	1.87_3	0.02_4	1.80_0
	40	1.80_2	0.03_0	1.81_1
	50	1.71_9	0.04_0	1.83_2
	60	1.66_5	0.04_1	1.82_4

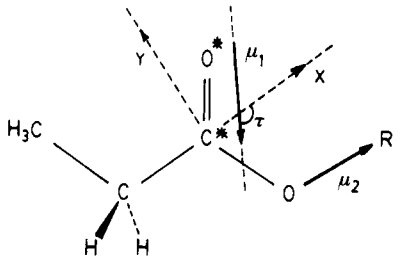

Figure 1. Schematic representation of the two contributions to the dipole moment of the phenyl propionate (R = Ph) molecule; μ_1 is the dipole moment of methyl propionate and μ_2 represents the effect of replacing a CH_3 by a phenyl group.

Table III
Summary of Dielectric Results of Phenyl and Chlorophenyl Propionates, CH_3–CH_2–COOR, in Cyclohexane Solutions

R	T, °C	$d\epsilon/dw$	$2n_1\,dn/dw$	μ, D
phenyl	20	1.78_7	0.12_4	1.68_9
	30	1.72_7	0.12_2	1.70_4
	40	1.66_0	0.12_1	1.71_3
	50	1.59_0	0.11_9	1.71_9
p-chlorophenyl	20	3.40_0	0.13_9	2.63_1
	30	3.18_3	0.14_1	2.61_0
	40	3.26_3	0.14_3	2.71_3
	50	3.07_0	0.14_5	2.69_6
m-chlorophenyl	20	3.02_6	0.10_1	2.49_2
	30	2.93_7	0.10_5	2.51_8
	40	2.82_7	0.10_9	2.53_0
	50	2.72_7	0.11_6	2.54_7
o-chlorophenyl	20	1.57_5	0.12_5	1.75_4
	30	1.47_3	0.12_7	1.73_6
	40	1.42_0	0.12_8	1.74_7
	50	1.35_1	0.13_1	1.74_1

± 0.04 D at 30 °C for OCPP to 2.60 ± 0.01 D at the same temperature for PCPP. On the other hand, the good agreement between the values obtained for all the compounds in benzene and cyclohexane seems to rule out any solvent effect on the dipole moments. A slight increase of μ with temperature can be seen in Tables II and III, respectively.

Theoretical Analysis

Phenyl Propionate and *p*-Chlorophenyl Propionate. The molecules of PP and PCPP can be formally obtained from methyl propionate (MP) by substitution of the O–CH_3 bond by O–R groups with R = phenyl and *p*-chlorophenyl for PP and PCPP, respectively.

The dipole moment of PP was calculated as the sum of two contributions: μ_1, which is the dipole moment of the methyl ester group, and μ_2, which will represent the effect of replacing the O–CH_3 by the O–R bond (see Figure 1). The value of 1.75_7 D was assumed for μ_1, which is the dipole moment of methyl propionate measured at 25 °C in benzene solutions,[6,16] with an orientation defined by[5] $\tau = 123°$. The μ_2 component is taken to be positive when it points away from the O atom, as shown in Figure 1, i.e., when the R group is less electronegative than the O atom. In phenyl esters,[5,10] the C*OPh angle exceeds CC*O by ca. 6–10° and therefore the OR bond is not exactly parallel to the x axis shown in Figure 1. Taking the difference between the two valence angles to be 7.5°,[10] $\mu = \mu_1 + \mu_2$ was calculated for several values of μ_2 ranging from +1 D (i.e., oxygen atom more electronegative than the R group) to −2 D; the results are summarized in Figure 2. It is clear from this figure that values of $\mu_2 = +0.3$ and +0.2 D are required to reproduce the experimental results of for PP at 20 °C in benzene (1.65 D) and cyclohexane (1.69 D) solutions, respectively. This result seems reasonable taking into account that the ether O–Ph bond is less polar than the similar O–CH_3 bond as proved by the dipole moments of 1.17, 1.17, and 1.35 D obtained for diphenyl,[6,17] methylphenyl,[6,18] and dimethyl[6,19] ethers, respectively, all of them measured at 25 °C in cyclohexane solutions. Therefore, the effect of replacing the O–CH_3 by a less polar O–Ph group is equivalent to introducing a small positive (i.e., pointing to the Ph group) value of μ_2.

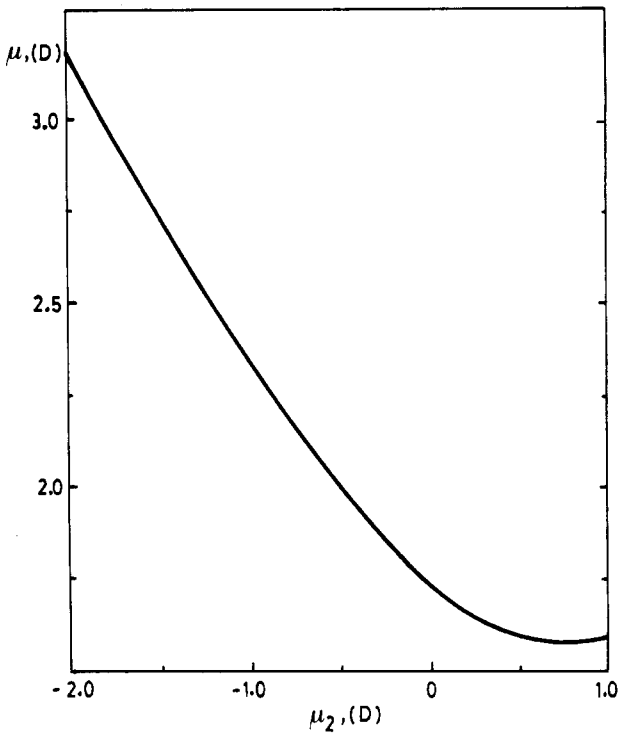

Figure 2. Dipole moment obtained by addition of μ_1 and μ_2 vectors (see Figure 1). The μ_2 component is taken to be positive when, as drawn in Figure 1, it points away from the O atom, i.e., when the R group is less electronegative than the O atom.

In order to reproduce the experimental values of the dipole moments of PCPP at 20 °C (2.56 D in benzene solution and 2.63 D in cyclohexane), it is required to use $\mu_2 = -1.3$ and −1.4 D. Comparison of the results obtained for PP and PCPP indicates that the difference in values of μ_2 required for these two molecules corresponds exactly to the dipole moment of a chlorobenzene molecule[5,6,20] (1.60 D), which is what could reasonably be expected taking into account that PCPP can be formally obtained from PP by introducing a molecule of chlorobenzene and eliminating a molecule of benzene. Thus, the dipole moment of PCPP can be obtained by addition of three contributions, namely, $\mu_1 = 1.75_7$, $\mu_2 = +0.2$ to +0.3, and $\mu_3 = -1.6$ D, representing respectively the dipole moments of the ester group, the effect of replacing an O–CH_3 by a O–Ph group, and the Cl–Ph bond (this last component points from Cl to Ph).

The dipole moments of both PP and PCPP do not depend on any rotation which could be affected by temperature; the only way of changing μ with T is through modifications of the valence angles which should be small close to room temperature. Consequently, small temperature coefficients should be expected for these two molecules. Experimental measurements in cyclohexane seem to confirm this prediction since they show no clear variation of μ with T. However, the values obtained in benzene solutions seem to show an increase of μ with increasing T; this variation of μ could be achieved with a modification of ca. 3–4° in either CC*O or C*OPh bond angles in the range of temperature 20–60 °C.

***m*-Chlorophenyl Propionate.** By use of an analysis similar to that employed above for the PCPP molecule, the dipole moment of MCPP can be obtained by addition of three contributions (see Figure 3), namely, $\mu_1 = 1.75_7$

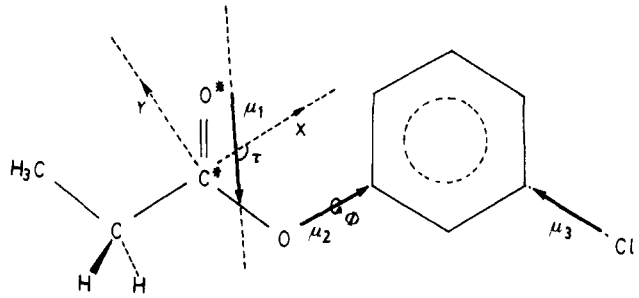

Figure 3. Molecule of *m*-chlorophenyl propionate shown in its all-trans conformation. The dipole moment of the molecule is obtained by addition of three components: $\mu_1 = 1.75_7$ D representing the ester group, $\mu_2 = +0.2$ to $+0.3$ D for the benzene ring, and $\mu_3 = 1.60$ D for the Cl–Ph bond. The conformation shown here with Cl and C* atoms in a trans orientation is taken as the origin of rotations ($\phi = 0$).

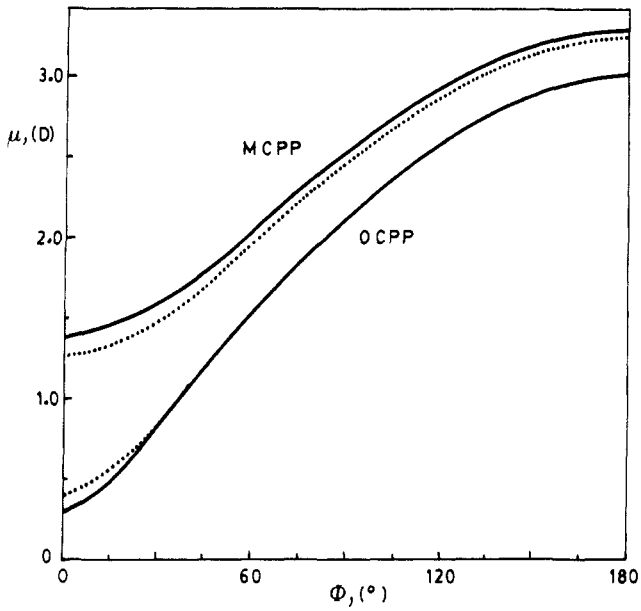

Figure 4. Dipole moments of the *m*- and *o*-chlorophenyl propionate molecules as a function of the rotational angle ϕ. Values for $180 < \phi < 260°$ are symmetrical with those calculated in the range $0 < \phi < 180°$ and are not shown here. Solid and broken lines represent values of μ calculated with $\mu_2 = +0.2$ and $+0.3$ D, respectively.

D for the ester group, $\mu_2 = +0.2$ to $+0.3$ D representing the effect of changing a O–CH_3 by a O–Ph group, and $\mu_3 = 1.60$ D for the Cl–Ph bond.

Once the modulus and orientation of the three contributions are determined, the dipole moment of the whole molecule will depend upon the direction of the O–Ph bond relative to CH_2–C* (i.e., the difference between the valence angles C*OPh and CC*O) and the rotational angle ϕ. We take a value of 7.5° for the first parameter[10] and calculate μ as a function of ϕ. The results of this calculation, summarized in Figure 4, indicate that the dipole moment of the molecule μ increases when the rotational angle increases from $\phi = 0$, where the two main contributions μ_1 and μ_3 partially cancel each other, to $\phi = 180°$, where they are almost parallel.

The conformational energy of the MCPP molecule should be practically identical with that of phenyl acetate, since the interactions produced by either the CH_3 group in the acid residue or the Cl atom in the meta position of the aromatic nuclei are negligibly small. Hummel and Flory[21] reported a conformational analysis of the PA molecule for which they found four minima of energy located at $\phi = \pm 60$ and $\pm 120°$, all of them equivalent due

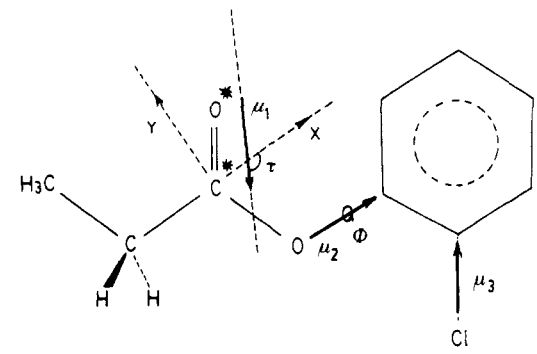

Figure 5. Molecule of *o*-chlorophenyl propionate shown in its all-trans conformation. See legend of Figure 3.

to the symmetry of the molecule.

According to the results shown in Figure 4, when $\mu_2 = +0.2$ D, the dipole moment of MCPP is 2.04 and 2.93 D respectively for $\phi = \pm 60$ and $\pm 120°$; the average of these two values gives $\langle \mu^2 \rangle^{1/2} = 2.52$ D, in excellent agreement with the experimental value of 2.49 D measured at 20 °C in cyclohexane solutions.

In the same way, taking $\mu_2 = +0.3$ D, one obtains $\mu = 1.95$ and 2.87 D for $\phi = \pm 60$ and $\pm 120°$ respectively, whose average gives $\langle \mu^2 \rangle^{1/2} = 2.45$ D, in good agreement with the value measured at 20 °C in benzene solutions.

Despite the fact that μ strongly depends on the rotation ϕ, it should be quite insensitive to the temperature, since all the minima have the same energy. The experimental values seem to agree with this conclusion; thus, even if they suggest a very small positive temperature coefficient, the variation of μ in the range of temperatures studied lies within the experimental error of the measurement. At any rate, this variation of μ, if real, could be produced by the adjustment of ca. 1–2° in the valence angles.

***o*-Chlorophenyl Propionate.** The dipole moment of the OCPP molecule can be calculated with the same scheme used above for MCPP, since the only difference between these two molecules is the orientation of the contribution μ_3 associated to the Ph–Cl bond (see Figure 5). The values of μ for the whole molecule, calculated as function of the rotational angle ϕ, are shown in Figure 4 where one can see that the difference produced by using $\mu_2 = +0.2$ or $+0.3$ D is negligible for $\phi > 50°$. In order to determine the conformational energy of OCPP as function of ϕ, we have taken as starting point the conformational analysis of PA[21] and evaluated the modifications produced in the energy when an ortho H is substituted by a Cl atom[22] as required to transform the ester group of PA molecule into that of OCPP, assuming that the differences arising from the CH_3 group in the acid residue of OCPP should be negligibly small. Thus, we find that the conformational energy of the OCPP molecule is similar to that of PA with two noteworthy differences: First at all, the minimum that appear at $\phi \simeq \pm 60°$ in PA is displaced to about $\phi \simeq \pm 75°$ in OCPP due to the interactions of Cl with C* and O* atoms which in this range of values of ϕ are attractive and reach their minima at $\phi \simeq \pm 75°$ for the Cl,C* pair ($d_{ClC*} = 3.55$ Å) and at $\phi \simeq 100°$ for Cl,O* pair ($d_{ClO*} = 3.35$ Å). However, as ϕ increases, the distances between Cl and the other two atoms decrease and the interactions change to strong repulsions. Thus when $\phi \simeq 120°$, $d_{ClC*} = 2.85$ Å and $d_{ClO*} = 2.75$ Å and they produce interactions of 7.52 and 5.85 kJ/mol, respectively. Consequently, the conformation $\phi \simeq \pm 120°$ has an energy of around 16.72 kJ/mol higher than that of $\phi \simeq \pm 75°$. Therefore, the second difference between the conformational energies of PA and OCPP molecules is the vanishing

of the two minima located at $\phi \simeq \pm 120°$ in PA; instead, the energy of OCPP increases continously as ϕ departs from ±75° reaching two maxima[23] at $\phi = 0$ and 180°.

According to the results of Figure 4, $\mu \simeq 1.80$–1.85 D for $\phi \simeq \pm 75°$, which is in excellent agreement with the experimental values of 1.75 and 1.79 D measured in cyclohexane and benzene solutions, respectively. The two minima of energy are identical both in energy and in value of μ; consequently, as in the case of MCPP, the dipole moment of this molecule should be almost independent of temperature despite the strong variation of μ with ϕ. The experimental results indicate that μ is roughly independent of temperature when measured in cyclohexane solutions, while in benzene it seems to have a very small positive temperature coefficient which could be produced by little variations (ca. 1–2°) of the valence angles.

We therefore conclude that the theoretical values of the dipole moments of these four molecules are in excellent agreement with the experimental results. In the case of MCPP and OCPP, the agreement could be taken as a experimental support for the conformational analysis of PA, reported by Hummel and Flory.[10]

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Registry No. PP, 937-41-7; OCPP, 60202-89-3; MCPP, 6603-24-3; PCPP, 61469-49-6.

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(21) See Figure 4 of ref 10.
(22) Conformational energy calculations were made with the same geometry and energy functions given in ref 10. Since energy minimization by allowing bond angle relaxation was not performed, unrealistic high values of energy when $\phi = 0$ or 180° due to the interactions of O* with either H or Cl were obtained. However, the energies calculated in the range $\phi = 40$–140° should be reasonably good since there are no strong interactions that require relaxation of either bond lengths or bond angles in this range of ϕ.
(23) A third difference between PA and OCPP molecules is the nonequivalence between $\phi = 0°$ and $\phi = 180°$ in OCPP. However, this difference is irrelevant for the present analysis.

Conformational Entropy Associated with the Formation of Internal Loops in Collagen

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ABSTRACT: The conformational entropy of formation of internal loops in the collagen triple helix is estimated. Computer simulation is used to generate random conformations of short polypeptide chains that are connected at both ends to unbroken triple helices. The internal disruption of the triple helix has been modeled as a trifunctional star (i.e. a molecule in which three disordered chains emanate from a single trifunctional branch point, not counting the triple helix itself) that is constrained so that the three ends remote from the branch point meet at a common site. Parameters describing short-range interactions in the branches of the trifunctional star are adjusted so that the characteristic ratio of a linear random chain agrees with that determined for denatured collagen. Excluded volume is introduced by considering atoms of the chain that participate in long-range interactions as hard spheres. The diameter of these spheres is selected so that the chain expansion is at the upper end of the observed range for denatured collagen in aqueous media. Excluded volume interactions reduce by no more than an order of magnitude, relative to the formation of three unrestricted random chains, the probability of formation of internal disruptions for loops containing 30 residues per branch.

Introduction

The triple-helical structure of collagen may contain localized regions of reduced stability, even under conditions where the triple-stranded helix is thermodynamically stable. Transient local unfolding of the triple-stranded helix may occur in such regions, resulting in the formation of internal loops by the three constituent chains. The probability of formation of such a loop depends on the local amino acid sequence, and hence it varies along the molecule. The frequency and location of prolyl and hydroxy-

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