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Conformational Properties of Poly(vinylidene bromide) and Poly(vinylidene fluoride)

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ABSTRACT: The conformational properties of trimer molecules modeling poly(vinylidene bromide) (PVDB) and poly(vinylidene fluoride) (PVDF) have been analyzed by the molecular mechanics method of Boyd et al., which takes into account both steric and electrostatic energy. The geometric and energy results show that the increase in steric hindrance on substituting Br for F outweighs the corresponding decrease in electrostatic effects. The geometric parameters calculated for PVDF agree with those estimated by Loufakis et al. from the length of the chain folds and those determined by Hasegawa et al. by X-ray diffraction. Total conformational energies were used to calculate a set of intramolecular interaction energies that by means of the rotational isomeric states model allowed estimation of the characteristic ratios C_r and dipole moment ratios C_m of PVDB and PVDF under unperturbed conditions. The results agree satisfactorily with available experimental values.

Introduction

In recent years, great efforts have been made to achieve a better understanding of the physical properties of poly(vinylidene halide)s. This is especially true in the case of poly(vinylidene fluoride) (PVDF), which has technological applications in hydrophones, loudspeakers, optical modulators, detectors, radiometers, and other devices, and there have accordingly been many studies of the various crystalline forms and conformations of PVDF in the solid state.[1] However, very little experimental work has been published on the properties of PVDF in solution,[2,3] the most interesting results being the estimation of the unperturbed dimensions of isolated chains in Welch's[2] viscosity and light diffraction study. For poly(vinylidene bromide) (PVDB), experimental data are even scarcer.

The unperturbed dimensions and dipole moments of polymers are generally expressed in terms of the ratios $C_r = \langle r^2 \rangle_0 / 2xl^2$ and $C_m = \langle \mu^2 \rangle / xm^2$, respectively, where x is the degree of polymerization, l the length of the C-C bond, and m the dipole moment of the carbon-halogen bond. In a conformational study of PVDF, which used the experimental value of C_r as a reference,[2] Tonelli[4] found that varying the proportion of head-head:tail-tail polymerization between 0 and 20% had very little effect on the calculated values of C_r and C_m when compared with other factors. This kind of irregularity, which in any case normally amounts to only about 5% of the polymer chain, may accordingly be ignored.

Boyd et al.[5,6] published a study of poly(vinylidene chloride) (PVDC)[6b] in which detailed conformational analysis of segments of the polymer chain was performed by using a molecular mechanics method in which not only C-C torsion angles but also all the bond lengths and bond angles, were varied. As had been done for PVDF (but without taking into account the possibility of head-head:tail-tail addition), they then estimated C_r and C_m (obtaining good agreement with experimental values) using a statistical procedure based on the rotational isomeric states model.[7]

In this article we report the results of a conformational study of PVDB and PVDF carried out by using the molecular mechanics method of Boyd et al.[5] together with the corresponding estimates of C_r and C_m obtained from the calculated conformational energies by the same statistical procedure based on the rotational isomeric states model.

Methodology

The general plan of the conformational calculations performed has been described elsewhere.[6,8] Steric energy, DE + NB, is determined by using a transferable force field including bond stretching terms $U(r_{ij})$, bending terms $U(\theta_{ijk})$, twisting terms $U(\phi_{ijkl})$ and terms for interaction between nonbonded atom pairs, NB. The total conformational energy, ET, is considered to be the sum of the steric contribution DE + NB and the electrostatic contribution EE.

To save computer time, the "optimal" geometry is taken to be the structure obtained by minimizing the steric energy DE + NB (by a modified Newton-Raphson method, with variation of all three kinds of internal coordinate, i.e., r_{ij}, θ_{ijk}, and ϕ_{ijkl}) while simulating the electrostatic energy EE by fixed partial charges; once the geometry of least energy has been determined, the electrostatic energy is calculated correctly for this structure and the total energy ET is obtained.

In calculation of EE it is assumed that the carbon-halogen bonds have intrinsic dipole moments μ_0 that create an electric field giving rise to induced dipole moments μ in each bond, that the induced moments in turn induce further moments in other bonds, and so on. The total intrinsic and induced moment of each bond is obtained by solving a system of equations,[6a] and EE is given by the work done on polarization and the interdipole interaction energies.

Application of the above calculations to model molecules provides information concerning both distortion with respect to the usual values of geometrical features (especially bond angles and torsion angles) and energy contributions, though the latter cannot be taken at face value and should rather be interpreted by comparison with other results obtained by using the same force field. Some of the geometrical results can be compared directly with available experimental values for the polymer.

It is also possible to derive for the polymer chain a set of a priori intramolecular interaction energies that can

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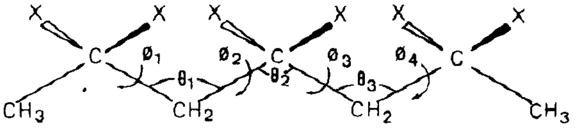

Figure 1. Nomenclature and numbering of the PVDB and PVDF trimer models 2,2,4,4,6,6-hexabromoheptane (X = Br) and 2,2,4,4,6,6-hexafluoroheptane (X = F).

be used to calculate statistical weights in accordance with the rotational isomeric states model and thence to compute values for the characteristic ratio C_r and the dipole moment ratio C_m.

Results and Discussion

(A) Conformational Calculations. The methods indicated above[5-8] were used to calculate the energies and conformational geometries of various conformers of the PVDB "trimer" model 2,2,4,4,6,6-hexabromoheptane (HBH) and the PVDF "trimer" model 2,2,4,4,6,6-hexafluoroheptane (HFH), for which the structure is shown in Figure 1.

The most striking feature of the geometries determined (Tables I and III) is the distortion of the skeletal bond angles θ_1, θ_2, and θ_3, which are appreciably wider in HBH (with values of θ_1 and θ_3 approaching 126° in one or two conformers and values of θ_2 in the range 106–119°) than in HFH (which has average values of 116°, 113°, and 116° for θ_1, θ_2, and θ_3, respectively). As is to be expected, they are likewise greater than those calculated previously[8c] for poly(vinyl bromide) (PVB) and poly(vinyl fluoride) (PVF).

The mean values of 113° and 116° calculated for HFH are close to the values 116.5° and 118.5° found for alternate PVDF C–C–C angles in the X-ray diffraction study of Hasegawa et al.[10] and likewise lie in the range 112–118° estimated by Loufakis et al.[1b] from simple conformational calculations together with the length of chain folds determined by X-ray diffraction.

Like the bond angles, the torsion angles θ_{ijkl}, whose usual values are 180° (T), 60° (G), or −60° (G'), are more distorted in HBH (by 15° or more) than in HFH (by 5° or less). The average lengths of the four skeletal bonds (not shown in Tables I and III) are 1.57–1.58 Å for HBH and 1.55 Å for HFH, whereas the normal, "relaxed" value, 1.54 Å, has been obtained for PVB and PVF,[8c] in which both steric and electrostatic effects are less intense.

To sum up, the increase in steric hindrance on substituting Br for F has a greater influence on the geometry of these molecules than the accompanying decrease in electrostatic effects. The same behavior was predicted for PVB and PVF,[8c] but in PVDB and PVDF it is more pronounced because there are twice as many halogen atoms per unit. The predicted angle and C–C distance distortions confirm the conclusion that in order to derive realistic conformational energies (and hence, subsequently, intramolecular interaction energies) it is necessary to allow the positions of all the atoms to change during optimization.

Tables II and IV list the energies calculated for the conformers included in Tables I and III, with the four contributions to the steric energy DE + NB ($U(r)$, $U(\theta)$, $U(\phi)$, and NB) all separately specified. The largest contributions are, roughly ex aequo, the bending energy, $U(\theta)$, and the energy of interaction between nonbonded atoms, NB, whereas in model molecules of PVB and PVF,[8c] NB had been clearly the largest contribution, with $U(\theta)$ a poor second. The increased relative importance of $U(\theta)$ in the poly(vinylidene halide) trimers can once more be attributed to the increase in steric and electrostatic effects caused by doubling the number of halogen substituents.

As in the poly(vinyl halide) models,[8c] the stretching energies $U(r)$ vary little from one conformer to another while the torsion energies $U(\phi)$ differ widely. The $U(r)$ contribution to DE + NB is the third in size in both PVDB and PVDF and in PVDB is generally two or three times $U(\phi)$, whereas this large proportion is not observed for PVB, PVF,[8c] or for PVDF.

In all the PVDB conformers, the steric energy DE + NB is very much larger than the electrostatic energy EE, whereas in PVDF they are of the same order, with EE even being larger in some conformers ($T_+T_+T_+T_+$, for example), doubtless because of the strong electrostatic repulsion between C–F dipoles (in $T_+T_+T_+T_+$ the C–F dipoles almost eclipse each other and are separated only by a CH_2 group).

A similar situation was found in the case of poly(vinyl halide)s,[8c] with the absolute value of EE being about 40% of DE + NB in PVB but making the larger contribution to ET in PVF.

(B) Statistical Calculations. The intramolecular interactions between bond pairs in the trimer of Figure 1 consist chiefly of steric and electrostatic repulsions between C–X pairs (X = F, Br, or H), which depend on the geometry of the C–C bonds of the skeleton. Figure 2 illustrates the σ interaction involving adjacent C–C bonds with T_+/G_- or T_-/G'_+ rotation angles[9] and two C–X bonds with a large electrostatic dipole interaction. The other interactions considered are α and α' (involving the distortions G_- and G_+, which are more stable than T/T forms), γ (in which $\phi_a/\phi_b = G_+/G_-$ or G'_-/G'_+), and γ' (in which $\phi_a/\phi_b = G_+/G_+$ or G'_-/G'_-).

Assuming them to be additive, the above interactions were calculated from the total energies listed in Tables II and IV by using a least-squares method previously applied to poly(vinylidene chloride)[6b] (Table V). For HFH, there were problems in convergence during the minimization process, perhaps because of HFH's greater electrostatic energy, as a result of which we found fewer conformers for HFH (Tables III and IV) than for HBH (Tables I and II). This in turn meant that E_r and $E_{r'}$ could not be calculated in the same way for HFH as for HBH; for HFH they were obtained from the experimental value of C_r for PVDF.[2] The results of reconstructing the total energies as the sums of the intramolecular interactions are satisfactory (Tables II and IV) and show that, in spite of the magnitude of the electrostatic effects, the additive interaction scheme is valid.

In general, the interactions previously calculated for poly(vinylidene chloride), PVDC,[6b] are closer to those now obtained for PVDF than to the PVDB values (Table V), suggesting that the increase in electrostatic effects on substituting F for Cl are less than the increase in steric hindrance on substituting Br for Cl.

The fact that the difference in E_σ between PVDB and PVDC is greater than the difference in $E_{\gamma'}$, which is quite small, may likewise be due to steric effects when Br is substituted for Cl. One of the most striking features of the energy results, the great difference between the stability of G_- and G_+ conformations ($E_{\alpha'} - E_\alpha$ being 8.90 kJ·mol^{-1} for PVDB and 13.16 kJ·mol^{-1} for PVDF), may be in part attributed to the nonbonded hydrogen···halogen repulsion.

For PVDC,[6b] the interaction parameters of Table V were used to construct statistical weight matrices in accordance with the rotational isomeric states model. Posi-

Table I
Calculated Geometry of 2,2,4,4,6,6-Hexabromoheptane

conformer	ϕ_1	ϕ_2	ϕ_3	ϕ_4	θ_1	θ_2	θ_3	ET, kJ·mol^{-1}
$G'_+T_+T_+G'_+$	-42.2	192.6	192.6	-42.2	123.8	106.6	123.8	125.0
$G'_+T_+T_-G_-$	-42.1	189.4	170.6	42.1	123.8	106.9	123.8	125.7
$T_+T_+T_+T_+$	200.3	200.4	200.5	200.4	125.4	105.8	125.4	134.4
$T_+T_+G'_+T_+$	200.1	197.9	-46.9	195.0	125.8	112.5	124.6	138.6
$T_+T_-G_-T_-$	180.5	178.9	45.1	165.5	127.8	112.2	124.2	144.5
$T_+T_+G_+T_+$	195.4	200.3	86.8	201.9	125.0	110.1	124.4	140.2
$T_+G_+G_+T_+$	201.0	73.6	73.6	201.0	125.8	119.0	125.8	149.6
$T_+G_+G_-T_-$	203.0	83.3	46.5	163.2	124.0	116.8	124.8	138.2
$T_+T_+T_-T_-$	199.9	197.7	162.3	160.1	125.3	106.4	125.3	136.5
$T_+T_+G'_+G'_+$	199.7	198.9	-55.0	-50.7	125.6	112.1	123.3	132.1
$G_-G'_-T_+T_+$	70.6	-44.9	200.9	199.5	124.0	111.7	125.6	140.9
$T_+T_+T_+G_+$	200.1	199.8	199.9	78.6	125.4	105.8	125.5	139.1
$T_+T_+T_-G'_-$	199.7	198.8	163.2	-79.2	125.3	106.4	125.4	141.2
$G'_+T_+T_+G_+$	-40.5	194.3	199.6	87.2	123.4	106.7	125.0	135.8
$G'_+T_+T_-G'_-$	-41.8	189.7	162.4	-80.4	123.8	106.5	125.2	135.7
$T_+G'_+T_-G_-$	195.9	-44.5	173.4	43.3	123.9	113.7	123.8	131.9
$T_+T_+T_+G'_+$	199.7	201.0	192.5	-41.7	125.2	106.2	123.9	129.4
$T_+T_+T_-G_-$	199.4	198.1	171.0	41.7	125.2	106.6	123.9	130.7

Table II
Calculated Conformational Energies of 2,2,4,4,6,6-Hexabromoheptane (kJ·mol^{-1})[a]

conformer	DE = NB	$U(r)$	$U(\theta)$	$U(\phi)$	NB	EE	ET	parameters
$G'_+T_+T_+G'_+$	120.4	13.4	52.0	2.5	52.5	4.6	125.0	$E_0 = 2E_\alpha = 127.7$
$G'_+T_+T_-G_-$	121.1	13.6	50.3	2.3	54.9	4.6	125.7	$E_0 = 2E_\alpha = 127.7$
$T_+T_+T_+T_+$	124.9	13.3	48.9	11.1	51.6	9.5	134.4	$E_0 = 136.5$
$T_+T_+G'_+T_+$	132.9	13.8	57.8	8.7	52.6	5.7	138.6	$E_0 = E_\alpha = 132.1$
$T_+T_-G_-T_-$	138.9	14.4	65.8	4.6	54.1	5.7	144.5	$E_0 = E_\alpha = E_\sigma = 140.4$
$T_+T_+G_+T_+$	132.1	14.1	56.0	11.2	50.8	8.1	140.2	$E_0 = E_{\alpha'} = 141.0$
$T_+G_+G_+T_+$	145.3	16.0	70.1	3.2	56.0	4.3	149.6	$E_0 = 2E_{\alpha'} = E_{\mathrm{r}'} = 149.6$
$T_+G_+G_-T_-$	133.2	14.6	64.9	2.9	50.8	5.0	138.2	$E_0 = E_\alpha = E_{\alpha'} = E_\mathrm{r} = 138.2$
$T_+T_+T_-T_-$	127.0	13.7	54.8	5.4	53.1	9.5	136.5	$E_0 = 136.5$
$T_+T_+G'_+G'_+$	126.7	13.7	53.3	6.7	53.0	5.4	132.1	$E_0 = 2E_\alpha = 127.7$
$G_-G'_-T_+T_+$	131.8	13.8	55.4	8.7	53.8	9.1	140.9	$E_0 = E_\alpha = E_{\alpha'} = 136.6$
$T_+T_+T_+G_+$	131.3	13.7	57.4	6.6	53.7	7.8	139.1	$E_0 = E_{\alpha'} = 141.0$
$T_+T_+T_-G'_-$	133.6	14.2	57.9	6.8	54.7	7.6	141.2	$E_0 = E_{\alpha'} = 141.0$
$G'_+T_+T_+G_+$	130.2	14.1	54.2	7.0	54.9	5.6	135.8	$E_0 = E_\alpha = E_{\alpha'} = 136.6$
$G'_+T_+T_-G'_-$	130.4	14.6	56.4	4.9	54.4	5.3	135.7	$E_0 = E_\alpha = E_{\alpha'} = 136.6$
$T_+G'_+T_-G_-$	127.7	13.8	53.4	7.6	52.9	4.2	131.9	$E_0 = 2E_\alpha = E_\sigma = 136.0$
$T_+T_+T_+G'_+$	122.7	13.3	52.9	4.4	52.1	6.7	129.4	$E_0 = E_\alpha = 132.1$
$T_+T_+T_-G_-$	123.9	13.7	53.2	4.2	52.8	6.8	130.7	$E_0 = E_\alpha = 132.1$

[a] DE = NB = steric energy, $U(r)$ = stretching energy, $U(\theta)$ = bending energy, $U(\phi)$ = twisting energy, NG = energy of interaction between nonbonded atoms, EE = total electrostatic energy, ET = DE = NB = EE = total conformational energy.

Table III
Calculated Geometry of 2,2,4,4,6,6-Hexafluoroheptane

conformer	ϕ_1	ϕ_2	ϕ_3	ϕ_4	θ_1	θ_2	θ_3	ET, kJ·mol^{-1}
$T_-G_+G_+T_-$	175.9	61.2	61.2	175.9	116.4	116.4	116.4	30.2
$T_+T_+G'_+G'_+$	183.0	187.8	-59.8	-59.7	114.9	113.9	118.1	32.5
$G'_+T_+T_+G'_+$	-59.5	189.7	189.7	-59.5	116.3	111.3	116.3	32.7
$T_+T_+T_+T_+$	180.8	180.8	180.8	180.8	115.1	111.0	115.1	38.4
$T_+T_+G'_+T_+$	184.3	188.7	-57.2	190.2	115.0	113.7	116.3	33.4
$G_-G'_-T_+T_+$	58.3	-91.5	180.3	180.3	117.5	112.6	115.0	46.0
$G'_+T_+T_-G_-$	-59.2	188.4	171.6	59.2	116.4	111.5	116.4	34.4
$T_+T_+T_+G'_+$	181.7	183.4	189.8	-57.4	114.9	111.3	116.3	35.1
$T_+T_+T_-G_-$	180.8	180.6	171.4	59.2	115.0	111.3	116.4	35.3
$T_+G'_+T_-G_+$	192.5	-58.3	179.4	63.4	116.7	114.2	116.5	35.8

Table IV
Calculated Conformational Energies of 2,2,4,4,6,6-Hexafluoroheptane (kJ·mol^{-1})[a]

conformer	DE = NB	$U(r)$	$U(\theta)$	$U(\phi)$	NB	EE	ET	parameters
$T_+T_+G'_+G'_+$	22.9	2.3	10.2	1.4	9.0	9.6	32.5	$E_0 = 2E_\alpha = 32.8$
$G'_+T_+T_+G'_+$	22.3	2.1	9.5	1.9	8.8	10.4	32.7	$E_0 = 2E_\alpha = 32.8$
$T_+T_+T_+T_+$	14.2	1.8	4.2	1.7	6.5	24.1	38.3	$E_0 = 37.8$
$T_+T_+G'_+T_+$	19.6	2.0	6.8	3.1	7.7	13.8	33.4	$E_0 = E_\alpha = 35.3$
$G_-G'_-T_+T_+$	26.0	2.5	9.2	5.4	8.9	20.0	46.0	$E_0 = E_\alpha = E_\alpha = 46.0$
$G'_+T_+T_-G_-$	22.7	2.2	9.6	1.9	9.0	11.7	34.4	$E_0 = 2E_\alpha = 32.8$
$T_+T_+T_+G'_+$	18.6	2.0	6.9	2.1	7.6	16.5	35.1	$E_0 = E_\alpha = 35.3$
$T_+T_+T_-G_-$	18.5	2.1	7.4	1.5	7.5	16.8	35.3	$E_0 = E_\alpha = 35.3$
$T_+G'_+T_-G_+$	25.3	2.4	11.0	2.5	9.4	10.5	35.8	$E_0 = 2E_\alpha = E_\sigma = 35.6$

[a] DE = NB = steric energy, $U(r)$ = stretching energy, $U(\theta)$ = bending energy, $U(\phi)$ = twisting energy, NB = energy of interaction between nonbonded atoms, EE = total electrostatic energy, ET = DE = NB = EE = total conformational energy.

Table V
Intramolecular Interaction Parameters Derived from the Total Conformational Energies (kJ·mol^{-1})

param	PVDB	PVDF	interaction[a]
E_0	136.46	37.82	base energy
E_α	−4.36	−2.51	G_- or G'_+ bond
$E_{\alpha'}$	4.54	10.65	G_+ or G'_- bond
E_σ	8.29	2.78	T_+/G_-, T_-/G'_+ pair
E_r	1.57	−6.69	G_+/G_-, G'_-/G'_+ pair
$E_{r'}$	4.06	3.81	G_+/G_+, G'_-/G'_- pair

[a] The slash in the pair interactions refers to interactions of a bond pair across an intervening CBr_2 or CF_2 group. The E_β parameter, which corresponds to T_+/T_+ or T_+/T_- interactions, has been taken to be zero.

Table VI
E_v Dependence of the Characteristic Ratio C_r and the Dipole Moment C_m (PVDF)[a]

E_v, kJ/mol	5.02	5.85	6.69	7.52	8.36	9.20
C_r	6.0	5.8	5.5	5.2	4.9	4.6
C_m	0.97	0.93	0.89	0.84	0.79	0.73

[a] The other PVDF parameters of Table V are assumed constant. Temperature = 190 °C.

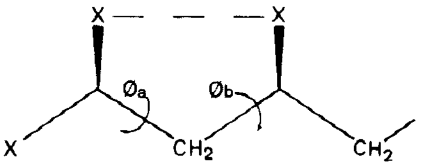

Figure 2. Scheme of the σ interaction: $\phi_a/\phi_b = T_+/G_-$ or T_-/G'_+, X = F or Br.

Table VII
Experimental and Calculated Values of the Characteristic Ratio C_r and the Dipole Moment C_m

	$C_r = \langle r^2 \rangle_0/2xl^2$ (t = 25 °C)		$C_m = \langle \mu^2 \rangle/xm^2$ (t = 60 °C)	
	calcd	exptl	calcd	exptl
PVDB	8.2[a]		0.74[a]	
PVDC	12.0[b]	8[c]	1.83[b]	≈0.8[b]
PVDF	5.7[a]	5.6[d]	0.84,[a] 1.03–0.8[e]	

[a] Calculated from the parameters of Table V. [b] Reference 5c. [c] Matsuo, K.; Stockmayer, W. H. *Macromolecules* **1975**, *8*, 760. [d] Determined at 190 °C,[2] at which temperature the value calculated for C_r in this study is 5.5 (see Table VI). [e] Calculated for t = 85 °C, and 0–20% *H–H*:*T–T* addition.[4]

tive and negative divergences from the standard angles T (180°), G (60°), and G' (300°) were considered separately by using mean values obtained from Table I for PVDB (G_+ = 80°, G_- = 40°, T_+ = 200°, T_- = 165°, G'_+ = 315° and G'_- = 280°) and from Table III for PVDF (G_+ = 65°, G_- = 55°, T_+ = 185°, T_- = 175°, G'_+ = 305°, and G'_- = 295°). Mean values were also used for the C–C–C angles: $\theta_1 = \theta_3$ = 125° and θ_2 = 110° for PVDB; $\theta_1 = \theta_3$ = 116° and θ_2 = 113° for PVDF.

Table VII compares the available experimental values of C_r and C_m with the values calculated by using the statistical weight matrices constructed as above. Values for PVDC and values calculated by other researchers for PVDF are also shown. As for poly(vinyl halide)s,[8c] the calculated C_r and C_m are greater for the chloro derivative than for either the bromo or fluoro derivative. If empirically C_r and C_m can be assumed to behave similarly in the PVB–PVC–PVF and PVDB–PVDC–PVDF series, then the experimental results for the two series together agree with these qualitative predictions (for the PVX series there are no experimental data for the fluoro derivative, and for the PVDX series experimental values for the bromo derivative are likewise unavailable).

For PVDF there is good quantitative agreement among the values of C_r obtained by Welch,[2] Tonelli,[4] and the present study, and the value of C_m calculated here from just the conformational energies and C_r is fairly close to that obtained by Tonelli[4] taking into account 0–20% of head–head:tail–tail polymerization.

Though the values listed in Table V could doubtless be estimated more accurately if suitable experimental data were available, the values of C_r and C_m obtained nevertheless show that, as in the case of poly(vinyl halide)s,[8c] their calculation from the total conformational energies of short oligomers allows a good first approximation to be obtained for conformation-dependent experimental quantities.

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