Table IV. Calculated Dyad and Triad Composition at Stereochemical Equilibrium[a]

	Polystyrene 20°	Polystyrene 140°	TPH 140°
f_m	0.398	0.432	0.486
F_I	0.143	0.173	0.235
F_H	0.510	0.518	0.501
F_S	0.347	0.309	0.264

[a] All calculations with $\tau^* = 1.00$ and η given by eq 28.

fraction of *meso* dyads in TPH is given by $F_I + {}^1/_2F_H$, *i.e.*, by[5]

$$(f_m)_3 = (1 + \eta + \eta\tau^*)/(1 + \eta)(2 + \eta\tau^*) \quad (33)$$

The occurrence of racemic dyads in excess over *meso* dyads is a direct consequence of $\eta > 1$. It is to be noted, however, that the equilibrium composition of the polystyrene chain differs markedly from that of TPH (or of DPP as well). Neighbor influences obviously are responsible for the differences. The fallacy of direct identification of the polymer composition at equilibrium with that of its oligomeric analog will be apparent from the illustrative calculations in Table IV.

In an all-syndiotactic chain of great length ($x \rightarrow \infty$) and subject to the condition $\omega = \omega' = \omega'' = 0$, the proportion of dyads that occur in the *tt* conformation is given by[20]

$$p_{tt}'' = 1 - 2/[4 + (\eta\tau^*)^2 + \eta\tau^*\sqrt{4 + (\eta\tau^*)^2}] \quad (34)$$

This result may be obtained by application of familiar eigenvalue methods to the matrix $\mathbf{U}_r^{(2)}$ given by eq 21. With η given by eq 28 and $\tau^* = 1.00$, we find according to eq 34 that $p_{tt}'' = 0.818$ at 20° and 0.752 at 140°. In assessing this indicated preference for the *trans* conformation, one should observe that eq 34 yields $p_{tt}'' = {}^1/_2$ in the limit $\eta = 0$, as follows from the rule that neighboring dyads cannot both be *gg* when the ω's are zero. A strong preference for the *tt* form is nevertheless indicated. This follows directly from the fact that η exceeds unity according to eq 28 at temperatures below about 200°.

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Stereochemical Equilibrium and Configurational Statistics in Oligomers of Poly(vinyl chloride)

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Abstract: Stereochemical equilibration of 2,4-dichloro-*n*-pentane (DCP) in DMSO at 70° in the presence of LiCl yields a mixture containing 36.4 ± 0.3% of the *meso* isomer. The statistical weight parameter (η) evaluated from this result is used for theoretical calculation of the proportions of various conformers in *meso* and racemic DCP, and also in the three diastereoisomers of 2,4,6-trichloro-*n*-heptane (TCH). Calculations for TCH are compared with estimates of Doskočilová and coworkers from nmr coupling constants. It is shown that the less-favored conformations, often ignored, contribute appreciably to the conformer populations of the TCH isomers.

Molecules of the series $H\text{-}(CH_2CHCl)_x\text{-}CH_3$, comprising poly(vinyl chloride) and its oligomers, are characterized by less severe steric interactions than the homologs of polystyrene[2] owing to the smaller size of the chlorine substituent compared with phenyl. Conformations in which a chlorine substituent is involved in a steric overlap with another chlorine atom or with a methylene group cannot therefore be so readily subordinated to the category of near-negligibility. A greater number of conformations must be taken into account, with appropriate weights assigned to each, and a larger set of parameters is required to describe adequately those conformations which make appreciable contributions. The task is by no means beyond reach of fulfillment, and definite inferences can be drawn from analysis of the limited experimental evidence available.

Both infrared and nmr spectroscopy[3-10] have been

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applied to the elucidation of the conformations of the diastereoisomers of 2,4-dichloropentane (DCP) and 2,4,6-trichloroheptane (TCH), *i.e.*, the oligomers of poly(vinyl chloride) with $x = 2$ and 3. The C–Cl stretching vibration, being affected by the disposition of substituents attached to the adjoining carbon atoms on either side, occurs at a frequency which can be identified with the local conformation.[11,12] The coupling constants for methine and methylene hydrogens provide the basis for the nmr method.[7–10] The two methods, supplemented by measurements of dipole moments,[6,8] agree on the preferred conformations. For *meso* DCP, the *tg* forms (right- and left-handed; see ref 2) are preferred; for racemic DCP, the preferred form is *tt*. Corresponding preferences are manifested by the diastereoisomers of TCH: *tgtg* and *gttg* for the isotactic, *tgtt* and *gttt* for the heterotactic, and *tttt* and *ttgg* for the syndiotactic species. Proportions of the different conformers for each have been estimated by Doskočilová and coworkers[9] from the infrared intensities for C–Cl stretching vibrations and from nmr spectra of the isomers.

Recently Schneider, *et al.*,[10] have pointed out that the infrared and nmr spectra of *meso* and racemic DCP cannot be fully explained in terms of their preferred conformations to the exclusion of all others. The infrared spectra also give evidence of less-favored conformations. A weak absorption at 645 cm^{-1} in the spectrum of the *meso* isomer was attributed to the $t\bar{g}$ conformer; $g\bar{g}$, *tt*, and *gg* forms may also occur in minor amounts. Frequencies at 718 and 685 cm^{-1} in the spectrum of the racemic isomers have been assigned to the *gg* and *tg* forms, respectively; a band of very low intensity at 706 cm^{-1} may be due to the $g\bar{g}$ conformer. (For the significations of *g* and $\bar{g}$, see ref 2.) According to Schneider and coworkers,[10] vicinal coupling constants from the nmr spectra of these compounds, and especially their dependence on temperature, are consistent with significant contributions from these less prominent conformations.

In this paper we present results of the stereochemical equilibration of DCP carried out in dimethyl sulfoxide (DMSO) in the presence of LiCl. The proportions of *meso* and racemic forms and the analytical evidence cited above on the conformations of individual isomers are interpreted according to the theory[13–16] applied in the preceding paper[2] to oligomers of polystyrene.

Experimental Section

2,4-Dichloropentane (DCP) was synthesized following the procedure given by Pritchard and Vollmer.[17] The *meso* and racemic isomers were partially separated using the Varian Aerograph A90-P3 chromatograph. A column, 200 cm × 6.5 mm, packed with 20% Carbowax on 60–80 Chromosorb W was used. It was operated at a temperature of 90° with a helium flow rate of about 60 ml/min. Nmr spectra[7,9,10] of the separated isomers confirmed that the racemic isomer had the shorter retention time on the column.

Atttainment of equilibrium between the two isomers of DCP was achieved at 70° in a saturated solution of LiCl in DMSO.[18] The concentration of LiCl was *ca.* 0.01 *M*.[18] The solutions, prepared in the manner described previously,[2,19] were sealed in ampoules under vacuum and maintained at 70° for varying periods of time. The ampoules were opened, water was added, and the DCP was extracted with *n*-pentane.

Analysis of the samples was carried out through use of the chromatographic column and procedure specified above. The relative amounts of the diastereoisomers were determined from areas of the peaks on the chromatograms, the areas being measured by the triangle approximation method. Mole fractions thus determined were confirmed within ±0.5% by values calculated from the heights of the peaks.

Results

Four partially separated samples of DCP in which the mole fraction f_m of the *meso* isomer varied from 0.160 to 0.743 were subjected to conditions promoting epimerization as described above. Results are summarized in Table I. Entries for equilibrated samples in the final column are the means of three separate chromatographic analyses agreeing within ±0.5%. Epimerization proceeds very slowly at 25° according to results for the first sample in the table. At 70°, however, equilibration appears to be complete after 7 days. The final values attained by each of the four samples are the same within experimental error. Two of the samples initially contained the *meso* isomer in excess, and in two of them the racemic isomers were in excess. Thus, the concordant, time-independent values of f_m may be identified with the state of equilibrium with full assurance. The results yield $f_m = 0.364 \pm 0.003$ for the equilibrated mixture of diastereoisomers at 70° in DMSO.

Table I. Epimerization of *meso* and Racemic 2,4-Dichloro-*n*-pentane

Temp, °C	Time, days[a]	Mole fraction, f_m, of *meso* isomer
	0	0.623
25	14	0.590
25	28	0.558
70	7	0.364
70	14	0.365
	0	0.190
70	7	0.364
70	14	0.364
	0	0.160
70	60	0.363
	0	0.743
70	60	0.363

[a] Samples dissolved in DMSO saturated with LiCl.

A somewhat lower equilibrium value of $f_m = 0.29$ was found by Billups and Kurtz[20] at 25°. They carried out the epimerization of DCP in CS$_2$ using AlCl$_3$ as the catalyst. The same value of f_m was obtained by approaching equilibrium in either direction. Substantial polymerization (20–30%) and rearrangement to *erythro*- and *threo*-2,3-dichloropentane occurred simultaneously with epimerization. The results of Billups and Kurtz[20] may have been vitiated by these side reactions. Differences in experimental conditions appear,

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however, to be the principal sources of the disparity between our result and theirs. The lower temperature of their experiments, the lower dielectric constant of CS_2 compared with DMSO, and possible complex formation between DCP and $AlCl_3$ may have contributed to the difference of result. Of these, the difference in temperatures probably accounts for the larger part of the disparity between our value of f_m and theirs (*cf.* below).

Discussion

The calculation of conformational energies by various empirical procedures is much in vogue. Such calculations rest on two assumptions: that conformational energies can be reckoned in terms of the interactions between pairs of nonbonded atoms or groups, with or without supplementation by torsional potentials ascribed to rotations about single bonds, and that the energies of interaction for nonbonded pairs can be represented by various semiempirical expressions for *intermolecular* forces. Until the origins of the hindrance potential affecting rotations about single bonds are adequately understood, results of such calculations should be viewed with circumspection. No doubt the main features revealed by such calculations can be relied upon. They should not be trusted in quantitative detail, however. Experimental evidence is essential for assigning the energies to be ascribed to various conformations with the accuracy required for precise statistical weighting.

Current computational schemes are notably deficient when the bond subject to rotation bears a substituent such as –O–, –F, or –NH– having nonbonded electron pairs. The marked preference for the *gauche* conformation in such instances is inexplicable by semiempirical calculations of the kinds mentioned, as we have pointed out elsewhere in greater detail.[21] Chlorine, when present as a substituent, may exert a similar effect. For these reasons, we prefer to estimate statistical weights by inference from other examples supported by experimental evidence.

Considering second-order interactions first, we again observe that interactions involving pairs of CH_3, CH_2, or CH groups separated by four skeletal bonds in the homologous chains $H\text{-}(CH_2CHCl)_x\text{-}CH_3$ can be likened to the corresponding interactions in polymethylene chains.[2] Hence, conformations (*gg* for *meso*, *gg* for racemic; see Table II) giving rise to steric overlaps of such pairs may be assigned the factor[2] $\omega \approx 0.034$ at 25°. The intergroup distance calculated for these conformations on the basis of skeletal bond angles of 112°[13,15] and rotational states at 0 and ±120° is 2.7 Å. The similarly calculated distance between Cl and CH_2 (or CH_3 in DCP) for conformations ($t\bar{g}$ and *gg* for *meso* dyads) that place this pair in a corresponding relationship is 2.8 Å. Since the van der Waals radius of Cl, *ca.* 1.7 Å, is *ca.* 0.2 Å less than the radius of CH_2, a smaller repulsion is indicated. Hence, ω' should exceed ω; we may assume in crude approximation that $\omega' \approx 0.10$. (For definitions of ω, ω', and ω'', see the preceding paper.[2])

The steric overlap in conformations (*tt* and $\overline{gg}$ for a *meso* dyad, for example) that place Cl atom pairs in proximity is less severe. The distance of separation is about 2.8 Å, or only 0.6 Å below the sum of their van der Waals radii. However, coulombic repulsions between the C–Cl dipoles (or the associated partial charges) may be expected to enhance the energy of such conformations to the extent of about 1 kcal $mole^{-1}$. We are thus led to postulate that $\omega'' \approx 0.05$ at 25°. Exact values of the ω's are not required for the following analysis provided that they are small, as earlier considerations indicate, and as following calculations demonstrate.

Statistical weights for various conformations of *meso* and racemic DCP are listed in Table II. They follow directly from the analysis given previously;[2,16] see especially eq 1, 5, 6, and 7 of the preceding paper.[2] Illustrative calculations of the fractions of various conformers of the *meso* and of the racemic isomers are presented in the last two columns. The parameters used for these calculations, given at the foot of the table, should be approximately representative of DCP (and its higher homologs as well) at a temperature in the neighborhood of 70°.

Table II. Statistical Weights and Conformer Fractions for *meso* and Racemic Dyads of 2,4-Dichloro-*n*-pentane

Conformation designation[a]	Statistical weights		Fractions calcd[b]	
	meso	Racemic	*meso*	Racemic
tt	$\eta^2\omega''$	η^2	0.076	0.864
tg[c]	2η	$2\eta\omega'$	0.863	0.049
$t\bar{g}$[c]	$2\eta\tau\omega'$	$2\eta\tau\omega''$	0.043	0.012
gg	ω	1	0.006	0.071
gg[c]	$2\tau\omega'$	$2\tau\omega$	0.012	0.004
$\overline{gg}$	$\tau^2\omega\omega''$	$\tau^2\omega'^2$	8×10^{-5}	1.8×10^{-4}

[a] For the identification of the rotational senses of various conformers designated in the first column, see ref 2 and 16. [b] Calculated for $\eta = 3.5$, $\tau = 0.50$, $\omega = 0.05$, $\omega' = 0.10$, $\omega'' = 0.05$. [c] These entries include the equivalent conformations obtained by reversing the order of the pair; *i.e.*, *gt* is included with *tg*, etc.

Table III reports calculated mole fractions of the *meso* isomer at equilibrium for values of the ω parameters in the neighborhood of the estimates offered above, with η chosen to achieve approximate agreement with experiment. As a reasonable estimate, τ was set equal to 0.50 for most of the calculations; its value is of little importance when the ω's are small. Equations 8 and 10 of the preceding paper[2] were used for these calculations, or, equivalently, the statistical weights for *meso* and racemic

Table III. Calculated Equilibrium Compositions of 2,4-Dichloro-*n*-pentane

η	τ	ω	ω'	ω''	f_m
2.5		0	0	0	0.408
3.2		0	0	0	0.363
3.5		0	0	0	0.346
4.5		0	0	0	0.298
3.5	0.50	0.10	0	0	0.347
3.5	0.50	0	0.10	0	0.348
3.5	0.50	0	0	0.10	0.377
3.5	0.50	0	0.20	0.10	0.376
3.5	0.50	0.05	0.10	0.05	0.363
3.5	1.0	0.05	0.10	0.05	0.372
3.5	0.10	0.05	0.10	0.05	0.356

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[21] See ref 15, pp 171–172.

DCP given in Table II were summed, and the appropriate ratios were taken.

The calculations in Table III show the equilibrium composition to be little dependent on ω and ω' when the ω's are small. The effect of ω'' is greater, but its value is not critical. The mole fraction composition depends predominantly on η. The experimental result, $f_m = 0.364 \pm 0.003$ at 70°, is reproduced by $\eta = 3.2$ and $\omega = \omega' = \omega'' = 0$, and also by $\eta = 3.5$, $\tau = 0.5$, $\omega = 0.05$, $\omega' = 0.10$, and $\omega'' = 0.05$. The former set of parameters would preclude the less-favored conformations (other than *gg* for the racemic form), evidence for the occurrence of which is cited in the introductory section. The latter set of parameters is therefore a more reasonable choice.

Letting $\eta = \exp(-E_\eta/RT) = 3.5$, we find $E_\eta = -850$ cal mole^{-1}, which represents the difference in energy between conformations in which Cl is *syn* to CH and those in which CH_3 is *syn* to CH (see Figure 3 of the preceding paper[2]). If E_η is treated as an energy, *i.e.*, if entropy contributions are ignored, then $\eta = 4.2$ at 25°. Treating other parameters similarly, we obtain $f_m = 0.33$ at 25°, a result somewhat higher than that found by Billups and Kurtz.[20]

The estimate of E_η above denotes an energy difference of -1.7 kcal mole^{-1} between the two principal conformers of racemic DCP, namely, the *tt* and *gg* conformers having statistical weights η^2 and 1, respectively.

Recent results of Goodman and Niu[22] on the stereochemical equilibrium between *meso* and racemic α,α'-dichlorodiethyl ether are of interest. At ordinary temperature they find $f_m = 0.117$, and at *ca.* $-25°$, $f_m = 0.096$. The corresponding values of η are 15.0 and 18.8, respectively. The shorter C–O bonds (1.43 Å), compared to the C–C bonds (1.53 Å) of DCP, enhance the various steric interactions. Assignment of values of zero to the ω's is well justified for this reason. The larger values of η, compared with η for DCP, may likewise be attributed to a larger first-order steric overlap of CH_3 by CH. The value of η may, as Goodman and Niu point out, be increased also on account of the coulombic attraction between Cl and CH in conformations placing them in the *syn* position relative to each other.

Fractions of the principal conformers in the three TCH diastereoisomers calculated from theory are compared in Table IV with estimates of Doskočilová and coworkers[9] from the nmr spectra of these compounds at 20°. The calculated values in the fourth column were obtained by use of a set of parameters, given at the foot of the table, considered appropriate for a temperature of 20°. In particular, the value of $\eta = 4.0$ is consistent with the analysis of the equilibration of DCP at 70°. Inasmuch as the experimental values in the last column of the table are approximate only, more refined calculations are unwarranted.

Table IV. Calculated and Observed Conformer Populations in 2,4,6-Trichloro-*n*-heptane at 20°

Isomer	Conformer	Statistical weight	Conformer fractions	
			Calcd[a]	Obsd[b]
Isotactic (*mm*)	*tgtg*[c]	$2\eta^2$	0.51	0.80
	gtgt	η^2	0.26	0.20
	Others		0.23	
Heterotactic (*mr*)	*tgtt*	η^3	0.42	0.55
	gttt	η^3	0.42	0.45
	gtgg	η	0.03	<0.05
	Others		0.13	
Syndiotactic (*rr*)	*tttt*	η^4	0.82	0.85
	ttgg[c]	$2\eta^2$	0.10	0.15
	Others		0.08	

[a] Calculated for $\eta = 4.0$, $\tau = 0.5$, $\omega = \omega'' = 0.03$, and $\omega' = 0.07$. [b] Results estimated by Doskočilová, Štokr, Schneider, Pivcová, Kolínský, Petránek, and Lím[9] from nmr coupling constants. [c] These entries include also the forms of reversed sequence obtained through rotation of the molecule as a whole.

It will be observed that nonpreferred conformers constitute appreciable fractions of the total conformer populations, according to the calculations. This is especially true of the isotactic isomer, where they comprise *ca.* 23% of the total. These results of calculations are, of course, directly dependent upon the values assigned to the ω's, which can only be estimated by inferences from other examples (see above). Nevertheless, the calculations call attention to the probable importance of conformers other than the principal ones. Their contributions will, of course, affect the observed nmr coupling constants, and hence the conformer fractions calculated for the main rotational isomeric species.

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