Structural Selectivities in the Reduction of Poly(vinyl chloride) with Lithium Aluminum Hydride and Tri-*n*-butyltin Hydride

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ABSTRACT: After ca. 98-99% reduction with $LiAlH_4$ in tetrahydrofuran at 100 °C, poly(vinyl chloride) (PVC) is converted into products containing vinyl chloride monads and *r* dyads in ratios of ~1.1 to 1.4. At this stage in the reaction, *m* dyads are not found, and the monad CHCl group is more reactive than an *r* dyad CHCl by a factor of ca. 3.8. Conformational analysis suggests that the preferential removal of *m* dyads is unlikely to result from a preferred S_N2 attack by $LiAlH_4$ upon the most stable conformers of *m* dyads and *mm* triads. However, the reactivity data can be accommodated by an S_N2 mechanism involving high-energy meso conformers, or by a mechanism involving a rate-limiting attack on halogen by a metallic electrophile. Extensive (>99%) reduction of PVC by Bu_3SnH in 2-methyltetrahydrofuran at ~80 °C leaves vinyl chloride monads unaccompanied by any dyads. This result is shown to be consistent with the presence of nucleophilic $Bu_3Sn\cdot$ radicals as intermediates. Comparisons with reductions by Bu_3SnH suggest that $LiAlH_4$ reduction is an unreliable tool for determining long branch points, methyl branches, and internal double bonds in PVC.

Reductive dechlorination with lithium aluminum hydride, followed by spectroscopic examination of the hydrocarbon product, has comprised a popular approach toward the elucidation of the microstructure of poly(vinyl chloride) (PVC).[1] However, the $LiAlH_4$ reduction of PVC has been shown to suffer from several serious disadvantages, including incomplete removal of halogen and the occurrence of various side reactions leading to undesirable structural complications.[2] Although it is now known that many of these difficulties can be avoided by using tri-*n*-butyltin hydride as the reducing agent,[2] the detailed chemistry of the $LiAlH_4$ reduction retains considerable intrinsic interest nonetheless. The present paper explores some structural consequences of the incomplete reduction of PVC by $LiAlH_4$ and comments further on PVC reductions using Bu_3SnH.

Results and Discussion

Stereoselectivity of $LiAlH_4$ Reductions. As noted earlier,[2] PVC reductions by $LiAlH_4$ are frequently incomplete even when performed under vigorous conditions. This behavior is illustrated by Figure 1A, which shows the ^{13}C NMR spectrum of the product obtained by reducing a typical sample of PVC, prepared by conventional free-radical polymerization, with excess $LiAlH_4$ in tetrahydrofuran (THF) for 7 days at 100 °C.[3] The strong resonance at 30.0 ppm arises from carbons contained in the unperturbed backbone methylenes, and the spectrum exhibits other resonances that can be assigned to carbons in isolated unreduced monomer units (monads),[1a,2] methyl branches[1a] (derived from pendant chloromethyl groups[2,4]), and isolated trans double bonds[2,4] (for spectral assignments, see Figure 2). Of particular interest, however, are the four resonances designated as a–d, which do not appear in the spectra of polymers that have been completely reduced.[1a,2]

The latter observation suggested that these resonances might also be associated with one or more structures containing halogen, and in order to investigate this possibility, another sample of $LiAlH_4$-reduced PVC (polymer R-23, see below) whose spectrum resembled Figure 1A was subjected to a further reduction using Bu_3SnH.[2] This treatment completely eliminated resonances a–d, as well as the resonances associated with isolated secondary chlorine. Thus resonances a–d did indeed appear to be associated with halogen, and their occurrence at a very late stage of the reduction process (>99% reduction, based on the isolated CHCl content) implied that they might be arising from the carbons of isolated vinyl chloride dyads.

Table I
Residual Halogenated Structures in $LiAlH_4$-Reduced PVC

	^{13}C NMR conditions[c]		R[a]		I[b]	
reduced polymer[c]	temp, °C	pulse rep time, s	from c CH_2[d]	from b CHCl[d]	from Cl-β CH_2[d]	from Cl-α CHCl[d]
S-80	110	3.0	2.5_4	2.8_5	3.0_0	4.0_1
R-23	110	3.0	1.8_8	1.8_9	2.1_5	2.5_0
E-80	115	4.0	*e*	3.0_2	*e*	3.5_6
E-54	115	4.0	*e*	1.3_0	*e*	1.5_0

[a] [(*r* dyad CHCl C)/2]/(1000 C); estimated accuracy, ±0.05. [b] (Isolated CHCl C)/(1000 C); estimated accuracy, ±0.05. [c] See Experimental Section for details. [d] For identification of resonances, see Figures 1 and 2. [e] Not calculated due to interference by dimethyl-d_6 sulfoxide.

Wilkes has recently investigated the structures of a series of saturated stereoregular polymers that were obtained by diimide reduction of some stereoregular copolymers of vinyl chloride and 1,3-butadiene.[5] These saturated polymers constitute an excellent model for partially reduced PVC, and their ^{13}C NMR spectra show that they contain vinyl chloride sequences whose configurations are predominantly racemic (*r*, syndiotactic) rather than meso (*m*, isotactic).[5] Resonances appearing in these spectra at ca. 60.8, 47.6, 38.9, and 26.5 ppm vs. Me_4Si (*o*-dichlorobenzene solvent, 100 °C, polymer concentration 20% w/v, chemical shifts estimated by us from copied traces[5]) can be assigned with confidence to carbons b, a, c, and d, respectively, of the *r* dyad in Figure 2. These values are in satisfactory agreement with the shift values of 60.9, 47.9, 39.3, and 26.6 ppm that are found for these carbons from the spectrum of Figure 1A, which was obtained under slightly different conditions (1,2,4-trichlorobenzene solvent, 110 °C, polymer concentration 33% w/v). Moreover, the relative intensities of the a–d resonances of Figure 1A are qualitatively consistent with these assignments, and the complete absence of *m*-dyad resonances from this spectrum can be inferred, not only from the data of Wilkes,[5] but also from the ^{13}C-NMR spectra of the stereoisomers of 2,4-dichloropentane.[6] Similar results were obtained for several other polymers that had been extensively reduced with $LiAlH_4$ (see Table I).

In line with these observations, other workers have observed that the racemic structures in PVC are resistant

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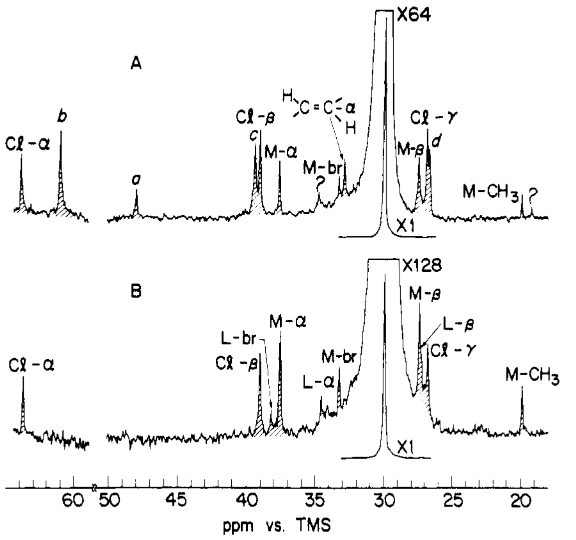


Figure 1. ^{13}C-NMR spectra (25.16 MHz) of PVC (S-80) reduced with: A, $LiAlH_4$; B, Bu_3SnH (one pass). See text for details (TMS = Me_4Si).

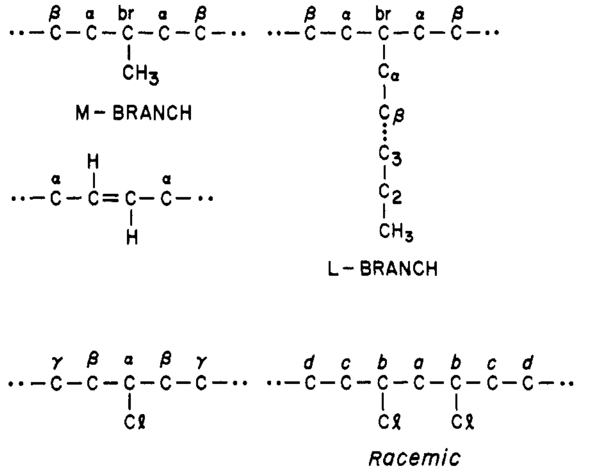


Figure 2. Structures found in reduced PVC.

to $LiAlH_4$ attack. Braun and Schurek[7] studied the $LiAlH_4$ reduction of some PVC samples whose original P_r values (r-dyad fractions) were in the range of 0.60 to 0.65. After about 95–97% reduction with excess $LiAlH_4$ in refluxing THF, the unreduced segments of these polymers were judged to be mostly racemic on the basis of IR evidence.[7] Using IR analysis, Millán et al.[8] found that the syndiotactic segments of PVC were relatively unreactive toward $LiAlH_4$ in THF at 45 °C in the early stages of the reaction.[9] This result was attributed to the preferential reduction of heterotactic triads.[8]

The original PVC's of Table I had P_m values (m-dyad fractions) ranging from 0.44 to 0.49 (Experimental Section). Thus the total absence of m dyads from these polymers after partial reduction with $LiAlH_4$ might seem to imply an enormous difference in the reactivities of the m- and r-dyad structures. However, further consideration of the situation suggests a possible alternative rationale.

If the reductions of the two types of dyad are regarded as kinetically separable processes, the reduction rates can be described by eq 1 and 2, where the k's are rate constants, R and M are the concentrations of the r and m dyads, respectively, and L^n represents the concentration of the reducing agent raised to the appropriate power.

$$-\mathrm{d}R/\mathrm{d}t = k_R L^n R \qquad (1)$$

$$-\mathrm{d}M/\mathrm{d}t = k_M L^n M \qquad (2)$$

Combination of these equations in order to eliminate the time variable, followed by integration within limits, gives eq 3, in which the subscripts 0 and x refer to initial

$$\frac{\ln (M_x/M_0)}{\ln (R_x/R_0)} = k_M/k_R \qquad (3)$$

concentration and concentration after partial reduction, respectively. In a typical reduction experiment, the P_m of the starting polymer (E-80) was 0.44, corresponding to an M_0 value of 220/(1000 C) and an R_0 value of 280/(1000 C). After 98.1% reduction, R_x was found to be 3.02/(1000 C) (Table I), and the ^{13}C NMR spectrum indicated that M_x could have been no greater than ca. 0.27/(1000 C) (as noted, no m dyads were actually found). Hence, from eq 3, $\ln (0.27/220)/\ln (3.02/280) = k_M/k_R = 1.5$. Thus the apparent absence of m dyads after extensive reduction may require only a small difference in relative reactivity, and it is amusing to note that an R_x/M_x ratio of 10^6 [i.e., $M_x = 3.02 \times 10^{-6}/(1000\ \mathrm{C})$] would necessitate a k_M/k_R ratio of only 4.0 for the polymer under discussion!

We realize, of course, that the preceding analysis is not entirely rigorous, since k_M, k_R, and (presumably) k_M/k_R will actually vary during reduction due to changes in the local environments of the meso and racemic groups. Nevertheless, this simple approach illustrates an important principle that generally applies to competitive kinetic situations, viz., that small differences in relative reactivity can produce very large differences in reactant concentration for reactions nearing completion.

Relative Reactivity of Monads and r Dyads Toward $LiAlH_4$. Our ^{13}C-NMR results show that r dyads and isolated secondary CHCl groups are the only "normal" halogenated structures in the polymer when its $LiAlH_4$ reduction is nearly complete. Thus, at this stage in the reaction, the removal of these structures can be described by

$$\underset{r\ \text{dyad}}{-\mathrm{CH_2CH(Cl)CH_2CH(Cl)CH_2}-} \xrightarrow[\mathrm{LiAlH_4}]{k_1}$$

$$-\mathrm{CH_2CH(Cl)CH_2CH_2CH_2}- \xrightarrow[\mathrm{LiAlH_4}]{k_2} -(\mathrm{CH_2})_5-$$

in which the k's can be regarded as pseudo-first-order rate constants since $LiAlH_4$ is now present in considerable excess. The disappearance rates of the two structures are then given by eq 4 and 5, where the isolated CHCl concentration is represented by I. Integration of these expressions within limits[10] yields eq 6 and 7, with the

$$-\mathrm{d}R/\mathrm{d}t = k_1 R \qquad (4)$$

$$-\mathrm{d}I/\mathrm{d}t = k_2 I - k_1 R \qquad (5)$$

$$R_x/R_0 = e^{-k_1 t} \qquad (6)$$

$$I_x/I_0 = e^{-k_2 t} + \frac{(R_0/I_0)}{(1 - k_2/k_1)}(e^{-k_2 t} - e^{-k_1 t}) \qquad (7)$$

subscripts 0 and x denoting initial and final concentration, respectively. Combination of eq 6 and 7 gives eq 8, which can be used to calculate k_2/k_1 if the ratios R_x/R_0, I_x/I_0, and R_0/I_0 are available.

$$\left(\frac{R_0}{I_0} + 1 - \frac{k_2}{k_1}\right) e^{(k_2/k_1)\ln(R_x/R_0)} + \frac{I_x k_2}{I_0 k_1} = \left(\frac{R_0}{I_0}\right) e^{\ln(R_x/R_0)} + \frac{I_x}{I_0} \qquad (8)$$

Under ideal circumstances, these concentration ratios would be computed from individual concentrations whose absolute values were known. However, the individual concentrations measured by proton-decoupled pulse Fourier transform ^{13}C NMR will differ from the true concentrations if partial saturation occurs (i.e., if pulse intervals are less than $\sim 5T_1$)[11] and if different nuclear Overhauser enhancement (NOE) factors apply to the analytical and reference signals (all concentrations are measured relative to the principal methylene resonance at 30.0 ppm). Nevertheless, the following considerations show that reliable values of k_2/k_1 can still be obtained under these conditions.

For a set of analyses carried out under identical circumstances, the experimental concentrations (subscript ex) are related to the true concentrations by eq 9, in which

$$\begin{aligned} R_x &= C_R R_{x,\mathrm{ex}} & I_x &= C_I I_{x,\mathrm{ex}} \\ R_0 &= C_R R_{0,\mathrm{ex}} & I_0 &= C_I I_{0,\mathrm{ex}} \end{aligned} \qquad (9)$$

the C's are proportionality constants. From these relationships, it follows that $R_x/R_0 = R_{x,\mathrm{ex}}/R_{0,\mathrm{ex}}$, $I_x/I_0 = I_{x,\mathrm{ex}}/I_{0,\mathrm{ex}}$, and $R_0/I_0 = C_R R_{0,\mathrm{ex}}/C_I I_{0,\mathrm{ex}}$. Thus all of the ratios of absolute concentrations can be replaced by ratios of experimental concentrations if $C_R = C_I$. Equality of the C's is most likely to occur when the analyses are based on resonances arising from carbons in similar molecular enivronments, since such carbons are likely to exhibit similar T_1's and NOE's. For example, comparable values of C_R and C_I seem likely for the methylene carbon resonances designated as c and Cl-β (see Figures 1A and 2). Comparable C's are also to be expected for the chloromethylene carbon resonances denoted as b and Cl-α, although these C's may differ significantly from those associated with the methylene signals. The pulse interval may have a pronounced effect on the values of C_R and C_I, but these values should still remain comparable to each other if they are associated with the same carbon type. Thus, to summarize, even though the values found for R and I may vary with experimental conditions and with the calculation method employed, they should still afford a reliable result for k_2/k_1 (from eq 8) if they are obtained in a consistent way. Moreover, different sets of mutually consistent concentration values should give the same value of k_2/k_1.

In the present work, self-consistent sets of values for R and I were obtained from analyses performed on pairs of polymers that had been reduced to different extents (Table I). Equation 8 was then solved for k_2/k_1 by a successive approximations technique, using a digital computer. In order to reduce the machine computation times, iterations were started with k_2/k_1 values estimated from eq 10, which

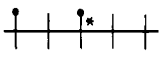
$$k_2/k_1 \simeq \left(\frac{\mathrm{R}_o + \mathrm{R}_x}{\mathrm{I}_o + \mathrm{I}_x}\right)\left(\frac{\mathrm{I}_o - \mathrm{I}_x}{\mathrm{R}_o - \mathrm{R}_x} + 1\right) \qquad (10)$$

can be derived by dividing eq 4 by eq 5 and then making the following substitutions: $\mathrm{d}R = R_0 - R_x$, $\mathrm{d}I = I_0 - I_x$, $R = (R_0 + R_x)/2$, $I = (I_0 + I_x)/2$.

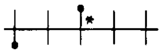
The reduced S-80 and R-23 polymers were analyzed under identical conditions (Table I). Thus the R and I values calculated for these polymers from the c and Cl-β methylene signals may be regarded as a self-consistent set of data in which R_0, R_x, I_0, and I_x are 2.5_4, 1.8_8, 3.0_0, and 2.1_5, respectively. Substitution of these quantities into eq 8 yields a k_2/k_1 value of 1.9_7. Similarly, the R's and I's computed from the b and Cl-α resonances of the reduced S-80 and R-23 polymers give a k_2/k_1 of 1.8_8, which is identical to the k_2/k_1 value calculated from the b and Cl-α data for the reduced E-80 and E-54 materials. The mean value of k_2/k_1 is 1.9_1 (mean deviation $\pm 0.0_4$), corresponding to a reactivity difference of 3.8_2 per chloromethylene unit, and the excellent agreement of the k_2/k_1 values obtained from the three data sets can be taken as evidence for the validity of our computational approach.

Mechanism of LiAlH$_4$ Reduction. During reductive dechlorination, the dyad CHCl groups of PVC are distributed among the five local environments experienced by the central CHCl moieties (asterisks) of partial structures **1–5**. The starting polymers had P_m values ranging from 0.49 to 0.44 (Experimental Section), corresponding to **1–3–5** ratios ranging from 24:26:50 to 19:31:49, respectively, for Bernoullian propagation.[12] Reduction of the central CHCl group of **5** removes one *m* dyad and one *r* dyad. Thus, if this process occurred preferentially, it could account for small increases in the overall *r* dyad–*m* dyad ratio during the early stages of reaction.[8] However, our finding of *r* dyad–*m* dyad ratios that are at least as high as 11:1 when the reduction is nearly complete must mean that the central CHCl groups of **1** and **2** are more reactive than those of **3** and **4**. The total reactivity (composite rate constant) of the central CHCl group in a given partial structure is represented by $\sum_i N_i k_i$, where N_i is the mole fraction and k_i the specific rate constant of the *i*th conformer of the structure in question.[13]


mm triad
1


m dyad
2


rr triad
3


r dyad
4


mr triad
5

• = Cl

Studies of the conformer populations for the stereoisomers of a model compound, 2,4,6-trichloroheptane (TCH), have shown that the preferred conformers of the *rr* and *mm* triads in PVC are the *tttt* and *gtgt* forms, respectively.[14] Backside (S$_N$2) attack on the central CHCl group of these conformers by a nucleophile, N$^-$, is depicted in Figure 3 (the electrophile, E$^+$, is, for the moment, ignored). We note that the S$_N$2 process with N$^-$ = AlH$_4^-$ is the mechanism most frequently considered to operate in the LiAlH$_4$ reduction of simple alkyl halides.[15]

From Figure 3 it follows that S$_N$2 attack at C-3 of the *gtgt mm* triad will be severely hindered by an axial interaction of N$^-$ with the bulky C-5 group. Moreover, stretching of the (C-3)Cl bond in the transition state for this reaction will relieve the strain associated with only one axial 1,3 H,Cl interaction, which involves the hydrogen atom on C-1. In contrast, N$^-$ experiences no axial interaction with a large group in the transition state for S$_N$2 attack at C-3 of the *tttt rr* triad, and in this case two axial 1,3 H,Cl interactions are relieved. These factors should tend to make C-3 of the *tttt rr* triad more reactive than C-3 of the *gtgt mm* triad toward backside nucleophilic displacement.

Similar considerations apply to the preferred conformers of dyad structures **2** and **4**, which are inferred to be the *gt* and *tt* forms, respectively, from studies on *m*- and *r*-2,4-dichloropentane (DCP).[14c,d,17] As shown in Figure 3, the asymmetic *gt m* dyad exists in equilibrium with its mirror image *tg* form. Both forms will, of course, be

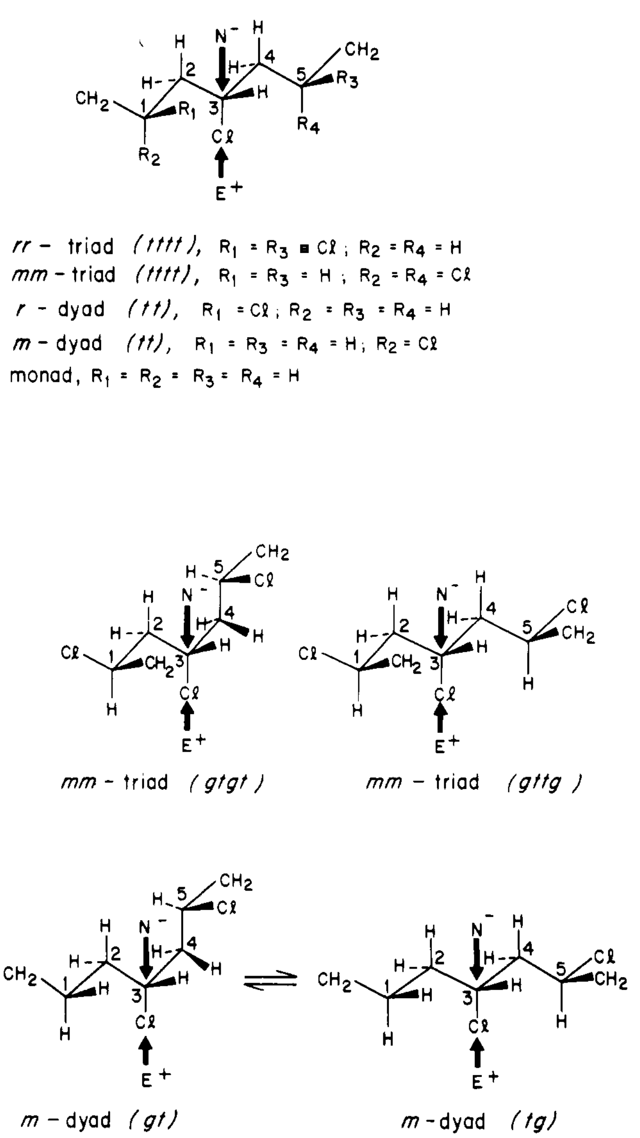


Figure 3. Conformations of some possible transition states for nucleophilic or electrophilic attack on PVC or on reduced structures derived therefrom.

present in identical concentration if the molecular environment of the *m* dyad is symmetrical. If the environment is not symmetrical (for example, if the *m* dyad is at the end of an *mm* triad or *mr* triad sequence), then the concentrations of the two forms will differ slightly,[14b–d] but in any case it is clear that structure 2 must spend a considerable fraction of its lifetime in the *gt* array. In accordance with our previous arguments, the S_N2 reactivities (at C-3) of the *tg m* dyad and the *tt r* dyad should be comparable to that of the *tttt rr* triad. However, an S_N2 reaction at C-3 of the *gt m* dyad should be slow for the reasons noted above in connection with the *gtgt mm* triad. The net reactivity of the *m* dyad $gt \rightleftarrows tg$ mixture should thus be relatively low, and it therefore seems reasonable to conclude that, on the basis of transition-state free-energy differences, the preferred conformers of structures 1 and 2 will both tend to be less reactive than the preferred conformers of either 3 or 4 toward S_N2 attack.

Turning now to other factors that have a bearing on relative reactivities, we note that equilibration studies[14c,d,18] and statistical calculations[14c,d] have shown that *r*-dyad structures in DCP, TCH, and PVC are thermodynamically favored over *m* dyads by concentration factors of about 1.8–2.6 in various media at 20–70 °C. However, the higher ground-state energy content of the *m* dyads is unlikely to reverse the reactivity order deduced above for 1–4, since the energy differences between the *m*-dyad- and *r*-dyad-containing conformers that have been considered thus far should be enhanced rather than reduced (or reversed) upon going to the congested transition states required for an S_N2 reaction. Furthermore, recent evidence[14b–d,17a] suggests that, in the case of 1 and 2, preferred conformers do not comprise significantly larger fractions of the total populations than is the case for 3 and 4. We therefore conclude that the higher overall reactivity observed for *m* dyads (vs. *r* dyads) in PVC is unlikely to result from preferential S_N2 attack on the preferred conformations of these groups.

Other *m*-dyad-containing conformers require consideration, and in the case of structure 1, a possible candidate for rapid reaction is the *gttg* form (Figure 3). However, this conformer is thought to comprise only about 20–28% of the total *mm*-triad population,[14b–d] and on the basis of previous arguments, its S_N2 reactivity should not be higher than that of the preferred conformers of 3 and 4. Another candidate is the *mm*-triad *tttt* conformer, for which a stronger case can be made. Relief of two axial 1,3 Cl,Cl interactions in the transition state, coupled with a relatively high ground-state free-energy content,[14d] should cause this conformer to be appreciably more reactive than the *tttt rr* triad or the *tt r* dyad. For similar reasons, the *tt m* dyad is also likely to react more readily than either of the latter structures.

Since the *tttt mm* triad and the *tt m* dyad comprise rather small fractions of the conformer populations of their respective groups,[14c,d,17] it is not possible to state categorically that the enhanced reactivities of these conformers are indeed responsible for the higher overall reactivity of the *m*-dyad structures in PVC. Nevertheless, the existence of this possibility means that the preferential removal of *m* dyads cannot be regarded as conclusive evidence against an S_N2 reduction process. The slightly higher reactivity found for monads vs. *r* dyads can also be accommodated by such a mechanism on the basis of one (or both) of the following assumptions: (a) the reactivity of the *r* dyad is lowered relative to that of the monad by steric interaction of the approaching nucleophile with the halogen on C-1 (Figure 3); (b) in the S_N2 transition state, the reacting carbon acquires a modicum of positive charge, which is destabilized by the electron-withdrawing inductive effect of the *r*-dyad C-1 halogen.

In any event, the overall situation is even more complex than the previous arguments imply, for the experimental facts also seem consistent with an alternative reduction mechanism involving a rate-determining attack on halogen by an electrophile, E^+. The electrophile could be lithium cation or some other metallic species,[16,19] including neutral Al(III) compounds formed during the reduction process.[19] Figure 3 shows that electrophilic attack on the C-3 chlorine atom will be hindered by two axial hydrogens (on C-1 and C-5) in the case of the *tttt rr* triad and the *tt r* dyad, but by only one axial hydrogen with the *gtgt mm* triad and the *gt m* dyad. The decreased transition-state encumbrance and relatively high ground-state energies of the latter conformers could lead to a higher overall reactivity of *m*-dyad-containing structures, as observed. Electrophilic attack on chlorine would undoubtedly generate some positive charge on the carbon skeleton of the polymer; thus the higher reactivity found for monads vs. *r* dyads can also be rationalized in terms of this mechanism by a γ-halogen inductive effect. Reversible C–Cl ionization resulting from electrophilic attack could lead to increased *r* dyad–*m* dyad ratios owing to stereochemical equilibration,[14c,d,18] but the

Table II
Branches and Double Bonds in Reduced PVC

reduced polymer[a]	polym temp, °C	reducing agent[a]	frequency (±0.1) per 1000 C M branch[b]	 L branch[b]	 *trans*-CH=CH
S-80	43[c]	$LiAlH_4$	1.9	<0.2[d]	1.4
		Bu_3SnH[e]	2.1	0.4	<0.2[d]
E-80	43[c]	$LiAlH_4$	2.0	<0.4[d]	1.2
S-54	75[c]	$LiAlH_4$	2.7	0.5	1.5
		Bu_3SnH[f]	2.8	0.6_5	<0.5[d]
E-54	75[c]	$LiAlH_4$	2.2	$<0.1_5$[d]	1.4
R-23	56	$LiAlH_4$	2.0_5	<0.2[d]	1.1
		$LiAlH_4/Bu_3SnH$[g]	2.6	<0.1[d]	1.1

[a] See Experimental Section for details. [b] For nomenclature, see Figure 2. [c] Reference 31. [d] Not detected. [e] "One-pass" reduction;[2] spectrum shown in Figure 1B. [f] "Two-pass" reduction.[2] [g] $LiAlH_4$-reduced polymer was subjected to a further reduction with Bu_3SnH.

available thermodynamic stability data[14c,d,18] suggest that equilibration, per se, cannot account for *r* dyad–*m* dyad ratios that are at least as high as 11:1 (see above).

The importance of electrophilic attack on halogen was recently demonstrated for the $LiAlH_4$ reduction of alkyl bromides,[19] and the literature contains several other examples of reactions where frontal attack of alkyl halogen by $LiAlH_4$ (or a derivative species) may be involved in a rate-determining step.[20] One of these examples is of particular interest within the context of the present work; this is the reduction of hindered 1,3-dihalopropanes to form cyclopropanes as well as the expected noncyclized products.[20a] Cyclization was attributed to the intervention of an organometallic intermediate,[20a] and in this connection it is of interest to note that organometallic complexes are indeed formed from $LiAlH_4$ and certain polyfluoroalkyl iodides.[21] Our ^{13}C NMR spectra show that no cyclopropane structures are produced during the $LiAlH_4$ reduction of PVC, presumably because the "normal" reduction of the polymer is not unduly retarded by steric factors. However, $LiAlH_4$ reduction of PVC in the presence of oxygen introduces hydroxyl groups into the resin,[22] whereas no hydroxyl groups are found in the product obtained from a chlorinated paraffin under similar reduction conditions.[22b] These observations can perhaps be regarded as evidence for the formation of oxidizable organometallic groups during the $LiAlH_4$ reduction of the polymer.[22]

In summary, the mechanism of the $LiAlH_4$ reduction of PVC remains uncertain at this time. The reactivity data seem to be consistent with either of the following alternatives: (a) an S_N2 displacement that occurs preferentially on monads and on the nonpreferred conformers of meso structures; (b) a rate-limiting electrophilic attack upon the low-energy conformers of various groups. The stereochemical arguments used to reach this conclusion should be applicable to other systems, and it would therefore be of interest to test these ideas with other reagents and substrates in situations where reaction mechanisms can be established by independent techniques. Such studies might be particularly useful in connection with attempts to modify the structure of PVC by nucleophilic substitution reactions.[1c,23]

Selectivity of Bu_3SnH Reduction. Figure 1B shows the ^{13}C-NMR spectrum of S-80 PVC that has been reduced with Bu_3SnH to the extent of 99.7%. Unlike the polymers reduced with $LiAlH_4$ to about this level of conversion, the Bu_3SnH-reduced polymer contains all of its halogen in isolated monad units. A similar result was obtained for polymer S-54 after 99.3% reduction with the organotin reagent. Thus the reactivity of monads relative to that of their dyad precursors must be lower for Bu_3SnH than for $LiAlH_4$.[24] The selectivities obtained with the two reagents cannot be compared directly due to differences in reaction temperature (about 20 °C higher for $LiAlH_4$) and solvent medium (2-MeTHF for Bu_3SnH, THF for $LiAlH_4$). Nevertheless, it is interesting to note that the altered selectivity found with Bu_3SnH is consistent with mechanistic considerations. Reductions of alkyl halides (R′X) with Bu_3SnH are free-radical chain reactions in which selectivity is determined by the following step: $R'X + Bu_3Sn\cdot \rightarrow R'\cdot + Bu_3SnX$.[25] Since the $Bu_3Sn\cdot$ radical has some nucleophilic character,[26] the rate of this step ought to be accelerated by electron-withdrawing substituents in R′.[27] Accordingly, enhanced reactivity toward Bu_3SnH of dyads relative to monads can be explained by the presence of an electronegative γ-chloro substituent in the R′ moiety of the dyads.

Branches and Double Bonds in PVC. Table II presents concentration data, obtained by ^{13}C NMR, for branches and internal trans double bonds in several reduced PVC's. Long branch points could not be identified conclusively in most of the $LiAlH_4$-reduced materials, apparently owing to side reactions occurring during reduction.[2] In agreement with this supposition, long branch points have been found by ^{13}C NMR in all of the Bu_3SnH-reduced polymers (including several polymers not listed in Table II) that we have examined to date.

The methyl branch values are essentially independent of the reduction method in the case of polymers S-80 and S-54. However, the methyl branch frequency of the $LiAlH_4$-reduced R-23 polymer seems to have increased significantly after a further reduction with Bu_3SnH. The second reduction removed several unassigned resonances that appeared in the spectrum of the $LiAlH_4$-reduced material, but we have been unable to associate these resonances with structures that are potential precursors of methyl groups. Nevertheless, these observations suggest that the $LiAlH_4$ reduction of PVC may not always be a reliable tool for quantitative methyl branch analysis.

Table II shows that, within the range of 43–75 °C, polymerization temperature has only a slight effect on the methyl branch and long branch frequencies. Total methyl contents per 1000 C, determined from IR measurements on samples reduced with $LiAlH_4$, are available for all of the polymers listed in Table II.[28] These values are 4.1 (S-80),[28a] 4.1 (E-80),[28b] 7.8 (S-54),[28a] 7.4 (E-54),[28b] and 5.7 (R-23);[28a] they were calculated from the absorbance of the methyl deformation band at 1378 cm^{-1} on the assumption that most of the methyls were contained in pendant *n*-butyl groups. Since this assumption is now known to be invalid and the extinction coefficient of the 1378-cm^{-1} band is known to depend strongly upon the local molecular environment,[29] correction of these methyl values[28] obviously is required.[30] If all of the methyls are considered to be present either in methyl branches (M-CH_3's) or at the ends of long chains (L-CH_3's), methyl branch contents can be calculated from the original IR data[28] using eq 11, where

$$\epsilon_1(\text{total CH}_3/1000\text{ C}) = \epsilon_2(\text{M--CH}_3/1000\text{ C}) + \epsilon_3(\text{L--CH}_3/1000\text{ C}) \quad (11)$$

ϵ_1, ϵ_2, and ϵ_3 are the reported[29] extinction coefficients of the 1378-cm^{-1} band for methyls in *n*-butyl branches, methyl branches, and long-chain ends, respectively. Assuming the presence of one L-CH_3 per number-average molecule, one obtains the following M-CH_3 values (per 1000 C) from this equation: 2.1 (S-80), 2.1 (E-80), 3.9 (S-54), 3.7 (E-54), and 2.9 (R-23). These results may be compared directly with the "M-branch" frequencies in Table II.

Table II also shows that all of the $LiAlH_4$-reduced polymers contained internal trans double bonds, whereas no groups of this type could be detected in the polymers reduced with Bu_3SnH. The double bonds may be primarily an artifact of the $LiAlH_4$ reduction method,[2] and this conclusion is supported by the results obtained with polymer R-23, which indicate that the double bonds in $LiAlH_4$-reduced PVC are not attacked directly by Bu_3SnH. The R-23 data do not completely exclude the possibility that double bonds are destroyed by intramolecular radical addition during the Bu_3SnH reduction of PVC itself. However, in keeping with earlier observations,[2] the ^{13}C-NMR spectra obtained in the present work provide no evidence for the presence of the alicyclic rings that would have resulted from such a process.

Molecular weight changes produced by ozonolysis have indicated that the total internal double bond contents (per 1000 C) of polymers S-80 and S-54 are only about 0.02 and <0.01, respectively.[28a] These values are not inconsistent with our results on the Bu_3SnH-reduced materials, since such low concentrations of double bonds would not have been detected by our measurements.

Experimental Section

Materials. The PVC samples employed have been described elsewhere in the literature.[28a,31] Some pertinent characteristics of these resins are as follows (polymer designation, polymerization method, number-average molecular weight determined by GPC, P_m determined by ^1H NMR unless noted otherwise): S-80, suspension, 58 100, 0.44;[31] E-80, emulsion, 62 900, 0.44;[31] S-54, suspension, 26 200, 0.48;[31] E-54, emulsion, 27 800, 0.49;[31] R-23, suspension,[28a] 37 700,[28a] 0.46 (our measurement by ^{13}C NMR[12b] in 1,2,4-trichlorobenzene solution at 120 °C).

Reductions with Lithium Aluminum Hydride. These reactions were carried out in purified THF solution at 100 °C under nitrogen, using ca. 1.25 mol of $LiAlH_4$ per mol of vinyl chloride monomer units.[3] Details of the experimental procedure have previously been described.[3]

Reductions with Tri-*n*-butyltin Hydride. Procedural details for this technique are given in earlier publications.[2] $LiAlH_4$-reduced R-23 polymer was subjected to a further reduction with Bu_3SnH in a xylene solvent mixture;[2] the other "one-pass" Bu_3SnH reductions were carried out in 2-methyltetrahydrofuran.[2]

Undesirable line broadening is occasionally observed in the ^{13}C NMR spectra of polymers that have been reduced with Bu_3SnH. We have recently found that this problem can be eliminated most conveniently by Soxhlet extraction of the reduced PVC into mixed xylenes through an Alundum thimble of 0.1-μ porosity, followed by precipitation of the polymer with excess methanol and processing in the usual way.[2] Use of this purification technique was, however, not required in the present work.

^{13}C NMR Measurements. The spectra were observed with a Varian XL-100 spectrometer modified for pulse Fourier transform spectroscopy and interfaced with a Nicolet Model 1080 computer. Protons were decoupled from the carbon nuclei using a random noise decoupling field. Free induction decays were stored in 8K computer locations using dwell times of 100 or 200 μs, corresponding to spectral windows of 5000 or 2500 Hz, respectively. The pulse angle was 90°, and the pulse repetition time ranged from 2.8 to 4.0 s. Hexamethyldisiloxane was used as an internal reference [2.0 ppm vs. tetramethylsilane (Me_4Si)], and the internal deuterium lock signal was provided by *p*-dioxane-d_8 or dimethyl-d_6 sulfoxide. Spectral accumulations ranged from about 14 000 to 67 000 scans.

Reduced PVC's were observed as 20–33% (w/v) solutions in 1,2,4-trichlorobenzene at 110–120 °C. At 110 °C, T_1 for the "normal" backbone carbons is approximately 1.3 s. The defect structure frequencies recorded in Table II were determined from the intensities of the M-α, L-α, and CH=CH-α resonances; for nomenclature, see Figures 1 and 2.

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References and Notes

(1) For brief reviews of earlier work in this field, see (a) K. B. Abbås, F. A. Bovey, and F. C. Schilling, *Makromol. Chem., Suppl.*, **1**, 227 (1975); (b) A. Rigo, G. Palma, and G. Talamini, *Makromol. Chem.*, **153**, 219 (1972); (c) J. Masojídek and J. Štěpek, *Chem. Listy*, **66**, 458 (1972).

(2) W. H. Starnes, Jr., R. L. Hartless, F. C. Schilling, and F. A. Bovey, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **18** (1), 499 (1977); *Adv. Chem. Ser.*, **No. 169**, 324 (1978).

(3) K. B. Abbås and E. M. Sörvik, *J. Appl. Polym. Sci.*, **19**, 2991 (1975).

(4) F. A. Bovey, K. B. Abbås, F. C. Schilling, and W. H. Starnes, Jr., *Macromolecules*, **8**, 437 (1975).

(5) C. E. Wilkes, presented at the Eighth Central Regional Meeting of the American Chemical Society, Akron, Ohio, May 21, 1976.

(6) C. J. Carman, A. R. Tarpley, Jr., and J. H. Goldstein, *J. Am. Chem. Soc.*, **93**, 2864 (1971); Y. Inoue, I. Ando, and A. Nishioka, *Polym. J.*, **3**, 246 (1972); I. Ando, Y. Kato, M. Kondo, and A. Nishioka, *Makromol. Chem.*, **178**, 803 (1977).

(7) D. Braun and W. Schurek, *Angew. Makromol. Chem.*, **7**, 121 (1969).

(8) J. Millán, F. Arranz, and E. Pinzón, *Rev. Plast. Mod.*, **27**, 361 (1974).

(9) For a related study, see J. Millán, F. Arranz, and E. Pinzón, *Rev. Plast. Mod.*, **27**, 529 (1974).

(10) S. W. Benson, "The Foundations of Chemical Kinetics", McGraw-Hill, New York, N.Y., 1960, pp 33 and 34.

(11) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, N.Y., 1972, p 30.

(12) (a) F. A. Bovey, *Acc. Chem. Res.*, 1, 175 (1968); (b) C. J. Carman, A. R. Tarpley, Jr., and J. H. Goldstein, *Macromolecules*, **4**, 445 (1971).

(13) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, " Conformational Analysis", Interscience, New York, N.Y., 1966, p 27.

(14) (a) Y. Abe, M. Tasumi, T. Shimanouchi, S. Satoh, and R. Chûjô, *J. Polym. Sci., Part* A-1, **4**, 1413 (1966); (b) D. Doskočilová, J. Štokr, B. Schneider, H. Pivcová, M. Kolínsky, J. Petránek, and D. Lím, *J. Polym. Sci., Part C*, **16**, 215 (1967); (c) P. J. Flory and A. D. Williams, *J. Am. Chem. Soc.*, **91**, 3118 (1969); (d) P. J. Flory and C. J. Pickles, *J. Chem. Soc., Faraday Trans. 2*, **69**, 632 (1973).

(15) J. S. Pizey, "Synthetic Reagents", Vol. I, Halsted Press, New York, N.Y., 1974, pp 244–247; H. O. House, "Modern Synthetic Reactions", W. A. Benjamin, Menlo Park, Calif., 1972, pp 98 and 99. In THF solution at the concentration used in the present work (ca. 1 M), $LiAlH_4$ apparently exists primarily as an equimolar mixture of the triple ions $LiAlH_4Li^+$ and $AlH_4LiAlH_4^-$.[16] These species are in equilibrium with low concentrations of solvent-separated ion pairs, $Li^+AlH_4^-$, and with even lower concentrations of the free ions Li^+ and AlH_4^-.[16] It is not clear which hydride species is the actual reducing agent for PVC, and it is possible that all of them are involved, since their order of reactivity may be the inverse of their order of abundance. These considerations do not affect the qualitative reactivity arguments made in the present paper.

(16) E. C. Ashby, F. R. Dobbs, and H. P. Hopkins, Jr., *J. Am. Chem. Soc.*, **95**, 2823 (1973); **97**, 3158 (1975).

(17) (a) J. Wu and H. J. Ache, *J. Am. Chem. Soc.*, **99**, 6021 (1977), and references cited therein; (b) B. Schneider, J. Štokr, D.

Doskočilová, S. Sýkora, J. Jakeš, and M. Kolínský, *J. Polym. Sci., Part C*, **22**, 1073 (1969), and references cited therein.

(18) W. E. Billups and A. N. Kurtz, *J. Am. Chem. Soc.*, **90**, 1361 (1968); W. E. Billups, A. N. Kurtz, and M. L. Farmer, *Tetrahedron*, **26**, 1095 (1970).

(19) J. L. Pierre, H. Handel, and R. Perraud, *Tetrahedron*, **31**, 2795 (1975).

(20) (a) M. S. Newman, G. S. Cohen, R. F. Cunico, and L. W. Dauernheim, *J. Org. Chem.*, **38**, 2760 (1973); (b) L. A. Paquette and P. C. Storm, *ibid.*, **35**, 3390 (1970), and references cited therein; (c) C. W. Jefford, D. Kirkpatrick, and F. Delay, *J. Am. Chem. Soc.*, **94**, 8905 (1972); (d) C. W. Jefford, U. Burger, M. H. Laffer, and N. Kabengele, *Tetrahedron Lett.*, 2483 (1973); (e) J. Hatem and B. Waegell, *ibid.*, 2023 (1973); (f) H. Yamanaka, T. Yagi, K. Teramura, and T. Ando, *J. Chem. Soc. D*, 380 (1971); (g) H. Yamanaka and K. Termaura, *Mem. Fac. Ind. Arts, Kyoto Tech. Univ. Sci. Technol.*, **22**, 92 (1973); *Chem. Abstr.*, 81, 24751u (1974); (h) Y. Kusuyama and Y. Ikeda, *Nippon Kagaku Kaishi*, 290 (1977); *Chem. Abstr.*, **86**, 189253z (1977).

(21) M. Hauptschein, A. J. Saggiomo, and C. S. Stokes, *J. Am. Chem. Soc.*, **78**, 680 (1956); R. S. Dickson and G. D. Sutcliffe, *Aust. J. Chem.*, **25**, 761 (1972).

(22) (a) J. D. Cotman, Jr., *J. Am. Chem. Soc.*, **77**, 2790 (1955); (b) H. Batzer and A. Nisch, *Makromol. Chem.*, **22**, 131 (1957).

(23) T. Suzuki, *Pure Appl. Chem.*, **49**, 539 (1977).

(24) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", Wiley, New York, N.Y., 1961, pp 166–168.

(25) D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.*, **90**, 7047 (1968).

(26) G. L. Grady, T. J. Danyliw, and P. Rabideux, *J. Organomet. Chem.*, **142**, 67 (1977).

(27) However, see R. C. Fort, Jr., and J. Hiti, *J. Org. Chem.*, **42**, 3968 (1977).

(28) (a) K. B. Abbås and E. M. Sörvik, *J. Appl. Polym. Sci.*, **20**, 2395 (1976); (b) unpublished results.

(29) C. Baker, W. F. Maddams, G. S. Park, and B. Robertson, *Makromol. Chem.*, **165**, 321 (1973).

(30) K. B. Abbås, *J. Macromol. Sci., Phys.*, **14**, 159 (1977).

(31) E. M. Sörvik, *J. Appl. Polym. Sci.*, **21**, 2769 (1977).

Structural Investigations on Poly(4-hydroxy-L-proline). 1. Theoretical Studies[+]

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ABSTRACT: Model building studies on poly(hydroxyproline) indicate that in addition to the well-known helical structure of form A, a left-handed helical structure with trans peptide units and with h = 2.86 Å and n = 2.67 (i.e., 8 residues in 3 turns) is also possible. In this structure which is shown to be in agreement with X-ray data of the form B in the next paper, the γ-hydroxyl group of an $(i + 1)$th Hyp residue is hydrogen bonded to the carbonyl oxygen of an $(i - 1)$th residue. The possibility of a structure with cis peptide units is ruled out. It is shown that both forms A and B are equally favorable from considerations of intramolecular energies. Since form B is further stabilized by intrachain hydrogen bonds, we believe that this is likely to be the ordered conformation for poly(hydroxyproline) in water.

Synthetic polypeptides containing L-proline and 4-hydroxy-L-proline have been extensively studied as models for the fibrous protein collagen, which contains large amounts of these imino acid residues. In spite of the close structural similarity between these residues, there are certain basic differences in their conformational features, as manifested in their homopolymers, viz., polyproline (PP) and poly(hydroxyproline) (PHP). Polyproline undergoes mutarotation in water and acid, from the form I (PP I) structure with all peptide bonds in the cis conformation, to the form II (PP II), in which all peptide bonds are in the trans conformation.[1-3] Similar transformations have also been observed for poly(*o*-acetyl-L-hydroxyproline).[3-5] On the other hand, PHP does not dissolve in most of the organic solvents, except strong acids like dichloroacetic acid.[5] Hence the type of transformations observed for PP in solution have not been observed for PHP. However, X-ray diffraction studies have indicated that PHP exists in two forms, designated as forms A and B.[5] Form A was shown to bear a general resemblance to PP II, but unlike the latter, the PHP structure is stabilized by a series of interchain hydrogen bonds between chains, involving γ-hydroxyl groups.[6] Since the X-ray pattern of form B was rather diffuse, it was not characterized in detail.[5]

Poly(hydroxyproline) is also more stable in solution than PP II, as indicated by the greater resistance of PHP to disruption by calcium chloride when compared to PP II.[7] The greater stability of an ordered PHP structure in solution can be either an intrinsic property of the isolated helix or the result of stabilizing intermolecular interaction, as in the solid state.[6] Other experiments, including our own, which are discussed in the subsequent paper, indicate that the polymer in solution does not form an aggregated structure but occurs as individual single chain helices. We should therefore be able to account for the extra stability of PHP in terms of intramolecular stabilization offered in some fashion by its hydroxyl group. This, in turn, might also explain the absence of mutarotation in PHP.

Further, we found that, contrary to what has been stated, the presence of the γ-hydroxyl group does not stereochemically hinder the formation of a PP I type structure, with all peptide bonds in the cis orientation. Therefore, the possibility of hydrogen-bond formation involving the γ-hydroxyl group was investigated for structures with all-trans peptide bonds as well as all-cis peptide bonds. Both direct hydrogen bonds and water-bridged hydrogen bonds, as proposed for the collagen structure,[8,9] were explored. A systematic conformational analysis was carried out and the various possible ordered conformations for PHP were, at each stage, checked against not only earlier experimental data but also our own

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